The Produce of Methyl Ester from Crude Palm Oil (CPO) Using Heterogene Catalyst Ash of Chicken Bone (CaO) using Ethanol as Solvent

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Abstract. Methyl Ester (methyl ester) is generally made by trans esterification using heterogeneous base catalyst. To simplify the separation, the heterogeneous catalyst is used, such as CaO, which in this case was isolated from chicken bones made by softening chicken bones and do calcination process. Some other important variables other than the selection of the catalyst is the catalyst dosage, molar ratio of ethanol to the CPO and the reaction temperature. The best result from this observe is at the molar ratio of ethanol to the CPO is 17:1, the reaction temperature is 70 °C and 7% catalyst (w.t) with reaction time for 7 hours at 500 rpm as a constant variable, got 90.052 % purity, so that this result does not get the standard requirements of biodiesel, because of the purity of the biodiesel standard temporary must be achieve > 96.5 %. This study aims to produce methyl ester yield with the influence of the reaction temperature, percent of catalyst and molar ratio of ethanol and CPO. The most influential variable is the temperature of the reaction that gives a significant yield difference of methyl ester produced. It’s been proven by the increasing temperature used will also significantly increase the yield of methyl ester.

1. Introduction
The world gradually towards energy crisis is very great due to the availability of fossil fuels such as petroleum, natural gas and coal are limited. Fossil fuels are categorized as a non-renewable energy sources that cannot be replaced in a relatively short time after exploited [1]. Biodiesel / Methyl Ester is one of the most potential alternative energy because it is renewable and environmentally friendly. Biodiesel is commonly produced by the trans esterification of oils or fats (vegetable oils and animal fats) with alcohol to produce alkyl esters, fatty acids, and glycerol as a byproduct [2].

Agricultural areas in Indonesia constitute 60% of the total land. This area is large enough to produce palm oil which is used as raw material for large-scale production of biodiesel [3]. Production of CPO (Crude Palm Oil) in Indonesia continues to increase each year until 2011 and 2012 CPO production reached 24.1 and 26.5 million tons [4].

Synthetic of Biodiesel / Methyl Ester from low-quality oil should be esterificated to reduce the levels of Free Fatty Acid (FFA). High FFA is undesirable during trans esterification process because it
cause the formation of soap, loss of yield, and the difficulty of separation of the product [5]. According to SNI, the standards of biodiesel should reach the level of purity> 96.5% [6].

Based on the literature reviewed, the catalyst of the chicken bones (CaO) is a heterogeneous catalyst which has been successfully used in the production of Biodiesel / Methyl Ester by trans esterification with a good performance, considering that a chicken bone is waste that can still be used as a catalyst. Farooq, et al., 2014 did the synthesize of biodiesel from waste cooking oil with chicken bones as catalyst that produces a yield of 89.33% [7]. Mohadi, et al., 2013 had previously done CaO preparation and characterization of chicken bones, where its percentage of CaO reached around 56.78% [8]. Therefore, the researchers examined the effect of chicken bones as catalyst in the manufacture of biodiesel from different sources, such ad from crude palm oil. Research purposes of this study to produce methyl ester yield with the influence of the reaction temperature, percent of catalyst and molar ratio of ethanol and CPO.

2. Method

2.1. Raw Material

The materials used in this study were derived from Palm Research Center located in Brigjen Katamso street, Medan and technis ethanol as a solvent derived from chemical store Rudang Jaya located in DR. Mansyur, Medan. Chicken Bone ash as a catalyst sourced from home eating KFC at Gajah Mada, Medan.

2.2 Analysis FFA (Free Fatty Acid)

For analysis of the levels of FFA CPO was done by standard titration AOCS (Official Method ca5a-40).

2.3 Calcination of Chicken Bone

Chicken bone calcination process is done by collecting chicken bones at KFC Medan, then the drying and pulverized using a ball mill, then burned with the furnace at temperatures 1000 °C for 4 hours to ashes and then filtered 100 mesh then the results, the CaO content analysis with AAS (Atomic Absorption Spectrometer) Shimadzu Brands and get 65% CaO content.

2.4 Esterification Process

Procedures of esterification is performed based on the research conducted by [9]. The esterification process use sulfured acid (H2SO4) as catalyst to reduce FFA (Free Tatty Acid) from the Crude Palm Oil (CPO).

2.5 Trans esterification Process

Procedures of trans esterification is performed based on the research conducted by Suriani et all., [9] starting from a chicken bone that has been refined using a ball mill put into furnace with calcination temperature of 1000 °C. The equipment used is a hot plate, furnace, digital balance, Ostwald viscos meter, ball mill, and oven. CPO that already esterified to reduce the levels of fatty acids, are incorporated into the trans esterification process ethanol is added in accordance with the variation. The experiments were performed with variations percent catalyst 5%, 6% and 7% and the variation of the molar ratio of methanol and CPO 13: 1, 15: 1, 17: 1 as well as variations in temperature of 60 °C, 65 °C and 70 °C with variations fixed reaction time of 7 hours and stirring speed of 500 rpm. The reaction product is then dried in the oven, then analyzed by GC-MS (Gas Chromatography-Mass Spectrophotometry) to determine the purity of the biodiesel produced.

2.6 Characterization

To see the purity of methyl ester using GCMS (Gas Chromatography Mass Spectrometry) type Shimadzu QP 2010 brand.
3. Result and Discussion

3.1. GC analysis CPO Materials

Raw materials used in this study is the CPO. Crude Palm Oil (CPO) the extraction results analyzed using GC to determine the composition of fatty acids acids contained therein. The results of this analysis can be seen in figure 1.

**Figure 1.** Composition of fatty acids CPO

From the figure 1 it can be seen that the unsaturated fatty acid composition of 55.086% and saturated fatty acid composition of 44.914%. From the calculations, then earned an average molecular weight of 270.942118 FFA CPO g / moll and an average molecular weight of triglycerides CPO 850.982348 g / mol. To do trans esterification FFA from CPO must < 1%. FFA content of CPO (Crude Palm Oil) before and after esterification can be seen in table 1.

| Esterification | Esterification | Decreases FFA |
|----------------|----------------|---------------|
| 5,141          | 0,475          | 90,07         |

Table 1. Decreases of FFA Before and After Esterification

The table is about the decreases of FFA before and after esterification
3.2. Influence of % Catalyst and Molar Ratio to Yield Methyl Ester
As for the effect of the acquisition of catalyst per cent methyl ester yield is shown in figure 2.

![Graph showing the effect of catalyst and molar ratio on yield](image)

**Figure 2.** The effect of catalyst of the molar ratio to yield.

The relation between the concentration of the catalyst to the yield and purity of the methyl ester with a variety of reaction time on the reaction time of 7 hours and the reaction temperature remained 65 °C can be seen in Figure 1. From Figure 2 it can be seen that the higher the percent of catalyst used chicken bones then yield generated will be even greater.

Research conducted by Yin Tang, et al. (2015) showed that the higher percent CaO catalyst is used, the resulting yield also increased significantly [10].

Among several catalysts, heterogeneous catalysts calcium oxide (CaO) are most often studied as a material catalyst in the manufacture of biodiesel for having alkalinity is high, the reaction activity in which the active site of the catalyst reacts with the reactants in the trans esterification high in mild reaction conditions, low solubility and non-toxic.

3.3. Influence of % Catalyst and Molar Ratio to Purify Methyl Ester
As for the effect of the acquisition of purity methyl ester catalysts are shown in figure 3.

![Graph showing the effect of catalyst and molar ratio on purity](image)

**Figure 3.** The effect of catalyst and the molar ratio to purity.

Farooq, et al have conducted research waste cooking oil trans esterification catalyst with chicken bones (CaO) in the manufacture of biodiesel. Comparison of the amount of the catalyst under study is from 1-8% and a maximum biodiesel / methyl ester yield (89.33%) achieved at 5% by weight, the molar ratio of 15:1, at temperature of 65 °C with a reaction time of 4 hours [11]. Maneerung, et al. (2016) conducted a study on the production of Biodiesel / Methyl Ester by transesterification of oils jelanta using CaO catalyst of chicken manure. In this study, the number of catalysts studied were 2.5, 5, 7.5, 10 and 20%. Optimum condition was obtained in the amount of catalyst which is at 7.5%, molar ratio of 15:1 with a temperature of 65 °C during 3 hours with high purity is at 97.2% [11]. When compared
with the research conducted by researchers, the best conditions in this study there at 7% percent of the catalyst with a molar ratio of 17: 1, 7 hours, the reaction temperature 70 ° C which gives purity methyl ester by 90.052 %, the experiments conducted by researchers worse still visible from the resulting purity, temperature and time are much larger. These results also show that the results are not meeting standards for biodiesel, where the purity of Biodiesel / Methyl Ester should reach <96.5%.

The relation between the concentration of the catalyst to the purity of the methyl ester with a variety of reaction time on the reaction time of 7 hours and the reaction temperature remained 65 ° C can be seen in Figure 3. From Figure 3 it can be seen that the higher percent chicken bone catalyst used then the resulting purity will the greater. Reaction trans esterification to get optimal methyl ester can be shown in table 2.

| Table 2. Reaction Trans esterification to Get Optimal Methyl Ester |
|-----------------|-----------------|-----------------|
| Ratio Molar | Temperature Reaction | % Purity of Methyl Ester |
| 17 : 1 | 70°C | 90,052 |

The table is about the maximum purity of trans esterification

3.4. Influence of Molar Ratio and Temperature to Yield Methyl Ester
As for the effect of the acquisition of purity methyl ester catalysts are shown in figure 4.

![Figure 4. The effect of molar ratio and temperature to yield](image)

The effect of the molar ratio and temperature to yield of methyl ester with a temperature variation of the catalyst remains 7% and 7 hours can be seen in figure 4. From figure 4 it can be seen that the higher the concentration the molar ratio of solvent used, the yield to be greater.

4. Conclusion
The esterification process is carried out on raw materials CPO can lower FFA levels by 87.6%, as was converted into methyl ester, and Chicken bone can be used as catalysts biodiesel by utilizing the CaO content therein. Results mester methyl highest yield is 90,052% obtained at 70 ° C operating conditions with a dose of the catalyst 7% (w / w), molar ratio of methanol: CPO at 17: 1 for 7 hours. This research has not qualified biodiesel standard for the highest purity only reaches 90,052%, while the purity standard biodiesel should reach > 96.5%
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