Production of biodiesel from used cooking oil using blood cockle shell (Anadara Granosa) ash as catalyst

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Abstract. Biodiesel is renewable energy that can be renewed, biodegradable and environmentally friendly. Transesterification is a reaction which is used to produce biodiesel where this reaction uses catalyst which was made from blood cockle shell ash which has been combusted at the temperature of 850°C for 3 hours and the amount of the ash being used was 8%, 10% and 12% (m/m). The ash used was dissolved into methanol with the mole ratio of methanol to oil of 9:1, 12:1 (n/n) to obtain calcium methoxide. Used oil was filtered then esterificated by 3% of catalyst (m/m), H₂SO₄ 98% and methanol:oil TG (6:1) to reduce the FFA until it is less than 1%. Transesterification was done at the reaction temperature of 65°C for 3 hours and constantly stirred at the speed of 700 rpm. Quantitatively, optimum biodiesel yield obtained was 56.51% at the condition of 12% (m/m) of blood cockle ash, 12:1 mole ratio of methanol to used oil. The specification of the biodiesel such as density, kinematic viscosity and flash point at this condition matched the standard of biodiesel SNI 04-7182-2006 and according to gas chromatography analysis, the purity of the biodiesel produced is 98.79%.

1. Introduction
Biodiesel can be produced by transesterification by reacting vegetable oil and methanol. Commonly, biodiesel (methyl ester) produced shows the same characteristic as conventional fuel. Production of biodiesel usually uses homogeneous catalyst. By using homogeneous catalyst, whether it is acid or alkali catalyst, will make formation reaction of biodiesel happen fast and obtain high conversion of biodiesel. However, one of the disadvantages of using homogeneous catalyst is it will be difficult to regenerate the catalyst because it has been mixed with oil and methanol so that the separation process of the catalyst from the product become complex. Using this catalyst is also not environmentally friendly because it needs a lot of water for the separation process. Many researches has been done to solve the disadvantage of using homogeneous catalyst and mostly focus in using heterogeneous catalyst. Some heterogeneous catalysts which have been used in producing biodiesel are KNO₃/Al₂O₃, MgO, SrO, CaO, etc. CaO is often used because CaO is more environmentally friendly. Utilization of CaO from clam shell waste such as oyster shell, blood cockle shell, batik clam shell, mud crab shell, golden apple and snail shell has been studied recently and has been used as the source of CaO and also has been evaluated its effectiveness as catalyst in producing biodiesel [1].

Biodiesel (methyl ester) is renewable energy which can be renewed, biodegradable and environmentally friendly because there is almost no carbon monoxide (CO), carbon dioxide (CO₂), sulphur dioxide (SO₂) hydrocarbon (HC) or other particles which can cause respiratory disease is released to the environment [2]. Blood cockle shell ash has a high content of CaO. The substances contained in ash catalyst can be seen in table 1.
Table 1. Primary content of blood cockle shell ash.

| Component | Concentration (%) |
|-----------|------------------|
| CaO       | 69.02%           |
| Water     | 0.02%            |

From table 1 above, we can see that the main substances contained in blood cockle shell ash is CaO. The function of catalyst is to activate reactant so that at certain condition, reaction rate constant increase. Potassium hydroxide (KOH) is the catalyst which is often used in methanolysis and ethanolysis of raw oil and coconut oil which resulted yield of 90%. But, using homogeneous catalyst has some disadvantages such as corrosive, hard to separate from product and catalyst cannot be reused [3]. Used oil has high free fatty acid content so esterification of free fatty acid needs to be done by acid catalyst like sulphuric acid to form methyl ester. Reaction of esterification can be seen in figure 1.

![Esterification](image1.png)

**Figure 1.** Esterification of fatty acid to form methyl ester.

Transesterification is the reaction of oil and fat to form ester and glycerol. Reaction of transesterification can be seen in figure 2.

![Transesterification](image2.png)

**Figure 2.** Transesterification of triglycerides to form methyl ester.

In this transesterification, there are three reversible reactions respectively. First, conversion of triglyceride become diglyceride, then to monoglyceride. And the final step is to glycerin and fatty acid methyl ester [4]. Catalyst is usually used to accelerate reaction rate and yield. Excess alcohol is also used for equilibrium because of reversible reaction so that reaction shift to product side. So, when NaOH, KOH or other catalyst is mixed with alcohol, it will form alkali solution. Methanol (CH3OH), ethanol (C2H5OH), propanol (C3H7OH) or buthanol (C4H9OH) is often used in this reaction but methanol is mostly used because it is cheaper than other alcohol [3,5].

Recently, there are a lot of industries use heterogeneous catalyst because of the advantages it offers and it is environmentally friendly such as non-corrosive, easily separated from product by filtration and can be used in a longer time period. Besides, heterogeneous catalyst can increase the purity because side reaction can be eliminated. Separation of heterogeneous catalyst from product can be done easily [6].

Some researches have been done in order to find cheap, environmentally friendly yet resulted high biodiesel yield heterogeneous catalyst. They are done by Aladetuyi (2014) which made a research about producing biodiesel from palm kernel oil by using cocoa pod ash as heterogeneous catalyst [7]. Besides, Olugbenga (2013) also did a research about producing biodiesel from vegetable oil by using cocoa pod ash as heterogeneous catalyst [8].
According to the data, Indonesia produces 34,382 ton of blood cockle each year so that the utilization of the blood cockle shell as catalyst is to reduce the waste. The blood cockle shell contains calcite (CaCO$_3$), the combustion of the shell is done to produce ash and to convert the content in it become CaO at the amount of 69.02%. The blood cockle shell ash which contains CaO will be reacted with methanol to produce calcium methoxide (Ca(OCH$_2$)$_2$) which can accelerate transesterification of vegetable oil in making methyl ester [6].

Aldes, et al. made methyl ester from used oil by using blood cockle shell as catalyst at temperature of 900°C by using the procedure which was introduced by viriya-empikul with some steps such as transesterification, esterification and distillation to get pure methyl ester. Used oil has a high content of free fatty acid (FFA) and if it is transesterificated by blood cockle shell ash (alkali) will form soap so it needs esterification before transesterification [9].

By considering those theory, the research of utilization of blood cockle shell ash as catalyst in producing biodiesel from used oil by esterification and transesterification is needed to be done so that large amount of biodiesel can be produced and blood cockle shell ash can be used as heterogeneous catalyst.

2. Materials and methods

2.1. Tool
The tools used in this research were beaker glass, three neck rounded flask, separating funnel, oven, desiccator, picnometer, erlenmeyer, condenser reflux, furnace, titration set, flask, thermometer, hot plate, viscosimeter ostwald, ball mill and filter paper.

2.2. Material
The material used as catalyst in this research was blood cockle shell which was collected from traditional market meanwhile the raw material to make biodiesel was used oil which was collected from restaurant. This research was done in research laboratory and chemical industry laboratory of Chemical Engineering Department, Faculty of Engineering, University of Sumatera Utara.

2.3. Procedure
2.3.1. Blood cockle shell ash preparation. The blood cockle shells were washed by water until clean. They were dried in the oven at the temperature of 110°C for 24 hours. Then, they were put in desiccator for 24 hours. The shells were crushed by using ball mill then they were calcinated by furnace at 900°C for 3 hours. The ash was put in the desiccator for 24 hours again and then it was sieved by 100 mesh sieve [9].

2.3.2. Esterification. 150 gram of used oil was reacted with methanol with 6:1 mole ratio of methanol to oil and 3% (m/m) of catalyst H$_2$SO$_4$ was added and reacted at the temperature of 60°C for 90 minutes with the stirring speed of 250 rpm. After reaction reached, sample was poured into separating funnel and was left for 2 hours at room temperature until it form 2 layers. Then the layer was separated between the ester and water. Esterificated sample was analyzed until the free fatty acid was below 1% and was heated in the oven at 110°C until the mass is constant [10].

2.3.3. Transesterification. 8% of blood cockle ash was stirred with methanol at the mole ratio of 9:1 (methanol to oil) in a beaker glass for 24 hours. Sample which has been esterificated from used oil was poured into the three neck rounded flask with thermometer, stirring motor and condenser reflux and was heated until 60°C. Then, the solution of the blood cockle ash and methanol was poured into the three neck rounded flask with oil in it. The mixture was heated until 65°C on a hot plate and was left for reaction for 3 hours at constant temperature and constant stirring speed of 700 rpm. The mixture was poured into separating funnel through filter paper and was left for 24 hours at room temperature for separation. Lower layer (glycerol) was separated so that only upper layer (biodiesel) was left. Biodiesel was washed by 50°C warm water in a separating funnel to dissolve catalyst and soap residue.
This washing process was done slowly until the water layer is clear. After it was washed, the biodiesel was dried at 110°C until there is not any gas left and the mass then weighed. Transesterification process was repeated for catalyst amount variable of 10% and 12% and the mole ratio of methanol to oil 9:1 [11,1].

The biodiesel produced was analyzed qualitatively and quantitatively. They are yield analysis, purity, density, kinematic viscosity according to SNI 04-7182-2006 standard which is shown in table 2.

| Parameter                          | Standard          |
|------------------------------------|-------------------|
| Density at 40°C, kg/m³             | 850-890           |
| Kinematic viscosity at 40°C, mm²/s (cSt) | 2.3-6.0          |
| Flash point, °C                    | Min. 100          |
| Free glycerol, % mass              | Max. 0.02         |
| Total glycerol, % mass             | Max. 0.24         |

3. Result

3.1. Raw material analysis
Gas chromatography was done to used oil as raw material to see the composition of fatty acid contained in it and to count the molecular weight of used oil (in triglyceride form).

![Chromatogram of composition of fatty acid in used oil.](image)

From the chromatogram in figure 3 above we can see the composition of fatty acid of used oil which is listed in table 3 below.

| Retention time (minute) | Component            | Composition (%) |
|-------------------------|----------------------|-----------------|
| 6.082                   | Caprylic acid (C₈:0) | 0.1265          |
| 10.098                  | Koproat acid (C₁₀:0) | 0.0311          |
| 13.648                  | Lauric acid (C₁₂:0)  | 0.3722          |
| 16.653                  | Myristic acid (C₁₄:0)| 1.0871          |
From the gas chromatography analysis, the most dominant fatty acid are palmitic acid \((C_{16:0})\) and oleic acid \((C_{18:1})\) with the amount of 39.7893% and 41.9186% respectively. Free fatty acid contained in used oil can be seen in table 4.

Table 4. Free fatty acid in used oil.

| Free Fatty Acid (%) | Before esterification | After esterification | % FFA decreased |
|---------------------|-----------------------|----------------------|-----------------|
| Palmitic acid \((C_{16:0})\) | 19.405 | 39.7893 | 0.819 | 73.70 |
| Palmitic acid \((C_{16:0})\) | 19.688 | 41.9186 | 0.860 | 73.20 |
| Stearic acid \((C_{18:0})\) | 21.713 | 4.5168 | 0.888 | 74.70 |
| Oleic acid \((C_{18:1})\) | 22.051 | 9.6923 | 0.901 | 75.10 |
| Linoleic acid \((C_{18:2})\) | 22.577 | 0.2870 | 0.942 | 76.46 |
| Linolenic acid \((C_{18:3})\) | 23.314 | 0.3446 | 0.956 | 76.82 |
| Arachidic acid \((C_{20:0})\) | 24.056 | 0.3896 | 0.3446 | 76.82 |
| Eikosenoic acid \((C_{20:1})\) | 24.467 | 0.3896 | 0.3446 | 76.82 |

From the table above, we can see that by esterification, the free fatty acid in used oil decreased until it reached under 1%.

3.2. Yield analysis
The relation between amount of catalyst used (% m/m) and biodiesel yield can be seen in figure 4.

![Figure 4. Effect of amount of catalyst used to biodiesel yield.](image)

Achami, et al. (2013) made a research of making biodiesel without catalyst for 2-6 hours where there is no methy ester produced [11]. There is a probability that biodiesel can be made without using catalyst but it need a lot of time. In figure 4, we can see effect of catalyst to biodiesel yield with different mole ratio of methanol and oil. In the ratio of 9:1 and 8% of catalyst, the yield is 6.3% and by increasing the catalyst to 10% and 12%, it resulted that the yield is also increase to 25.71% and 26.94% respectively. In the ratio of 12:1 and 8% of catalyst, the yield is 36.04% and by increasing the catalyst to 10% and 12%, the yield is also greater. This indicates that the transesterification depends on CaO catalyst from blood cockle shell catalyst. The bigger yield obtained in this research caused by the catalyst has reacted with methanol and has fully formed calcium methoxide meanwhile the lower yield
caused by the catalyst has not reacted with the methanol and the reaction did not shift to the product side and it caused reactant reacts more with reactants and lower the activeness of the catalyst. The reaction of CaO with triglyceride form glycerol and soap. This reaction will take some biodiesel formed and biodiesel which get caught in the emulsion so that it formed more glycerol and soap than biodiesel [12,13,16].

From figure 4, we can also see that the best condition in making biodiesel is by using 12% of catalyst and with 12:1 mole ratio of methanol to oil gave 56.51% yield, the highest yield obtained in this research. The result of using blood cockle shell ash as catalyst resulted higher yield and purity than the research before in making biodiesel from used oil using CaO catalyst which was done by Hilary Ruto and Christopher Enwerewadu using 12:1 mole ratio of methanol to oil where the yield they obtained was 46.92% and Aldes, et al. did not show the yield and purity from their research [9,14].

3.3. Analysis of the purity of biodiesel

The relation of amount of catalyst to the purity of biodiesel can be seen in figure 5 below.

![Figure 5. Effect of amount of catalyst used to the purity of biodiesel.](image)

From figure 5, we can see the effect of amount of catalyst from blood cockle shell ash to the purity of biodiesel. The figure above shows that, at the mole ratio of methanol to oil of 9:1, the purity of biodiesel increased from 8% of catalyst to 10% of catalyst. The purity reached 98.42%. However, the purity decreased to 97.33% when 12% of catalyst was used. Meanwhile, at 12:1 of mole ratio of methanol to oil, increasing amount of catalyst from 8%, 10% and 12% also increased the purity of biodiesel. The highest purity of the biodiesel obtained was 98.79% by using 12% catalyst and 12:1 methanol to oil ratio. 12% catalyst was mixed with 12:1 methanol to oil ratio caused more calcium methoxide was formed so that collision between triglyceride molecule with alcohol become more effective and product is formed faster in a certain time [12]. Figure 3 shows gas chromatography result of highest biodiesel. This result shows that the purity of biodiesel produced was 98.79% meanwhile the other are monoglyceride and internal.

3.4. Density analysis

Density is intensive magnitude which is related to heat value and power produced by diesel machine per volume of fuel [5].

| Catalyst (% m/m) | Density (kg/m³) 9:1 methanol to oil ratio | Density (kg/m³) 12:1 methanol to oil ratio |
|------------------|--------------------------------------------|--------------------------------------------|
| 8                | 887.69                                     | 873.37                                     |
| 10               | 877.89                                     | 872.44                                     |
| 12               | 874.62                                     | 856.23                                     |
Table 5 shows that the more catalyst used and the bigger mole ratio resulted smaller density of biodiesel. It is caused by termination of glycerol from triglyceride has happened so that compound with smaller molecule was formed. Density was intensive magnitude which is related to heat value and power produced by diesel machine per volume of the fuel. According to Indonesia National Standard (SNI 04-7182-2006), density of biodiesel at 40°C is 850-890 kg/m³. From the research, the density of biodiesel obtained is about 856.26-877.89 kg/m³ so that the biodiesel produced meet the standard of biodiesel. If the density of biodiesel is bigger than the standard then it can not be used because it will increase emission and cause damage to the machine [2].

3.5. Viscosity analysis
High viscosity diesel oil will make the process of forming mist particle harder in atomization of fuel in machine and the combustion will not be perfect. But, when the viscosity is too low, it will cause leakage in fuel injection pump. The viscosity of biodiesel produced is as follows.

| Catalyst (% m/m) | Kinematic viscosity (cSt) | Kinematic viscosity (cSt) |
|------------------|--------------------------|--------------------------|
|                  | 9:1 methanol to oil ratio | 12:1 methanol to oil ratio |
| 8                | 5.876                    | 5.722                    |
| 10               | 5.873                    | 5.102                    |
| 12               | 5.772                    | 4.082                    |

According to Indonesia National Standard (SNI 04-7182-2006), kinematic viscosity of biodiesel at 40°C is 2.3-6.0 cSt. The result of this research shows the kinematic viscosity of biodiesel produced about 4.082-5.876 cSt. The kinematic viscosity of biodiesel produced has met the standard of biodiesel kinematic viscosity [15].

4. Conclusions
From this research, it can be concluded that blood cockle waste can be used as catalyst to produce biodiesel. In this research, the maximum yield of biodiesel was 56.51% and the purity was 98.79% at the condition of 65°C reaction temperature, 12:1 methanol to oil molar ratio, 12% of catalyst and 3 hours of reaction time.

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