The utilization of chicken bones as heterogeneous catalyst (CaO) in the production of fatty acid ethyl ester from crude palm oil by using ethanol as solvent

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1. Introduction

This world is going to undergo great energy crisis caused by the limited fossil fuel such as crude oil, gas and coal [1]. This fossil fuel is categorized as non-renewable source of energy which can not be produced in a short time after it has been used [2]. Fatty acid ethyl ester is also known, as biodiesel is one of the most potential alternative energy because it is renewable and environmentally friendly. Fatty acid ethyl ester is usually produced by transesterification process of oil or fat (vegetable oil or animal fat) with alcohol to produce fatty acid alkyl ester and glycerol as byproduct [3]. Fatty acid ethyl ester mixture can be used as ignition compression of diesel machine with or without modification. Combustion of fatty acid ethyl ester is clearer, easy to use, biodegradable, non-toxic and free of sulphur and aromatics [4].

Production of CPO in Indonesia is increasing year to year until it reached 24.1 million tons in 2011 and 26.5 million tons in 2012 [5]. CPO contains free fatty acid which can be converted into fatty acid ethyl ester. This acid is converted to fatty acid ethyl ester by transesterification using alcohol which makes CPO a good potential raw material in producing fatty acid ethyl ester [6]. The production of fatty acid ethyl ester from low quality oil is begun with esterification to reduce the free fatty acid content. The high free fatty acid content is not wanted in transesterification because it can cause soap formed during the process which resulted lower yield and harder to separate the product [7]. Transesterification of vegetable oil or animal fat by using alcohol with the present of catalyst is the main process of producing biodiesel. There are a lot of catalyst which can be used, such as alkali.
catalyst, acid catalyst and enzyme catalyst [8]. Regeneration of homogeneous catalyst after transesterification is hard and resulted toxic waste. The research of alternative catalyst to substitute homogeneous catalyst has been done recently and researches has found that heterogeneous catalyst has some advantages than homogeneous catalyst such as it is easily separated from the product, it can be reused, low water content and more biodegradable [2].

By considering the description above, further research about producing fatty acid ethyl ester using chicken bones ash as heterogeneous catalyst is needed to be done to find out more heterogeneous catalyst which can be used in producing fatty acid ethyl ester and resulted high yield of fatty acid ethyl ester.

2. Materials and methods
2.1 Raw materials and tools
The main raw materials used in this research are crude palm oil as the material which will be converted into fatty acid ethyl ester by transesterification and chicken bones as heterogeneous catalyst to produce fatty acid ethyl ester. The tools used in this research are erlenmeyer, magnetic stirrer, hot plate, separating funnel, beaker glass, measuring glass, digital scale, stirring rod, thermometer, furnace, three neck rounded flask and oven.

2.2. Calcination of chicken bones
The chicken bones was collected and boiled for 20 minutes. Then, it was dried under the sun for a few days. It was crushed by using ball mill and combusted by furnace at 1000°C for 4 hours until it formed ash. It was sieved by using 100 mesh sieve [9].

2.3. Esterification
150 g of CPO was poured into three neck rounded flask which was equipped by reflux condenser, thermometer and magnetic stirrer. Methanol was poured into the flask with the ratio of methanol to CPO at 6:1 and 3% of H$_2$SO$_4$ was added. The reaction temperature was maintained at 60°C for 90 minutes at 250 rpm stirring speed. After the reaction was done, the mixture was poured into separating funnel and was left until it formed two layers which was methanol at the upper layer and the lower layer consisted triglyceride, methyl ester, residual free fatty acid and residual catalyst. The lower layer was separated and washed by 150 ml of aquaest twice. Then, it was dried in the oven at 110°C until the mass is constant. The FFA of the oil should be under 5% after esterification then transesterification can be done.

2.4. Transesterification
5% (w/w) of chicken bones ash was put into a beaker glass and then ethanol was added at the ratio of 13:1 (ethanol to CPO) and was left for 24 hours. Then, CPO was poured into a three necked rounded flask which was equipped with reflux condenser, thermometer and magnetic stirrer over a hot plate. The chicken bones ash and methanol mixture was poured into the flask. The mixture was heated by hot plate until it reached 60°C and the temperature was maintained constant at 500 rpm stirring speed. After the reaction was finished, the mixture was poured into separating funnel and was left until it formed two layers. The lower layer, a mixture of the catalyst, ethanol and glycerol, was separated from the upper layer. The upper layer was washed until it was clean. Then, it was dried by using an oven. This procedure was repeated for another variable of this research.

3. Result and discussion
3.1. Analysis of crude palm oil as raw material
Gas chromatography was done to find the composition of fatty acid in crude palm oil and to find out the molecular weight of crude palm oil (in triglyceride form). The figure above shows the composition of the crude palm oil which can be seen in Table 1.
Table 1. Fatty acid composition of CPO (crude palm oil).

| Peak Number | Retention Time (minute) | Component                  | Composition (% w/w) |
|-------------|-------------------------|----------------------------|---------------------|
| 1           | 13.656                  | Lauric acid (C_{12:0})     | 0.1896              |
| 2           | 16.670                  | Myristic acid (C_{14:0})   | 0.8921              |
| 3           | 19.421                  | Palmitic acid (C_{16:0})   | 38.7914             |
| 4           | 19.704                  | Palmitoleic acid (C_{16:1})| 0.1573              |
| 5           | 21.734                  | Stearic acid (C_{18:0})    | 4.6474              |
| 6           | 22.075                  | Oleic acid (C_{18:1})      | 42.5686             |
| 7           | 22.614                  | Linoleic acid (C_{18:2})   | 11.9100             |
| 8           | 23.352                  | Linolenic acid (C_{18:3})  | 0.3003              |
| 9           | 24.106                  | Arachidic acid (C_{20:0})  | 0.3932              |
| 10          | 24.519                  | Elcosenoic acid (C_{20:1}) | 0.1501              |

Table 1 shows the composition of unsaturated fatty acid is 55.086% and the composition of saturated fatty acid is 44.914%. The average molecular weight of CPO free fatty acid is 270.942118 g/mol and the average molecular weight of CPO triglyceride is 850.982348 g/mol.

3.2. Analysis of free fatty acid in crude palm oil

High level of free fatty acid in crude palm oil can prevent the reaction to happen and it cause soap formed while transesterification process is done. So that, free fatty acid analysis was done. The free fatty acid level can be seen in table 2.

Table 2. Free fatty acid level of crude palm oil.

| Before esterification | After esterification | %FFA reduced |
|-----------------------|----------------------|--------------|
| 1.330                 | -                    | -            |
| 5.141                 | 0.475                | 90.07        |

Table 2 shows the FFA of CPO before esterification. The first FFA analysis of the CPO resulted 1.330% and was used in transesterification without esterification. The result was soap formed after the process. The next FFA analysis of CPO resulted 5.141% and esterification was done to the CPO. The FFA of the CPO after esterification become 0.475%.

Transesterification is affected by the free fatty acid level of the raw material so that the free fatty acid level should be as low as possible [1]. Esterification was done to reduce free fatty acid of CPO. The higher the free fatty acid in CPO will cause the more possibility of soap formed. The soap formed will cause the separation process is harder to be done and it will increase the viscosity and the separation cost also [10]. In table 2, we can see that after esterification the free fatty acid reduced was 90.07%.

3.3 The effect of catalyst concentration (%w/w) to fatty acid ethyl ester yield

The concentration of catalyst used in this research was 5%, 6% and 7% (%w/w). The effect of catalyst concentration to fatty acid ethyl ester yield can be seen in figure 2. The effect of catalyst concentration to yield at 7 hours of reaction time and different molar ratio can be seen in figure 2. It shows that the more the chicken bones catalyst used caused the higher the yield obtained. The research which was done by Yin Tang, et al. (2015) showed that the higher the CaO catalyst used the higher the yield obtained [11]. Among some catalysts, calcium oxide (CaO) is the most used in producing fatty acid ethyl ester because it has high alkali, it can react well with the reactant in transesterification, low solubility and non-toxic.
3.4 Effect of temperature to fatty acid ethyl ester yield.

The temperature used in this research were 60, 65 and 70°C. The effect of temperature to yield of fatty acid ethyl ester is shown in Figure 3 below.

Figure 3. The Effect of temperature to fatty acid ethyl ester yield.
Temperature variation is one of the most important variable in producing fatty acid ethyl ester. Figure 3 shows the effect of temperature to fatty acid ethyl ester yield. It shows that the higher the temperature used caused the higher the yield of fatty acid ethyl ester obtained. Temperature affects reaction and result of fatty acid ethyl ester producing. Higher temperature can decrease the viscosity of oil and increase the reaction. However, if the temperature is higher than the optimum temperature, the production of fatty acid ethyl ester will decrease. Reaction temperature must be lower than boiling point of alcohol so that the alcohol does not evaporate [13].

Puneet and Sharma (2016) [14] has done a research on producing biodiesel by using methanol and ethanol in different temperature variation. It was found that the optimum reaction temperature was 61.3°C at 8.42: molar ratio, 1.21% of catalyst and 2 hours of reaction time which resulted 77.4% yield of biodiesel [13]. Kaur and Amjad (2013) has also done a research by using Li/ CaO as catalyst and ethanol as solvent in producing biodiesel from cotton seed oil. It was found that the optimum temperature was at 65°C and at 12:1 molar ratio, 5% of catalyst and 2.5 hours of reaction time. The yield obtained was 98% [14].

Figure 3 shows that the yield increased as the temperature gets higher. The best condition in this research was at 70°C, 17:1 molar ratio which resulted 90.052% of fatty acid ethyl ester yield. If this research is compared with the research by Kaur and Amjad [15] and Puneet and Sharma [14] as mentioned above, it was found that this research has lower yield than Kaur and Amjad research. However, the yield of fatty acid ethyl ester in this research is higher than the yield obtained in Puneet and Shamar research although the time, temperature, catalyst concentration and molar ratio used were higher than theirs but it resulted the higher yield of fatty acid ethyl ester.

4. Conclusion
Some conclusions can be concluded from this research, they are:

- Esterification is the reaction between fatty acid and alcohol to produce ester. Esterification is a must done process if the free fatty acid of crude palm oil is high because it will form soap.
- Chicken bones is waste which can be used as heterogeneous catalyst (CaO).
- According to this research, the highest yield was 90.052% at the condition of 7% of catalyst, 17:1 molar ratio and 70°C of reaction temperature.

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