The Effect of Adding Shrimp Shell Catalyst on the Quality of Biodiesel from Used Cooking Oil

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Abstract: Shrimp shell contains 40-50% calcium carbonate so that it can be used as a CaO catalyst in the manufacture of biodiesel using waste cooking oil. High levels of free fatty acid in waste cooking oil can be reduced by the esterification process using an acid catalyst. Biodiesel is produced by transesterification process using a heterogeneous catalyst of calcium oxide (CaO) from shrimp shells calcined at 1000°C for 3 hours. The esterification and transesterification processes are carried out using microwaves. The transesterification process was carried out with a variable weight percent catalyst (0%, 1%, 3%) and microwave power (150 W, 300 W). The characteristics of the biodiesel produced indicate that the parameters of density, flash point, and sentane number have met the standard, while the parameters of viscosity and water content have not met the standard. The yield of biodiesel produced increased along with the increase in the percentage of CaO catalyst concentration of shrimp shell waste and the microwave power used.

1 INTRODUCTION

Vaname shrimp is the product of pond cultivation in Indonesia. Based on the Central Statistics Agency in 2019, Java Island produced 144,873 tons of vaname shrimp. The large production of vaname shrimp has resulted in the generation of shrimp shell waste. Shrimp shell contains 45%-50% calcium carbonate, 25%-40% protein, and 15%-20% chitin (Sari et al, 2011). The content of the shrimp shells can be used as a CaO catalyst in the manufacture of biodiesel. One of the main ingredients for making biodiesel is used cooking oil.

Used cooking oil is a waste that is often found in households because of the large use of cooking oil. The used cooking oil produced can cause problems to the environment, especially pollution of water bodies (Glisic and Orlović, 2014). Used cooking oil contains fatty acids. Fatty acids are reacted with alcohol to produce esters which are the main compounds for making biodiesel (Darmawan and Susila, 2013). Therefore, this study was conducted to analyze the quality of biodiesel from used cooking oil using shrimp shell CaO catalyst.

2 METHODS

In this research there were several variables written in Table 1.

Table 1.

CaO Catalyst Of Shrimp shells (%)	Microwave Power in the Transesterification Process (Watts)	
	150	300
1	P1	P2
2	P3	P4
3	P5	P6

2.1 Production of Leather CaO Catalyst

Shrimp shells were cleaned using clean water and heated at 120°C for 1 hour then placed in a desiccator for 10 minutes (Yasar, 2019). Shrimp shells were mashed and sieved through a 100 mesh sieve (Petrus et al., 2015). Shrimp shell powder was calcined at 1000°C for 3 hours (Khodijah, 2017). Shrimp shell powder was tested by XRF to determine the CaO content.

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2.2 Sample Preparation Process

Waste cooking oil was filtered with filter paper to remove impurities. Then the sample was heated to remove the water content at a temperature of 105°C for 1 hour (Sartika et al., 2015).

2.3 Esterification Process

Waste cooking oil was mixed with methanol (mole oil-methanol ratio 1:5) and 0.5% (w/w) H_2SO_4 catalyst (Murni et al., 2016) then irradiated by microwave (Figure 1.) in a microwave for 20 minutes with a power of 450 W and stirred with a magnetic stirrer. (Ansori and Wibowo, 2018). Furthermore, the esterification results are left in a separatory funnel which aims to separate the methanol, oil, and H2SO4 in the top layer and the bottom layer was a mixture of oil and methyl ester (crude biodiesel). Then the crude biodiesel was washed with warm distilled water (60°C) with a ratio of product weight and distilled water used 1:1 (Pahlevi et al., 2015) and the top layer in the form of crude biodiesel was separated from the bottom layer in the form of washing water containing catalyst and residues. residual methanol using a separating funnel. (Pahlevi et al., 2015). Furthermore, the sample was heated in an oven (110°C) to reduce the water content in crude biodiesel (Suryanto et al., 2018). Finally, the samples were measured for density and % FFA.

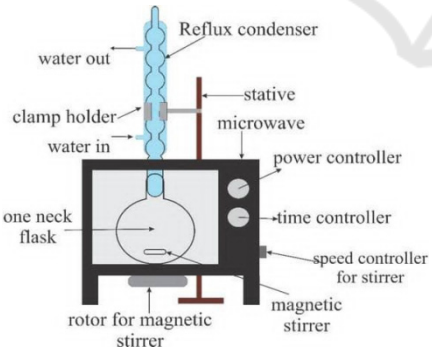

Figure 1: Microwave for Esterification.

2.4 Transesterification Process

Crude biodiesel was mixed with a mixture of shrimp shell CaO catalyst according to the specified variable with methanol with an oil ratio of 1:9 into a one neck flask (Ansori and Wibowo, 2018). Then, the sample was irradiated by microwaves using a microwave with microwave power according to the specified variable while stirring with a magnetic stirrer for 10 minutes. After that, the sample was put into a separatory funnel and allowed to stand at room temperature to form two layers (biodiesel and glycerol) (Sartika et al., 2015). Crude biodiesel was washed with warm water (60°C) with a ratio of product weight and distilled water used 1:1 (Pahlevi et al., 2015) and separation of two layers (crude biodiesel and biodiesel (FAME) (Pahlevi et al., 2015). The sample was heated in an oven (110°C) to reduce the water content in crude biodiesel (Suryanto et al., 2018) and lastly, the calculation of biodiesel yield on all variables of this study.

2.5 Analysis of Biodiesel Characteristics and CaO Catalysts

The characteristics of biodiesel tested in this study were samples that had the highest yield (3% catalyst at 300 Watt microwave power). The characteristics of biodiesel consist of density, viscosity, Free Fatty Acid (FFA), biodiesel yield, water content, Flash point, sentane number, X-Ray Fluorence (XRF) and Gas Chromatography Mass Spectroscopy (GC-MS).

Density testing in this study used a pycnometer. According to Dewi (2015) and Cahyati and Pujaningtyas (2017), the working principle of this test was that a clean and dry pycnometer was weighed to determine the mass of an empty pycnometer. First, Crude biodiesel to be tested was heated at a temperature of 40°C and then put into the pycnometer until it was full. Close the pycnometer and make sure there are no bubbles. The sample was cleaned and the pycnometer containing the sample is weighed. Then, record the mass of the pycnometer and the sample.

$$\text{Density } (\rho) = \frac{(\text{pycno mass} - \text{sample(gr)}) - (\text{empty pycno mass(gr)})}{\text{sample volume (ml)}} \quad (1)$$

Viscosity testing in this study using the Ostwald viscometer. According to Sinta et al. (2016), the working principle of this test was the Ostwald viscometer in a container filled with water at a temperature of 40°C (artificial water bath) in a vertical position. A certain amount of sample was pipetted into reservoir A. The liquid was brought to reservoir B and its surface crosses the line m, so reservoir A was still half filled. The viscometer and its contents were left in a container of water for 10 minutes to reach the desired temperature. Liquid B was sucked or blown to slightly above the m line. The liquid was allowed to flow freely. Record the time it takes for the liquid to flow from M to N, this step was repeated several times.

$$\text{Kinematic viscosity } (\mu k) = C \times t \quad (2)$$

Where:
C= Ostwald viscosity constant (0.4994 cSt/second)
t = time required for sample from point A to point B

FFA testing was carried out on waste cooking oil before and after the esterification process. Determination of FFA levels refers to SNI 01-3555-1998 concerning Oil and Fat Test Methods.

$$\text{FFA content } (\%) = \frac{(MxVxT)}{10 \times m} x100\% \quad (3)$$

Where:
M = molecular weight of fatty acids (grams)
V = volume of NaOH required for titration (ml)
T = normality of NaOH m = weight of sample (grams)

The calculation of the conversion of reducing FFA levels in waste cooking oil was carried out to determine the decrease in FFA levels using the esterification process.

$$\text{FFA reduction } (\%) = \frac{(\%FFA_{before} - \%FFA_{after})}{\%FFA_{before}} x100\% \quad (4)$$

1. Biodiesel yield was the percentage of conversion of oil into biodiesel (Efendi et al., 2018). The amount of yield produced according to Zuhra et al. (2015) can be calculated using the following formula:

$$\text{yield} = \frac{W_{biodiesel}}{W_{oil}} x100\% \quad (5)$$

Where:
$W_{biodiesel}$ = weight of methyl ester (biodiesel) from washing and separation
W_{oil}= weight of waste oil and fat used in the reactor

2. Moisture content in waste cooking oil refers to SNI 01-3555-1998 on Oil and Fat Test Method using the gravimetric method. Samples that already have a fixed weight can be calculated for their water content by the formula:

$$Ka = \frac{m_1 - m_2}{m_1} x100\% \quad (6)$$

Where:
Ka = moisture content (%)
m_1 = sample weight (grams)
m_2 = sample weight after drying (grams)

Flash point testing was used to determine the indication of the boiling distance. This test was carried out with reference to SNI 7182:2015 regarding Biodiesel using the ASTM D 93 method. The tool used for the flash point test was the Pensky-Martens closed cup tester.

The cetane number test was used to determine the ability of the fuel to ignite quickly after being injected. This test was carried out with reference to SNI 7182:2015 regarding Biodiesel.

XRF test aims to determine the composition of the elements in the calcined shrimp shell powder. The most important component in calcined shrimp shell powder was CaO.

Gas Chromatoraphy Mass Spectroscopy (GC-MS) Test

Analysis of fatty acid composition in (Waste Cooking Oil) used GC-MS method.

3 RESULTS AND DISCUSSION

3.1 Density

Testing the density of biodiesel was carried out at a temperature of 40°C using a pycnometer. The biodiesel quality requirements for the density parameter regulated in ISN 7182:2015 are 850 – 890 kg/m^3. Biodiesel with the highest yield has a density value of 858.69 kg/m^3. The density value in this study has met the standards that have been set. The smaller density value indicates that there has been a breakdown of glycerol from triglycerides, so that a compound with a smaller molecular size is formed (Petrus et al., 2015).

3.2 Viscosity

Viscosity testing using an Ostwald viscometer at a temperature of 40°C. Viscosity in biodiesel based on ISN 7182:2015 concerning biodiesel has a value of 2.3-6 cSt. The result of viscosity testing on biodiesel waste cooking oil which has the highest % yield is 14.77 cSt. This value is not included in the standard range that has been set. Triglycerides have a higher viscosity than methyl esters, this is what causes high biodiesel viscosity if the transesterification reaction is not perfect (Zulhardi et al., 2018). Several approaches have been proposed to reduce the viscosity of biodiesel so as to improve the flow properties of biodiesel at low temperatures which include mixing with diesel fuel, the use of additives, physical modification, fractionation crystallization, and winterization (Sukarno, 2012).

3.3 Flash Point

The flash point test refers to ISN 7182:2015 regarding Biodiesel using the ASTM D 93 method. The tool used for the flash point test is the Pensky-

Martens closed cup tester. The minimum requirement for flash point parameters for biodiesel is 100°C. Flash point test results show 205.83°C. The test results indicate that the flash point parameter has met the requirements. According to Permana et al, (2020), the higher the flash point of biodiesel, the safer it will be to use because it will minimize the occurrence of explosions due to heating.

3.4 Water Content

Testing the water content using the oven drying method. The water content value that has been determined in ISN 7182:2015 regarding biodiesel is a maximum of 0.05%-volume. Based on the research that has been done, the results obtained water content of 0.58%. The water content contained in biodiesel is above the maximum level. The biodiesel heating process is carried out to evaporate the water content after the washing process using water in biodiesel. The results of the water content that exceeds the standard cannot be used as fuel because the water content in the methyl ester can form paraffin crystals at cold temperatures which can clog the fuel flow. The water content can also cause corrosion of the engine (Busyairi., et al 2020). One approach to reduce water content is to use the dry washing method in the purification process. The dry washing method uses magnesium silicate as a substitute for the role of water in absorbing contaminants in biodiesel (Ayu & Zibbeni, 2012).

3.5 Centane Number

Centane number is one of the test parameters to determine the quality of diesel fuel combustion. The minimum requirement for the cetane number for biodiesel based on ISN 7182: 2015 is 51. The biodiesel cetane number in this study based on the test results is 0 because the cetane number value is outside the test range (20-100). This value is a sign that biodiesel has a cetane number that is outside the reading range of the analysis tool, which is between 20 - 100. The raw materials used in this study contained 52.51% saturated fatty acids and 47.49% unsaturated fatty acids. According to Damayanti., et al (2020), a higher content of saturated fatty acids than unsaturated fatty acids will cause the biodiesel cetane number in this study to be high (> 100). Based on these data and the results of previous studies, it can be used as a reference that the biodiesel centane number value in this study is above 100. The resulting centane number value exceeds the minimum cetane number value in the specified SNI standard. So that the value of the centane number in this study has met the standard.

3.6 Fatty Acids Methyl Ester Level

Fatty Acids Methyl Ester analysis was carried out using Gas Chromatography-Mass Spectrometry (GC-MS). Based on the results of GC-MS analysis, the dominant FAME components are Octanoic acid, methyl ester and Decanoic acid, methyl ester with area percentages of 46.4% and 43.07%, respectively. The compounds contained in the GC-MS test results indicate that the triglycerides contained in the waste cooking oil have been converted into methyl esters. According to ISN 7182-2015 regarding biodiesel, it is stated that the minimum methyl ester content is 96.5%. In this study, the methyl ester content produced was 95.31%. This value does not meet the standard so it can be seen that there are still some triglyceride components that have not been converted to FAME (Oktavian., et al 2019).

4 CONCLUSIONS

Characteristics of biodiesel produced from used cooking oil (waste cooking oil) indicates that the parameters of density, flash point, and the acid number has met the standard, while the viscosity and parameters water content does not meet the standard..

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