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RESEARCH PAPER

Utilization of Waste Shells as CaO Catalyst in Biodiesel Production from Used Cooking Oil

Umei Latifah Azzahro*, Wisnu Broto

[a] Industrial Chemical Engineering Technology Study Program, Department of Industrial Technology, School Vocational School, Diponegoro University. Jl. Prof Soedarto, SH, Tembalang, Semarang, 50275, Indonesia.
E-mail: azzahlatifah20@gmail.com

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Abstract: This research is motivated by the depletion of energy reserves while the need continues to grow. Biodiesel is an alternative fuel produced from vegetable oil, animal fat, waste oil, etc. This study aims to determine the best transesterification treatment variables and the most significant main effect using the 2 level 3 factorial design method and operating times of 50 minutes and 70 minutes. The maximum transesterification condition was found by adding a 4% (w/w) CaO catalyst, 70 minutes of transesterification time, and 70 ^{o}C of operating temperature. The biodiesel characteristics obtained were a viscosity value of 4.8908 cSt, a density of 853.2 kg/m^3, a yield of 78.1%, and a cetane number of 39. The most significant effect was the percentage of catalysts.

Keywords: biodiesel, used cooking oil, oyster shells, transesterification

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INTRODUCTION

Fossil energy can be depleted, and its presence in nature decreases over time. Meanwhile, the need for energy is inversely proportional to the availability of existing energy. Based on the Presidential Regulation of the Republic of Indonesia No. 5 of 2006 on the energy policy to develop alternative energy to replace fuel, various efforts to produce energy by searching for renewable alternative energy have been carried out [1].

Biodiesel is one of the renewable energy types with many advantages, including being an environmentally friendly fuel because it is safe, renewable, non-toxic, and biodegradable. In addition, emissions of CO, CO_2, SO_x, NO_x, and unburned fires are reduced by up to 50% [2].

Used cooking oil can be processed into biodiesel. It can be done because used cooking oil is also vegetable oil, a derivative of CPO (Crude Palm Oil). The utilization of vegetable oil as raw material for biodiesel has several advantages, including the ease of obtaining vegetable oil, the easy and fast process, and the high conversion rate (95%).

The content of used cooking oil in the form of fatty acid triglycerides is characteristically similar to palm oil. Thus, used cooking oil can be utilized as a raw material in biodiesel manufacture [3].

Blood clam (*Anadara granosa*) is a popular shellfish in Indonesia. The abundance of clam blood (*A. granosa*) in Indonesia, according to the Directorate General of Indonesian Capture Fisheries (2012), is 48,994 tons. The shells contain chemical mineral compounds, including chitin, calcium carbonate, calcium hydroxyapatite, and calcium phosphate. In addition to chitin, clam shells also have calcium carbonate ($CaCO_3$), which physically can adsorb or absorb other substances into the pores of its surface. In this study, blood clam shells can be used as an alternative source of CaO catalyst for the transesterification reaction [4].

Transesterification is a process in which the raw material in the form of triglycerides reacts with a short-chain (C1/C2) alcohol with the addition of a catalyst that can be carried out using homogeneous or heterogeneous catalysts. Heterogeneous catalysts have many advantages, such as reusability, easier separation of product and catalyst, and

reduced wastewater generated [5]. The transesterification reaction is carried out at temperatures close to the boiling point of methanol (60-70 ^{o}C) at atmospheric pressure. Therefore, in this research on making biodiesel, materials in the form of used cooking oil and shells will be used as CaO catalysts.

MATERIALS AND METHODS

Chemical and equipment.

The main ingredient used to make biodiesel is used cooking oil. At the same time, the additional materials are dara shells as a catalyst for CaO, methanol, sulfuric acid (H_2SO_4), KOH, phenolphthalein Indicator (PP), and aquadest.

The tools used in this research are three neck flasks, magnetic stirrer, hot plate, back cooler, stative, clamp, thermometer, hose, grinder, furnace, oven, pycnometer, ostwald viscosimeter, burette, and erlenmeyer.

Method

This study uses the transesterification method, where the initial processing of raw materials is in the form of CaO catalyst calcination, esterification, and transesterification (Table 1).

Tabel 1. Research Design

Run	Variable			Analysis
	T (minutes)	s (^{o}C)	k (%)	rendement
1	50	50	2	v
2	70	50	2	v
3	50	70	2	v
4	70	70	2	v
5	50	50	4	v
6	70	50	4	v
7	50	70	4	v
8	70	70	4	v

*t : transesterification time; *s : transesterification temperature; *k : concentration of CaO catalyst

Fixed Variable

The fixed variables used were calcination temperature (900 ^{o}C), calcination time (4 hours), esterification temperature (60 ^{o}C), stirring speed (600 rpm), esterification time (60 minutes), methanol esterification concentration (20% v/v), and sulfuric acid concentration (5% v/v).

Research Process

The first stage is the calcination of the CaO catalyst followed by using a 900 ^{o}C furnace for 4 hours. Next, biodiesel esterification was conducted at a temperature of 60^{o}C for 60 minutes with a stirring speed of 300 rpm. The next stage is biodiesel transesterification followed by a temperature of 50 ^{o}C and 70 ^{o}C for 60 minutes with a stirring speed of 300 rpm. The sample analysis was carried out to determine the density, viscosity, yield, FFA, and cetane number values.

RESULTS AND DISCUSSION

CaO calcination

CaO catalyst was measured using a 900 ^{o}C furnace for 4 hours in the Undip Natural Medicine Laboratory Building. The formation of CaO can be observed with the decreasing weight of the material from 112 gr to 91 gr. It occurs due to the release of CO_2 gas from the thermal decomposition of $CaCO_3$ into CaO, where CO_2 gas is another product of the decomposition [6].

Biodiesel Esterification

The characteristics of used cooking oil before the esterification process is shown in Table 2.

Table 2. Before esterification

	Standard Properties	
Density	Kg/m^3	907.6
Viscosity	cSt	37.87
FFA	%	4.17

This high level of FFA will form soap in the transesterification process if it is added with a CaO base catalyst. Thus, the esterification process must be carried out first to reduce the FFA content of used cooking oil using an acid catalyst H_2SO_4.

The characteristics of the oil after the esterification process can be seen in Table 3.

Table 3. Post Esterification

	Standard Properties	
Density	Kg/m^3	814.2
Viscosity	cSt	34.52
FFA	%	2.37

The FFA content of the oil after esterification decreased from 4.17% to 2.37%.

The decrease was due to the esterification process reacting the free fatty acids contained in the oil and methanol with the help of an acid catalyst [7]. The esterified oil then proceeds to the next stage, namely the transesterification stage.

Biodiesel Transesterification

This transesterification step is done by varying the temperature, time, and concentration of CaO catalyst with % yield response, as shown in Table 4.

Table 4. Transesterification Test Data

run	Variable			Analysis
	t (minutes)	s (^oC)	k (%)	rendement
1	50	50	2	70.4
2	70	50	2	71.8
3	50	70	2	73.3
4	70	70	2	74.2
5	50	50	4	75.6
6	70	50	4	76.4
7	50	70	4	77.8
8	70	70	4	78.1

The best treatment was chosen based on the high value of effectiveness produced, with each parameter having a different priority value weight. The weight of the parameter values determined at this transesterification stage is % yield.

Table 5. Characteristics of the Maximum Results

	Standard Properties	
Density	Kg/m^3	853.200
Viscosity	cSt	4.8908
Rendement	%	78.100
Setana Number		39.000

Based on the calculated effectiveness index value, the best treatment result is the eighth variable combination with the treatment of adding 4% CaO catalyst (m/v), transesterification time of 70 minutes, and operating temperature of 70 ^oC. The characteristics produced by these treatments have met the biodiesel quality standards based on Indonesian National Standard (abbreviated as SNI) SNI 7182:2015 and American Society for Testing and Materials (ASTM) ASTM D 613, which are shown in Table 5.

The eighth variable was the best treatment in this study because it had the highest yield value compared to the other variables, 78.1 %. The greater the concentration of catalyst in the solution, the lower the activation energy of a reaction so that more products will be formed [8].

Biodiesel Analysis Test

The biodiesel production by the transesterification reaction was carried out with 3 variations of variables, namely temperature, time, and catalyst content. Furthermore, the biodiesel was tested in density, viscosity, % yield, and cetane number.

Density

The biodiesel density values obtained from the 8 treatments are presented in Table 6.

The biodiesel density values obtained have met the SNI-7182:2015 standard, which ranged from 850 – 890 kg/m^3, except for treatment 1 where the density value was 891.2 kg/m^3. It is because the washing process is not optimal, causing the water content to be bound to the methyl ester so that it is difficult to separate.

Table 6. Biodiesel Density

Run	Density (kg/m^3)	SNI ($kg/m^{3)}$
1	891.2	850-890
2	888.2	
3	884.4	
4	879.2	
5	862.4	
6	856.4	
7	854.4	
8	853.2	

The density obtained is by the existing theory. The longer the time and the greater the temperature used, the reactant particles will move faster. The intensity of collisions between particles will be more intense and more effective, thereby reducing the viscosity value of biodiesel [9].

Viscosity

The viscosity values obtained in this study can be seen in Table 7. Most of the biodiesel viscosity values obtained have met SNI requirements – 7185: 2015 of 2.3 – 6.0 cSt. However, in treatments 1, 2, and 3, the viscosity value exceeds the expected SNI value. Since the reaction temperature is too low, and the reaction is less than complete,

they still contain unreacted (unconverted) triglycerides.

The viscosity obtained has met the existing theory, which is directly proportional to the density value. The lower the viscosity value of the oil tested, the lesser the density value. In theory, the longer the reaction takes place, the more fatty acids will be converted into methyl esters (biodiesel). The levels of glycerol and residual triglycerides in biodiesel will also decrease (Table 7).

Table 7. Biodiesel Viscosity

Run	Viscosity (cSt)	SNI (cSt)
1	7.7757	2.3-6.0
2	7.2385	
3	7.0751	
4	6.8416	
5	6.6992	
6	6.3264	
7	5.9085	
8	4.8908	

The higher the catalyst concentration, the viscosity tends to decrease because the more percentage of the catalyst given, the faster the triglycerides break down into three fatty acid esters, reducing the viscosity [10]. The yield of biodiesel for each treatment can be seen in Table 8.

Table 8. Biodiesel Yield

Run	% rendement
1	70.4
2	71.8
3	73.3
4	74.2
5	75.6
6	76.4
7	77.8
8	78.1

Based on the transesterification process that has been carried out, the effect of CaO catalyst concentration in the range of % w/w catalyst from 2% to 4% has increased biodiesel yield. It happens because the function of the catalyst is to lower the activation energy. The greater the concentration of the catalyst in the solution, the lower the activation energy of a reaction. Thus, more products will be formed. Increasing the concentration of the catalyst will cause an increase in biodiesel yield [8].

A catalyst concentration of 4% is a condition that produces a maximum biodiesel yield which is 78.1%. If the concentration of CaO catalyst is continuously increased to 4.5%, the formed yield will decrease. Adding an excessive catalyst concentration will encourage the reaction to form soap. In the product washing process, the presence of soap will produce a white emulsion. The more soap is formed, the less biodiesel is produced [11].

Figure 1. Cetane Number Results

The cetane number obtained from the best treatment (eighth treatment) is 39. It means that the quality of biodiesel in terms of cetane number is still below the standard of SNI – 7182: 2015, which should be 51 (Figure 1).

The low cetane number is related to the fatty acids contained in biodiesel—especially the %FFA of used cooking oil before the transesterification stage where %FFA is still 2.37%. On the other hand, the %FFA requirement is <2% to enter the transesterification stage. Thus, the high content of FFA means that biodiesel contains high levels of fatty acids with long carbon chains. It causes a low cetane number and a low combustion rate [12-14].

Fuels with low cetane numbers can cause diesel engines to run slower and have higher emissions due to inefficient combustion. The low cetane number also makes the engine difficult to start. Meanwhile, fuel with a high cetane number will burn faster and make the combustion process more efficient [15-17].

Design Factorial Analysis

Design factorial analysis is needed to determine the most influential main effect in the study from the variables that have been determined.

This study used a factorial design method of 2 level 3 variables with variations in operating temperature, operating time, and the catalyst level used—responses obtained in

density, viscosity, and yield. The acquired data is presented in Table 9.

Table 9. Biodiesel Test Data

No	Variable			Analysis		
	t	s	k	% r	d	v
1	50	50	2	70.4	891	7.8
2	70	50	2	71.8	888	7.2
3	50	70	2	73.3	884	7.0
4	70	70	2	74.2	879	6.8
5	50	50	4	75.6	862	6.7
6	70	50	4	76.4	856	6.3
7	50	70	4	77.8	854	5.9
8	70	70	4	78.1	853	4.9

Information : t: time (minutes); s: temperature (^{o}C); k: catalyst content (%); r: yield (%); d: density (kg/m3); v : viscosity (cSt)

To analyze the data above, the upper limit is marked (+) while the lower limit is marked (-) to facilitate calculations, as shown in Table 10.

Table 10. Data Analysis

No	t	s	k	ts	tk	sk	tsk
1	-	-	-	+	+	+	-
2	+	-	-	-	-	+	+
3	-	+	-	-	+	-	+
4	+	+	-	+	-	-	-
5	-	-	+	+	-	-	+
6	+	-	+	-	+	-	-
7	-	+	+	-	-	+	-
8	+	+	+	+	+	+	+

After being calculated using the factorial design method, data is depicted in Table 11.

Table 11. Data Interpretation

Effect	
Result mean	74.70
T	0.85
S	2.30
K	4.55
Ts	-0.25
Tk	-0.30
Sk	-0.35
Tsk	0.00

From the data interpretation table above, it can be seen that the most influential main effect is the catalyst. High CaO content gives higher base strength. The greater the base strength, the higher the catalytic activity of the catalyst. Hence, the yield of biodiesel produced is also higher.

CONCLUSION

Based on the research that has been done, it can be concluded that virgin clam shells can be used as an alternative to heterogeneous base catalysts for biodiesel production by calcining at 900 ^{o}C for 4 hours. In addition, the best transesterification condition was obtained in the eighth treatment with the addition of 4% CaO catalyst (m/v), a transesterification time of 70 minutes, and an operating temperature of 70 ^{o}C to obtain the highest yield of 78.1%. Furthermore, the most significant main effect in this study is the concentration of the catalyst. This data is obtained from calculations using the 2 level 3 variable factorial design methods.

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