The effects of catalysts type, molar ratio, and transesterification time in producing biodiesel from beef tallow

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Abstract. The high level of air pollution from combustion emissions and the lack of petrodiesel feedstock sources becoming a problem that can not be ignored. Therefore, to overcome these problems researchers developed alternative fuels that are environmentally friendly such as biodiesel. Biodiesel is produced through a transesterification reaction that reacts vegetable oils or animal fats with an alcohol assisted using an alkaline or acidic catalyst. This research was conducted to find out the influence of catalyst type, molar ratio of alcohol and fat, and transesterification reaction time to the yield and the characteristics of biodiesel produced. The transesterification reaction takes place at 65°C, and the catalyst weight is 1.5% by weight of beef tallow. Variations of catalyst type are NaOH and MgO, methanol molar ratio of 6:1, 9:1, and 12:1, and transesterification time for 1 hour, 2 hours, and 3 hours. The results showed that the optimum condition of the reaction using NaOH catalyst, molar ratio 6:1, and time for 1 hour with yield value 43.64%, density 0.84392 gr/ml, viscosity 5.7057 cSt, flash point 113.5°C, calorific value 9296.9 cal/gr, acid number 0.00992, and sulfur content 39 gr/kg.

1. Introduction
Fuel Consumption as renewable energy in Indonesia is low, less than 10% of total energy consumption, so some research on renewable energy will continue to be developed. Beef tallow is rarely consumed by people because it can cause cardiovascular disease. So it is very potential to be converted into biodiesel which is one of the environmentally friendly fuel. Biodiesel is a renewable fuel produced from vegetable oils or animal fats which used for diesel engines. The advantages of using biodiesel are renewable raw material, produce lower NOx emissions, and safer in terms of storage. Biodiesel is a fuel for diesel engines in which the raw materials of manufacture and the fatty acid composition of natural origin, such as vegetable oils and animal fats. Beef tallow potentially can be used as biodiesel because of its big availability, economical rates, and rarely consumed by the public because it can cause a variety of cardiovascular diseases.

Biodiesel with raw materials such as beef tallow can be obtained through a transesterification reaction with the aid of a homogeneous catalyst NaOH [3]. The use of homogeneous catalysts have various drawbacks such as difficulty in separation between the product and the catalyst, liquid phase operation that restricted certain operating conditions, and can not be regenerated for reuse. To overcome this problem, one solution being developed is the use of a heterogeneous catalyst in the manufacture of biodiesel. Biodiesel production using heterogeneous catalysts is very potential for economical production processes due to its reusable properties [5].
2. Beef Tallow
Beef tallow is one of many residual material from soap industry, but when this market is overloaded, the fats are disposed in a sanitary landfill. Beef tallow is one of the ingredients to make biodiesel which has fatty acid content. The qualities of beef fat are determined by color, solidification temperature of fatty acids, free fatty acid content (FFA), saponification number, and iodine number. Tallow fatty acid content at the most is palmitic, oleic and stearic. These fatty acids when reacted with an alcohol and a catalyst, it can be formed biodiesel (FFA less than 0.5%) and soap (FFA more than 0.5%). Free fatty acids from tallow are about 0.51-7.0%.

3. Methods
The study was conducted using two-stage reaction method, esterification and transesterification. The raw materials used are beef, magnesium carbonate, methanol, and sodium hydroxide. The variations used in this research are catalyst type, molar ratio of methanol and fat, and transesterification reaction time. The steps on this research are: Wash off the beef tallow and wipe off the dirt, then cut into small pieces, Melt the beef tallow by boiling them and stir. Enter into the oven at 110°C for 1 hour to remove the water content. Magnesium oxide catalyst preparation was carried out by inserting the MgCO₃ powder into the oven at 70°C. for 5 hours to remove the moisture content, Calcination MgCO₃ at a temperature of 800°C for 2 hours to produce MgO. Beef tallow that have been heated and in liquid conditions are incorporated into the reflux apparatus. Esterification of beef fat using methanol with methanol ratio and oil 9:1. Add the H₂SO₄ 1M catalyst as much as 0.5% by weight of cow fat. The mixture was reacted at 60° C. for 3 hours. The results of this reaction formed two layers of methanol and methyl ester in the upper layer, and the bottom of the form of triglycerides. This lower layer will be used for transesterification reaction stage, Triglycerides of previously introduced cow fat esterification are incorporated into a three-neck flask equipped with reflux condensers, thermometers and magnetic stirrers. Enter the catalyst (NaOH and MgO) variations of 0.8% by weight of triglycerides into methanol according to the variation in their molar ratio with oil (6:1, 9:1, and 12:1), during the specified time variation (1 hour, 2 hours, and 3 hours). The reaction product is inserted into the separating funnel, let stand for one day and it will form two layers. The top layer is methyl esters, methanol, and unreacted triglycerides and a lower layer of glycerol. While the use of MgO catalyst consists of three layers with the bottom layer of solid MgO mixture and a number of glycerol. Wash methyl ester that has been produced using aquadest temperature of 85°C until the color of washing water is not clouded. The product is heated at 105°C for 10 minutes to remove the moisture inside it.

4. Results
If the free fatty acid content of more than 0.5% would require esterification stage to reduce the levels of free fatty acids. Free fatty acid content of waste tallow derived from 0.52% titration method that needs to be done first esterification and transesterification reaction is then performed. Based on the results of research conducted biodiesel produced meets the quality of Indonesian National Standard (SNI) no. SNI 7182: 2015 in terms of viscosity, flash point, sulfur content, and acid numbers.
4.1. The Effects of Catalyst Type, Transesterification Time, and Molar Ratio to Biodiesel Yield

![Figure 1](image1.png)

Based on Figure 1, the highest yield average is obtained from the use of NaOH catalyst type. This is due to the alkaline effect of each catalyst, although NaOH and MgO are both alkaline catalysts. However, the alkaline effect of NaOH is greater on its catalysis power than MgO [6]. The yield of biodiesel produced decreases with increasing transesterification time. The highest yield was obtained at 1 hour reaction time. The reaction time is too long it will result in a decrease in the weight of the resulting methyl ester, due to the reversible reaction of the transesterification reaction resulting in the hydrolysis of the ester (saponification). The yield of biodiesel obtained decreased with increasing molar ratio between methanol and fat. This occurs because excessive use of methanol also results in the formation of high glycerol. The tendency of reactants to produce this glycerol results in triglycerides that should form methyl esters reduced.

4.2. The Effect of Catalyst Type, Transesterification Time, and Molar Ratio to Density

![Figure 2](image2.png)

The highest average density was obtained when using a MgO catalyst with a value of 0.8418 g/cm³. This is due to the residual impurities of MgO heterogeneous catalyst that are still trapped in biodiesel during the less than perfect purification process so that the mass of biodiesel is greater. Based on Figure 2, the highest average density was obtained during transesterification reaction time for 1 hour. The reaction of this biodiesel production is reversible, so the use of time is too long it causes a back reaction that actually causes a saponification reaction resulting in reduced methyl ester weight. The use of the methanol molar ratio causes a reversible reaction to form the reactant, so the biodiesel density becomes more decreased due to lower methyl ester density than triglyceride density [4]. In addition, the graph deviations that occur can be caused by the less than
perfect purification stage so that the biodiesel density obtained has varying values [1].

4.3. The Effect of Catalyst Type, Transesterification Time, and Molar Ratio to Viscosity

Based on Figure 3, the largest average viscosity is obtained when the NaOH catalyst is used. This occurs because the reaction between NaOH and methanol that form a sodium methoxide compound so as to attack the carbonyl group triglycerides stronger to form methyl ester than MgO catalyst. The average viscosity value decreases when reaction time is carried out for 3 hours, and the highest viscosity is obtained at 1 hour reaction time. This is because the transesterification reaction of biodiesel is reversible so that when the reaction equilibrium has been reached the product can react back so that the reaction time will no longer affect the reaction. The highest average viscosity is obtained when the use of 6:1 molar ratio. This shows that the greater the molar ratio of methanol and fat the viscosity obtained decreases. This varied viscosity value is due to the slightly fat soluble nature of methanol, so this solubility can decrease the viscosity of the resulting biodiesel.

4.4. The Effect of Catalyst Type, Transesterification Time, and Molar Ratio to Flash Point

Based on Figure 4, it is seen that the highest flash point average is obtained when the use of NaOH catalyst. The alkaline properties of NaOH catalysts are greater than MgO, causing the greater likelihood of triglycerides to form methyl esters so that the resulting flash point increases when using NaOH. The highest value of flash point is obtained during transesterification time for 1 hour. Excessive reaction time also causes the reaction to form a sapling reaction. The impurity content contained in biodiesel such as the result of soap, residue, and methanol reacting reaction causes
the flash point value to decrease. The highest flash point average is obtained when the molar ratio between methanol and oil is 6:1. This is due to the excess methanol in it. The low methanol flash point results in a higher molar ratio between methanol and oil causing the decrease in the resulting flash point biodiesel.

4.5. The Effect of Catalyst Type, Transesterification Time, and Molar Ratio to Heat Value

![Figure 5. The Effect of Catalyst Type, Transesterification Time, and Molar Ratio to Heat Value](image)

Based on Figure 5, it shows that the average highest heating value is obtained when the use of MgO catalyst, because the heterogeneous base catalyst is easy in terms of separating the product from the catalyst used, so that the resulting biodiesel product is free from the presence of the catalyst which leads to a decrease in the heating value. The highest average heating value was obtained during transesterification time for 3 hours. This is because the reaction of transesterification is back and forth so that when the reaction has reached equilibrium, the reaction time is too long it actually causes the reaction to turn toward the reactant so that the calorific value (heat required from the combustion process) is increasing.

High molar ratio of methanol and fat produces calorific values that tend to increase. Excessive use of methanol results in the formation of glycerol and makes it difficult to separate from the product. The presence of glycerol causes the calorific value of the produced biodiesel product to increase.

4.6. The Effect of Catalyst Type, Transesterification Time, and Molar Ratio to Sulfur Content

![Figure 6. The Effect of Catalyst Type, Transesterification Time, and Molar Ratio to Sulfur Content](image)

Based on Figure 6, it shows that the average value of the lowest sulfur content is obtained on the use of MgO catalyst. According to Indonesian National Standard (SNI 7182:2015), biodiesel must have a maximum sulfur of 50 mg / kg, because the resulting product has a biodiesel content ranging from 21 to 48 mg / kg in terms of sulfur content of biodiesel produced has met the standard.
Excess reaction time causes the reaction to turn into reactants because the reaction is reversible so that the biodiesel produced tends to be small. This sulfur content is also influenced from the compound used such as methanol and the catalyst is not pure so it is estimated there are impurity compounds that cause sulfur content is increasing.

The greater the molar ratio between methanol and fat used, the sulfur content contained in the product is also increasing. Excess amounts of methanol tend to make transesterification reactions produce more glycerol. The presence of glycerol and other impurities resulted in increased sulfur content in biodiesel samples.

4.7. The Effect of Catalyst Type, Transesterification Time, and Molar Ratio to Total Acid Number

Based on Figure 7, it shows that the highest average Total Acid Number value is obtained at the time of use of MgO catalyst. This is due to the basic nature of the transesterification catalyst used. NaOH tends to have a larger base properties than the MgO catalyst.

Based on Fig 8, shows that the longer reaction time, the acid number (total acid number) is greater. In addition, Fig 8. also shows that the greater the molar ratio of methanol and fat used, the higher the total acid number produced. The high total acid number is linear with the high sulfur content present in the product. Sulfur has an acidic properties so that if the amount is high then the amount of potassium hydroxide needed to neutralize the sample (total acid number) is also high.

4.8. Fourier Transform Infrared Spectrum Analysis (FT-IR)
Based on Figure 8, the results of FT-IR analysis obtained showed some spectrum changes between beef tallow and methyl ester. Biodiesel there was a peak loss of 693,64 cm$^{-1}$, 1595,76 cm$^{-1}$, and 1027,31 cm$^{-1}$ in beef tallow and peak appearance of 1737,82 cm$^{-1}$ in the spectrum IR methyl ester Biodiesel. The peaks of the missing and emerging spectrum indicate that the reaction transesterification was carried out successfully converted beef tallow seed oil into biodiesel. It was found that biodiesel has a functional group alkane, alkene, alkyne, esters, and alcohol.

5. Conclusion
The use of NaOH catalysts yields high yield, viscosity, and flash points compared to the use of MgO catalysts. The greater the molar ratio between methanol and oil in the transesterification reaction, the yield, density, viscosity, and flash point decrease. The longer the reaction time of transesterification, yield, density, viscosity, and flash point decrease. Optimum condition in the production of biodiesel from cow’s fat when using NaOH catalyst type, 6:1 molar ratio, and reaction time for 1 hour. Biodiesel products produced based on viscosity analysis, flash point, acid number, and sulfur content have fulfilled Indonesian National Standard (SNI).

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