

Potential Use of Natural Zeolite and Green Shells in Biodiesel Production

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Abstract – As energy needs continue to rise in line with the use of fossil energy, which is difficult to renew, other alternative energy is needed to continue to meet current and future energy needs. One alternative energy that is easy to produce is biodiesel. One of the raw materials that is quite widely used and developed in making biodiesel is waste cooking oil. According to statistical data, Indonesia can produce waste cooking oil of 5.06 tons per year. Waste cooking oil contains free fatty acids that can be processed into biodiesel using the help of heterogeneous catalysts. One source of heterogeneous catalysts that can be used is CaO, which can be found in green shells, where the CaO contained can be taken through the calcination process of green shells. To maximize the waste cooking oil processing process, an adsorption pretreatment process can be carried out. The adsorption process is carried out to reduce the FFA levels and acid numbers contained in waste cooking oil so that the transesterification reaction process can run optimally. Natural zeolite can be used as a good adsorbent to purify and lower the acid number of waste cooking oil. This study aims to find the best operating conditions in producing biodiesel made from waste cooking oil with a pretreatment adsorption process using natural zeolite and green shell catalyst through the factorial design method, where from the results of the research carried out, it was found that the density and viscosity met the SNI, the biodiesel yield produced was 45-65% and the cetane number test on samples 3 and 7 was 34,7 and 34,2 which did not meet the SNI. The operating temperature and amount of catalyst used in the biodiesel manufacturing process produce biodiesel with good density, viscosity, and yield, namely at a temperature of 60°C and a catalyst content of 6 grams. The operating temperature of 65°C produces a smaller density because the boiling point of alcohol is 64.7°C, so the reaction process is not perfect.

Keywords: Biodiesel; Green shells; Natural Zeolite; Transesterification; Waste cooking oil.

Introduction

Along with the increasing need for energy, the difficulty of renewing fossil energy that is currently used poses a challenge for the government, especially in the aspect of replacing fossil energy with renewable energy. Dependence on petroleum or fossil fuels can be reduced by using very large biodiesel fuels where the feedstock can be developed on a large scale (Putri et al., 2018).

One of the materials that can be processed into biodiesel is waste cooking oil, which still contains free fatty acids. The process of processing biodiesel from waste cooking oil is carried out through two reactions, namely esterification, which aims to reduce FFA content in materials, and transesterification, with the aim of converting triglycerides into methyl esters using catalysts that accelerate the reaction. The process of running the reaction can be assisted by a catalyst.

The catalysts used in biodiesel production are heterogeneous catalysts and homogeneous catalysts. Biodiesel production using homogeneous catalysts is fast but requires additional steps to remove catalytic contamination from products, thereby increasing production costs (Kurniasih, 2018). Another alternative is the use of heterogeneous catalysts, that is, catalysts with different phases between reactants and products. Heterogeneous catalysts that can be used in transesterification reactions include CaO and MgO. CaO is usually produced by pyrolysis of materials such as limestone, clam shells, eggshells, snail shells, or other mollusk shells.

Green shells are one source of CaO, with a content of 84% (Akbar et al., 2019). In addition to using green shells as catalysts, natural zeolite with large pores, large surface area, active sites, and deep cavities in crystals is also added. Catalytic reactions with natural zeolites depend on the diffusion of reagents and reaction products influenced by the size of the oral cavity and the groove system (Hartono et al., 2017).

Previous studies on biodiesel production have been widely conducted and found, including the research of Arifin et al. (2016) which discusses the use of snail shells as heterogeneous catalysts in the transesterification process of making biodiesel from waste cooking oil, where the study aims to determine the effect of heterogeneous base catalysts of snail shells used in transesterification reactions with dry washing methods on the yield and quality of biodiesel based on Biodiesel quality standards according to SNI No. 04 – 7182-2006. In addition, research conducted by Hartono et al. (2017) aimed to determine the optimization of biodiesel manufacturing using natural zeolite Bayah Banten as a heterogeneous catalyst. The methods used are acid transesterification and base transesterification using methanol and catalysts. The catalysts used are homogeneous H_2SO_4 catalysts and heterogeneous natural zeolite catalysts obtained from Bayah Banten that can reduce the FFA content in waste cooking oil.

In this research, natural zeolite was used as an adsorbent in the pretreatment process of waste cooking oil before processing it into biodiesel through a transesterification reaction. This pretreatment process is carried out to reduce the FFA content and acid number of used cooking oil so that the transesterification reaction can run smoothly and no saponification reaction occurs due to the high acid number. In this research, a heterogeneous catalyst obtained from green mussel shells through a calcination process was also used to help the transesterification reaction process in making biodiesel. The combination of natural zeolite, an acid catalyst, and green mussel shells as a base catalyst in this research is expected to produce high biodiesel yields and meet existing SNI standards.

From the description above, this research aims to find the best operating conditions in the process of making biodiesel from used cooking oil, which begins with an adsorption pretreatment process using natural zeolite and with the help of a green mussel shell catalyst and using the factorial design method. By conducting research with updates in the form of combining natural zeolite as an acid catalyst used as an adsorbent and green shell as a base catalyst, the author hopes that this research can produce biodiesel with good quality and in accordance with SNI so that it can be implemented in making alternative biodiesel energy.

Materials and Methods

Materials and instruments

In making biodiesel using waste cooking oil as raw material, waste frying oil from various brands such as Fortune, Bimoli, Filma, and Sania is used. This waste cooking oil comes from the remains of frying crackers and dishes that need to be fried on a household kitchen scale. Waste cooking oil was collected for approximately 2 months to reach a volume of approximately 3 liters. The green shells that will be processed into heterogeneous catalysts were obtained from the Karangayu Market, Semarang. Meanwhile, the natural zeolite used as an adsorbent in the adsorption pretreatment process was obtained from Bantul, Yogyakarta. The process of making biodiesel from waste cooking oil uses methanol as an additional feedstock in the transesterification reaction, HCl as a material used in the activation process of natural zeolite, and water for the cooling process. Chemicals were purchased at the Indrasari Chemical Store in Semarang. The equipment used in this research for the transesterification reaction process consists of a hose, reflux cooler, three-neck flask, thermometer, magnetic stirrer, and aluminum foil, which can be seen in Figure 1 below. To analyze the acid number and FFA content of waste cooking oil and biodiesel produced, the natural zeolite pretreatment process, making green shell catalysts and washing the biodiesel, additional equipment in the form of an Erlenmeyer, glass beaker and separating funnel were used.

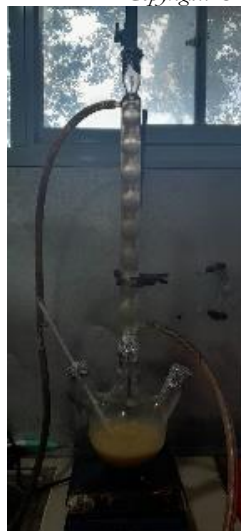


Figure 1. A Series of equipment for the transesterification reaction process.

Variable Design

The process of making biodiesel from waste cooking oil in this study uses a fixed variable, and the change variable can be seen in the tables below:

Table 1. Fixed variable.

Number	Name of Variable	Quantity	Unit
Activation of Natural Zeolite			
1	Natural zeolite weight	100	gram
2	HCl volume	500	ml
3	HCl immersion temperature	50	°C
4	HCl soaking time	2	hours
5	Drying temperature natural zeolite in an oven	130	°C
6	Drying time	3	hours
Manufacture of Green Shell Catalyst			
1	Green shells weight	3	kg
2	Drying temperature green shell in oven	110	°C
3	Calcination temperature	900	°C
4	Calcination time	4	hours
Pretreatment of waste cooking oil (adsorption using natural zeolite)			
1	Waste cooking oil volume	400	ml
2	Natural zeolite weight	40	gram
3	Magnetic stirrer rotating speed	400	rpm
4	Heating temperature	60	°C
5	Reaction time	1	hour
Biodiesel production			
1	Waste cooking oil after adsorption volume	50	ml
2	Methanol volume	100	ml

Table 2. Variable changes.

Number	Name of Variable	Value
1	Transesterification Time (T)	60 minutes (+)
		50 minutes (-)
2	Transesterification Temperature (S)	65°C (+)
		60°C (-)
3	The ratio of material and solvent (R)	1 : 6 g/g (+)
		1 : 4 g/g (-)

Procedures

The process of making biodiesel from waste cooking oil is carried out through the stages of activating natural zeolite, making a green shell catalyst, adsorption pretreatment process, making the biodiesel with transesterification process, and analyzing the biodiesel.

1. Activation of natural zeolite

Natural zeolite will be activated using HCl solution for 2 hours with a heating process at 50°C, then washed using aquades until the pH reaches neutral. After that, the drying process is carried out using an oven and then pounded and sifted until the size of the natural zeolite becomes smooth.

2. Green shell catalyst-making

Green mussel shells are washed and dried in the sun for 2 days and then dried using an oven for 3 hours. After drying, puree the green mussel shells and then calcine it for 4 hours. The shells resulting from the calcination process will be ground and sifted until the results are smooth and free from impurities.

3. Waste cooking oil adsorption pretreatment process

After going through the process of analyzing the FFA levels and acid numbers, 400 ml of waste cooking oil will go through an adsorption process with the addition of 40 grams of natural zeolite as an adsorbent. The adsorption process was carried out on a magnetic stirrer hot plate with a rotation speed of 400 rpm and a temperature of 60°C for 60 minutes. After that, the waste cooking oil is cooled and filtered to remove any remaining natural zeolite residue.

4. Biodiesel making

Biodiesel production is carried out through a transesterification process where for one biodiesel sample, 50 ml of waste cooking oil is used, which has been adsorbed, and 100 ml of methanol and green shell catalyst are added according to the variables. The variables used can be seen in Table 2. where the variable determination was carried out using the 2-level Factorial Designs method with three factors. The rotation speed used is set at 400 rpm. After the reaction is complete, the biodiesel is waited until it cools and separates into two layers (biodiesel on top and glycerol on the bottom). After that, the process continues with the washing process using distilled water. Then, analysis is carried out in the form of FFA content, acid number, viscosity, density, and cetane number tests.

Results

Waste cooking oil adsorption process using natural zeolite

The pretreatment process of waste cooking oil adsorption to be used as raw material for making biodiesel is carried out at a temperature of 60°C with the addition of natural zeolite of 5 grams in each sample and accompanied by stirring at a speed of 400 rpm.

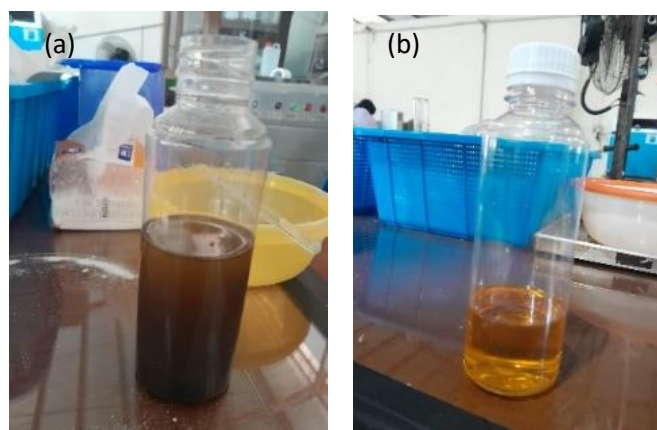


Figure 2. Visualization of used cooking oil (a) before adsorption and (b) after adsorption using natural zeolite.

Figure 2. Shows the difference in waste cooking oil before going through the adsorption process and after the adsorption process using natural zeolite. There are quite a lot of differences seen in the color of the oil. Used cooking oil that has been adsorbed is clearer in color than before it was adsorbed.

Acid number and FFA content analysis using titration method

Analysis of FFA content and acid numbers is carried out by titration method using KOH, which previously had the sample stirred with technical alcohol at 400 rpm for 30 minutes. According to Sudarmaji et al. (1984), FFA content and acid numbers can be calculated using the following formula:

$$\text{FFA Content} = \frac{V \times N \times \text{BM}_{\text{palmitic acid}} \times 100\%}{G \times 1000} \quad (1)$$

$$\text{Acid Numbers} = \text{FFA Levels} \times \frac{\text{BM}_{\text{KOH}}}{\text{BM}_{\text{palmitic acid}} : 10} \quad (2)$$

Where, V = KOH volume used for titration, N = KOH normality, G = Biodiesel mass

Figure 3. shows the results of FFA content analysis and acid number from biodiesel samples.

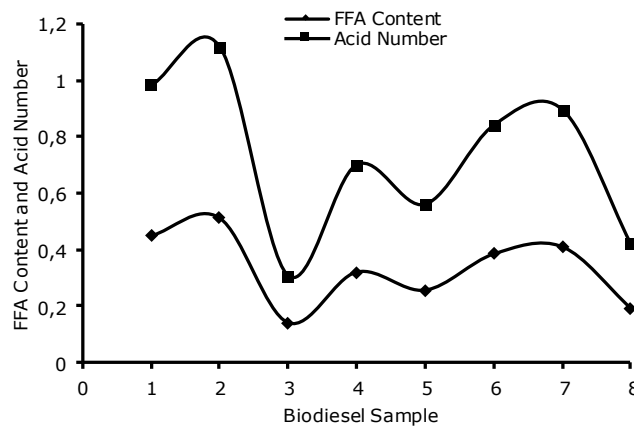


Figure 3. FFA content and acid number analysis results.

Density Analysis

Figure 4. shows the results of density analysis using a pycnometer.

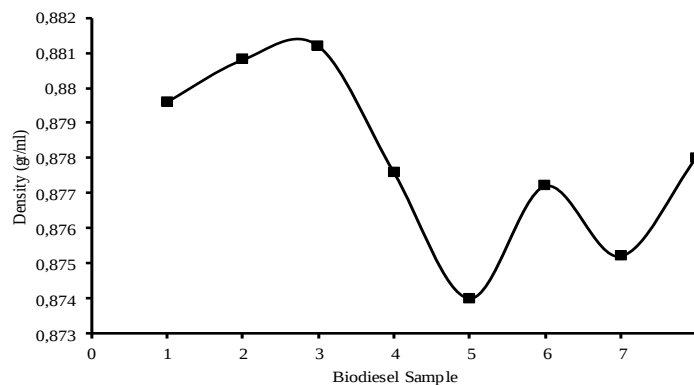


Figure 4. Density analysis results.

From Figure 4, it can be seen that the results of the density analysis are still fluctuating. Analysis of biodiesel density in this study obtained results in the range of 0.87-0.88 gram/ml. This result meets SNI standards, which are 0.85-0.89 grams/ml.

Viscosity Analysis

A viscosity analysis is carried out using an Ostwald viscometer to measure the viscosity of the biodiesel produced. Figure 5 shows the results of viscosity measurements.

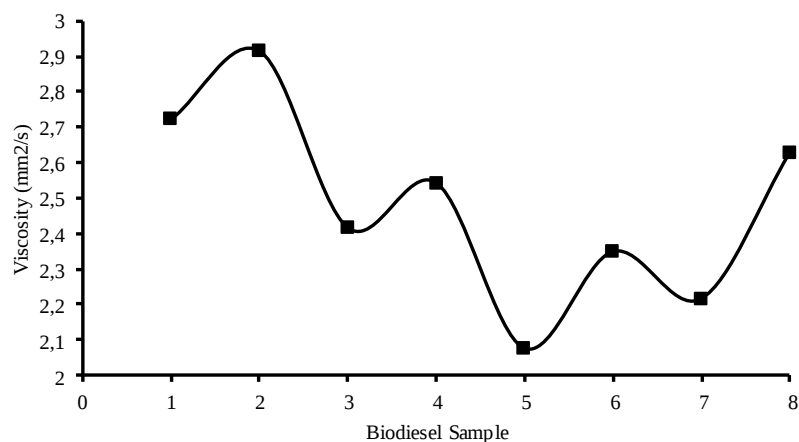


Figure 5. Viscosity Analysis Results

In Figure 3, it can be seen that samples with a catalyst content of 4 grams have a lower viscosity value than samples with a catalyst content of 6 grams. The viscosity analysis results obtained are in accordance with SNI 04-7182-2006, which ranges from 2.3-6 mm²/s.

Yield Analysis

Biodiesel production made from waste cooking oil with pretreatment adsorption using natural zeolite and green shell catalyst resulted in a 45-68% biodiesel yield. The results of the yield analysis can be seen in Figure 6.

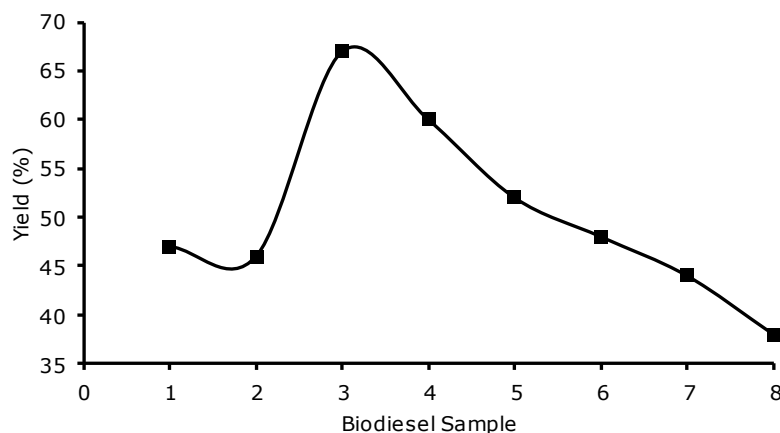


Figure 5. Yield Analysis Results

Cetane Number Analysis

To test the feasibility of using biodiesel for engines, cetane number measurements were carried out using the ASTM D 613 method, which can be seen in Table 1.

Table 1. Cetane Number Analysis

Number	Sample	Analysis Results
1	3	34,7
2	7	34,2

Discussion

Based on the FFA content analysis and acid number results, natural zeolite can be used as a good adsorbent for cooking oil waste. The pretreatment process is considered to reduce the acidity of waste cooking oil so that the coating reaction in making biodiesel can be avoided. From Figure 3, it can be seen that the results of FFA content and biodiesel acid numbers are still fluctuating. This is not in accordance with the theory based on research conducted by R. Hartono in 2017, where FFA content will decrease along with the increase in reaction temperature. This decrease is caused by increasing temperature, the collision between particles getting bigger so that the reaction will run faster, and the reaction constant is higher.

According to Hartono (2017), the greater the variation in the number of catalysts used, the density of biodiesel will decrease because using heterogeneous catalysts (zeolite) can reduce the coating reaction, and the density will decrease along with the increase in reaction temperature. Figure 4 shows that for reactions with a temperature of 65°C, a density smaller than the density of a sample with a reaction temperature of 60°C is obtained. This is because, at a temperature of 65°C, the reaction of making biodiesel becomes imperfect because the boiling point of methanol is 64.7°C, so the methanol will quickly evaporate before the perfect biodiesel process occurs. However, methanol evaporation can be controlled using a reflux process during the reaction.

In Figure 5, it can be seen that samples with a catalyst content of 4 grams have a lower viscosity value than samples with a catalyst content of 6 grams. This is in accordance with research conducted by R. Hartono in 2017, where the higher the concentration of catalyst, the viscosity tends to decrease because the more percent of the catalyst given, the faster the breakdown of triglycerides into three fatty acid esters, which will reduce viscosity by 5-10 percent. For samples 6 and 8, with a reaction temperature of 65°C, there was an increase in density. It is still not in accordance with the existing theory regarding the reaction temperature; the higher the reaction temperature, the more viscosity value will decrease (Irawati, 2018).

In the biodiesel yield analysis, the results were obtained in the form of samples increasing in sample 3 and decreasing along with the increase in temperature of the transesterification reaction. Rising temperatures will cause collisions between particles to get bigger, so the reaction runs faster, and the reaction constant is greater (Hartanto, 2017). In this study, cetane number measurements were carried out in samples 3 and 7. The cetane number produced has not met the SNI standard of at least 51. According to Tri Lestari (2017), a higher cetane number will ensure a good start and minimize the formation of white smoke.

Conclusion

Based on the results of research and discussion, it can be concluded that natural zeolite can be used as a good adsorbent in the waste cooking oil adsorption pretreatment process. This can be seen from the decrease in FFA levels and the acid number of used cooking oil from FFA levels of 1.99% and an acid number of 4.35 mg KOH/g to FFA levels of 1.09% and an acid number of 2.38 mg KOH/g. Green shells have good potential for acting as catalysts for the biodiesel production process. This research shows that using a green mussel shell catalyst can produce relatively high biodiesel yields, namely in the 40–70% range. The catalyst level added to biodiesel will affect the amount of biodiesel yield produced because the catalyst and biodiesel yield levels are directly proportional. Maximum operating conditions for making biodiesel using green shells, which begin with the adsorption pretreatment process of used cooking oil using natural zeolite, produce good biodiesel, and the analysis results for FFA content, acid number, density, and viscosity are in accordance with SNI at a temperature of 60 °C for 60-minute reaction with a catalyst content of 6 grams. The biodiesel produced in this research does not comply with SNI for analyzing its cetane number. The author suggests using more optimal equipment with new technology and adding variations in biodiesel analysis based on existing SNIs to determine the quality and shortcomings of the biodiesel produced.

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