Utilization of Avocado Seed Waste as Raw Material for Producing Biodiesel with CaO Catalyst from Eggshell

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Abstract. Avocado is one of the plants that thrives in the tropical area such as Indonesia. Avocados produce waste in the form of avocado seeds because it is less used. The oil from avocado seeds contains triglyceride as raw materials in biodiesel synthesis. Biodiesel is an alternative diesel oil from the transesterification of vegetable oils or animal fats with the addition of catalyst. The objective of this study was to utilize avocado seed waste as raw material in the production of biodiesel and eggshell waste as source of CaO catalyst. The various effect of reaction conditions, such as methanol-to-oil molar ratio (3:1–12:1), reaction time (30–120 min), and amount of catalyst loading (1–7% wt) were investigated. Catalyst reusability was also studied. Result showed that the highest biodiesel oil was obtained from reaction with the condition of 6:1 methanol-to-oil ratio, 60 min reaction time, 5% wt amount of catalyst loading, and the catalyst can be reused up to 3 reaction cycles with the yield above 75%. The physico-chemical properties of biodiesel produced met the SNI standard of biodiesel quality.

1. Introduction
Currently, the need to develop renewable alternative fuels has been increasing due to the increasing in energy demand as the population and industry increased [1]. Regarding alternative fuels, biodiesel is a promising type of fuel because of its enviromental friendliness such as low toxicity, low CO₂, sulfur and benzene-free emission product, and also has high cetane number [2]. Biodiesel is a mixture of methyl esters resulting from the transesterification reaction of vegetable oil or animal fats with alcohol with the aid of an acid or base catalyst [3].

Transesterification reaction can be conducted homogenously or heterogenously. A heterogenous catalytic process is more advantageous than a homogenous one. A heterogenous catalyst easier to separate and reuse, the homogenous catalyst presents problems in separation and purification of the product, the use of homogenous catalyst is not environmentally benign because the washing step for catalyst removal produces a large amount of waste water [4]. CaO, an active and base catalyst, is widely used for transesterification of vegetables oil. Eggshells, which contain CaCO₃ for about 94%, can be used as raw material to obtain CaO through the calcination process [5].

The purpose of this study is to obtain the optimum condition for biodiesel production by transesterification process of avocado seed oil using methanol as solvent and CaO from eggshells as
catalyst, to study there usability of the catalyst, and to characterize the physicochemical properties of the biodiesel and compare to the SNI standard.

2. Materials and method

2.1. Materials
Avocado seeds and egg shells were obtained from food sellers around Banda Aceh. Chemicals used to produce biodiesel were methanol that purchased from PT. Jeungki Mali Medical, n-hexane as solvent for the extraction process and FFA analysis process also purchased from PT. Jeungki Mali Medical. Other materials used were deionized water for biodiesel washing, phenolphthalein indicator and NaOH 0.1 N for FFA analysis process.

2.2. Oil extraction from avocado seeds
Avocado seed was cut manually using knife and then crushed in blender. The sample was dried in oven at 110˚C for 2 h. A 50 g sample was extracted using n-hexane 250 ml at 65˚C for 4 h [5]. The avocado seed oil produced was characterized for free fatty acid (FFA), viscosity, and density.

2.3. Catalyst preparation
Eggshell were dried in oven at 110˚C for 2 h, crushed in blender and sieved at 60 mesh. Egg shell powder was calcined in furnace at 900˚C for 2 h [6]. The catalyst was characterized using XRD and SEM method.

2.4. Transesterification process
Various parameters were investigated to study their effect on the biodiesel yield. The parameters studied were methanol-to-oil ratio (1:3–1:12), reaction time (30–120 min), and amount of catalyst loading (1–7%wt). The operating temperature was kept constant at 65˚C for all the parameters studied.

Reactions were conducted in a three-neck rounded flask. The reactor was equipped with a magnetic stirrer and thermometer. Specific amount of oil, methanol, and catalyst were placed in reactor, and the reactions were run at the various conditions stated above. After the reaction, product was centrifuged to separate the catalyst, then the biodiesel and glycerol were separated using separating funnel, left for 12 hours and biodiesel produced was washed with aquadest to remove methanol from the product [7].

3. Result and discussion

3.1 Avocado seed oil analysis
The avocado seed oil that obtained from extraction was analyzed for FFA, density, and viscosity. FFA is the most important thing in producing biodiesel. For transesterification reaction, FFA should be below 1% [8]. The result from characterization shown in Table 1.

| Analysis     | Result |
|--------------|--------|
| FFA (%)      | 0.42   |
| Viscosity (poise) | 0.47   |
| Density (g/mL)   | 0.86   |

Table 1. Characterization of avocado seed oil
3.2 Catalyst characterization

CaO catalyst from eggshell was analyzed using XRD to identify the components in catalyst after calcination process. Figure 1 shows the diffractogram of the analysis.

![Catalyst diffractogram](image)

**Figure 1.** Catalyst diffractogram after calcination at 900°C for 2 h

As shown in Fig.1, XRD spectrum showed CaO component (JCPDS No.82-1690), CaCO₃ (JCPDS No.47-1743), and Ca(OH)₂ (JCPDS No.01-073-5492) [9]. CaO is the active phase for transesterification process available in high intensity than CaCO₃ and Ca(OH)₂.

3.3 Transesterification of Avocado Seed Oil

3.3.1. Effect of methanol-to-oil molar ratio on biodiesel yield

The stoichiometric ratio for transesterification using methanol requires 3 moles of methanol for 1 mole of triglyceride. Reactions were performed at 65°C for 60 min with 5 wt % catalyst by varying the molar ratio of methanol-to-oil from 3 to 12. The result is shown in Figure 2.

![Effect of methanol-to-oil molar ratio](image)

**Figure 2.** Effect of methanol-to-oil molar ratio on biodiesel yield at 60 min reaction time and 5 wt % catalyst loading

The result, as illustrated in Fig. 2, showed that the best methanol-to-oil molar ratio was 6:1, resulted in 85.3% yield. At 9:1 and 12:1 methanol-to-oil molar ratio, biodiesel yield decreased because of the high amount of methanol used in the reaction, which increased solubility and made the glycerol barely separated [10]. At the methanol-to-oil molar ratio of 3:1, the yield also decreased because the amount of methanol used in the reaction was less than the 6:1 molar ratio reaction and produced excess triglyceride[11].
3.3.2. Effect of various reaction time on biodiesel yield

Biodiesel yield from the transesterification reaction was also influenced by reaction time. The reaction was conducted at 65°C, 6:1 methanol-to-oil molar ratio, and 5 wt % catalyst loading amount. The result is shown in Figure 3.

![Figure 3](image.png)

Figure 3. Effect of various reaction time on biodiesel yield at the condition of 6:1 methanol-to-oil molar ratio and 5 wt % catalyst

Figure 3 shows that the best reaction time for transesterification was 60 minutes with biodiesel yield of 85.3%. Biodiesel yield was decreased at reaction time 90 and 120 minutes because the transesterification process was heated too long that affected the quality of the oil. When the reaction run for 30 minutes, the biodiesel yield was also decreased because the mixing process of methanol, oil, and catalyst has not been completed and the reaction run slowly [12].

3.3.3 Effect of various catalyst loading amount on biodiesel yield

Various catalyst loading amounts ranged from 1 to 7 wt % on the basis of oil weight was investigated. The reaction was conducted at 65°C, methanol-to-oil molar ratio of 6:1, and the reaction time of 60 minutes. The result is presented in Figure 4.

![Figure 4](image.png)

Figure 4. Effect of various catalyst loading amount on biodiesel yield at the condition of 6:1 methanol-to-oil molar ratio and 60 min reaction time

Figure 4 shows that the best catalyst loading amount was 5 wt %, resulted in 85.3% yield. Biodiesel yield decreased at 1 and 3 wt% catalyst because of insufficient active phase available for the reaction to occur. Reaction with 7 wt% catalyst loading also yielded lower biodiesel, due to high amount of catalyst produced emulsion and gel that increased viscosity [13].

Based on the above result, the best biodiesel yield was 85.3% resulted from the reaction with the condition of 6:1 methanol-to-oil molar ratio, 60 min reaction time, and 5 wt% catalyst loading.
3.4 Characterization of biodiesel

3.4.1 Physical properties of biodiesel

The analysis of the physical properties of biodiesel according to SNI 7182-2012 includes viscosity and density. Based on the analysis of the best product, viscosity value was 4.23 cSt and the density was 0.86 g/mL. This value shows that biodiesel is not only made from good raw materials, but also with good processing. The characterization result is shown in Table 2.

| Analysis Method | Result | SNI |
|-----------------|--------|-----|
| Viscosity (cSt)  | 4.23   | 2.3–6.0 |
| Density (g/mL)  | 0.86   | 0.85–0.89 |

3.4.2 Chemical properties of biodiesel

Methyl ester that produced from the best operating condition was analyzed using GC-MS to determine the components of the fatty acid in biodiesel. The result from characterization shown in Figure 5 and Table 3.

Figure 5 shows that there are five peaks of the avocado seed oil methyl ester compound. Then each peak on the GC chromatogram was identified by a mass spectrophotometer, where each compound has a specific mass fragmentation pattern. Based on Table 3, the highest esters of avocado seed biodiesel is methyl oleate that indicated by peak number 4 with result of 57.39%.

Figure 5. Chromatogram of avocado seed biodiesel from GC-MS analysis

3.5. Reusability of catalyst

Heterogeneous catalyst can be reused in the reaction after being separated from the product. The result of reusability test of the catalyst is shown in Figure 6.

Based on the figure, biodiesel yield slightly decreased from 85.3% from reaction with fresh catalyst to 81.77% and 77% from reaction with the second and third cycle, respectively. This was caused by the decreasing of the active phase of CaO on the catalyst surface, which can be proven by the XRD analysis in Figure 7.

The figure shows that the large CaO content in fresh catalyst decrease significantly after the catalyst was used for three times in the transesterification process. A small amount of CaO reacts with
the atmospheric CO$_2$ and produce CaCO$_3$ which is a passive component in transesterification reaction[14].

Figure 6. Transesterification using reusable catalyst

Figure 7. Diffractogram of CaO catalyst; (a) fresh catalyst, (b) reused catalyst; 1)CaO, 2)CaCO$_3$, 3)Ca(OH)$_2$

In addition, biodiesel yield decreased by the deactivation of the catalyst due to blockage of catalyst pores by triglyceride from the oil during the reaction [15], thereby reducing the amount of active pores on the catalyst surface as seen from the SEM analysis that shown in Figure 8.

Figure 8 (a) shows the surface of the catalyst before reaction, the pores of the catalyst still visible. Meanwhile, in Figure 8 (b) the catalyst pores have been covered by oil during the reaction process.

Figure 8. Result of SEM analysis of CaO from eggshell; (a) fresh CaO, (b) reusable CaO
4. Conclusion
Avocado seed oil can be used as raw material for biodiesel synthesis over CaO from eggshell as catalyst. The best operating condition for the transesterification reaction was 6:1 methanol-to-oil molar ratio, 60 min reaction time and 5 wt% catalyst loading amount. The catalyst can be reused up to 3 reaction cycles with the biodiesel yield more than 75%. Characterization of the product showed that the highest ester compounds of biodiesel from avocado seed oil was methyl oleate and the physical properties of biodiesel produced met SNI 7182-2012.

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