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Synthesis of Biodiesel from Waste Cooking Oil Using Heterogeneous Catalyst (CaO) Based on Duck Eggshell with Transesterification Reaction

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Abstract

Biodiesel is produced from esterification and transesterification reactions of various vegetable oils such as coconut oil, palm oil, seed oil, soybean oil, etc. Waste cooking oil has the potential as a raw material for making biodiesel due to its abundant availability. The use of the CaO catalyst from duck eggshells can increase biodiesel quality. This study aimed to obtain the best catalyst with a high yield in biodiesel production using the transesterification method. The initial stage begins with activating the impregnated duck eggshell catalyst with various concentrations of KOH in distilled water (10 g KOH/100 mL, 15 g KOH/100 mL, 20 g KOH/100 mL, and 25 g KOH/100 mL). Followed by biodiesel synthesis steps using temperature variations in transesterification (45˚C, 55˚C, and 65˚C) in reaction times of 1, 2 and 3 hours using 2% catalyst concentration to the amount of waste cooking oil and a molar ratio of methanol: oil (7:1). The experimental results showed that transesterification of waste cooking oil could be improved with the presence of a CaO heterogeneous catalyst. The values of density, Free Fatty Acid (FFA), viscosity, and the acid number obtained was adjusted to the parameters using SNI:7182:2015. Only the total ester parameter (96.02%) and the cetane number (40.4) did not meet the requirements.

Keywords: biodiesel, duck eggshell, waste cooking oil

1 Introduction

The use of process technology in the industrial sector, such as boilers, furnaces, and motor equipment, requires a large amount of energy and fuel. This sector's total final energy demand is projected to increase from 297 million BOE (barrel oil equivalent) in 2017 to 1,352 million BOE in 2050 or increase with an average growth rate of 4.7% per year. The industrial sector currently uses a lot of gas, coal, and electricity, besides diesel oil and fuel oil. In 2050 consumption of these energies is expected will increase to replace more expensive fuel oil, so it is crucial to accelerate the development of industrial-scale biofuels [1–3].

Biodiesel is a type of biofuel that can replace diesel fuel. Biodiesel is produced from raw materials derived from vegetable oils, animal fats, and waste cooking oil [4]. Biodiesel can be produced from biological resources that contain triacylglycerol (TAG). Biodiesel is commonly referred to as fatty acid alkyl ester (FAME). The production of biodiesel has some advantages in that raw materials are easy to obtain and cheap. The production is easily customized to the needs, eco-friendly, non-toxic, biodegradable, low viscosity, and has a high cetane number [5,6].

Heterogeneous catalysts have now received greater attention than homogeneous catalysts in biodiesel manufacture. One example of waste materials that can be used as alternative energy for making biodiesel is duck eggshells. Calcium carbonate (CaO) contained in duck eggshells has a high content so that it can be used as a heterogeneous catalyst through the calcination process. In the calcination, duck eggshells are heated at high temperatures to form CaO. The CaO formed is carried out by the impregnation process by KOH [7]. CaO is the best catalyst with added value as a potential source of calcium; abundant and inexpensive, it has a relatively low impact because the separation is simple [8].

Wiyata and Broto [9] studied biodiesel manufacturing from waste cooking oil by utilizing duck eggshell waste as a CaO catalyst. The results showed that the best transesterification conditions were adding 4% CaO catalyst (m/v), transesterification time of 70 minutes at 70ºC; the highest yield was 78.1%. The biodiesel characteristics obtained have a viscosity value of 3.8246 cSt, a density of 864.8 kg/m3, 81.4 % yield and a cetane number of 38.0. Research by Suryandari et al. [10] was biodiesel synthesis through transesterification of waste cooking oil based on heterogenous catalyst of CaO from waste chicken eggshell and obtained the best calcination conditions produced at 900°C for 2 hours.

Based on the data obtained from several references, the next research is to produce biodiesel from waste cooking oil using heterogeneous catalysts from duck eggshells. In this study, duck eggshells were calcined at 800ºC for 4 hours. Furthermore, the eggshells were impregnated using the concentration of KOH in aquadest (10 g KOH/100 mL; 5 g KOH/100 mL; 20 g KOH/100 mL; 25 g KOH/100 mL) with temperature variations 45˚C, 55˚C, and 65˚C, variation of reaction time 1, 2 and 3 hours. The fixed variables are the methanol: oil molar ratio of 7: 1 and the use of a 2% catalyst concentration to the amount of waste cooking oil in the biodiesel synthesis process.

2 Research Method

The research was conducted in Laboratory of Sekolah Tinggi Analis Kimia Cilegon. The research begins with the synthesis of heterogeneous CaO catalysts and continues with biodiesel production.

Tools used in this research: 50 mesh sieve, burette, funnel, separator flask, Erlenmeyer, furnace, beaker, heater, blender, watch glass, filter paper, three-neck flask, analytical balance, oven, magnetic stirrer, pycnometer, dropper, thermometer, and viscometer.

The ingredients used are methanol, aquadest, duck eggshells, PP Indicator, 0.1N Potassium Hydroxide (KOH), waste cooking oil, methanol, and 6% Sodium Hydroxide (NaOH).

Catalyst Activation Stage

The duck eggshells that have been obtained are washed and dried using an oven at 110ºC for 24 hours. The dried duck eggshells were crushed and sifted using *screeneer* 50 mesh. Furthermore, the eggshells obtained from sifting were calcined at a temperature of 800ºC for 4 hours. Duck eggshells are reheated in the oven at 110ºC for 24 hours. Next, the duck egg shell was impregnated with KOH at 60°C for 2 hours and heated in an oven at 60°C for 8 hours. The result was separated with filter paper and dried in an oven at 110°C for 24 hours. Then, duck eggshells were calcined at a temperature of 450°C for 4 hours.

Cooking Oil Cleaning Stage

Waste cooking oil was heated at 100-115°C for 30 minutes to remove the water. After that, the oil was put into a separatory funnel, and neutralization process was carried out using 4 mL of 6% NaOH solution for every 100 mL of oil to reduce the levels of FFA. The waste cooking oil was reheated at 40ºC with stirring for 10 minutes to accelerate the reaction in reducing the FFA levels. The oil is filtered through filter paper to separate large solid impurities.

Biodiesel Synthesis Procedure

Biodiesel synthesis was carried out by the transesterification method. In the transesterification stage, the ratio of the molar ratio of oil:methanol 1:7. The catalyst concentration used was 2% of the amount of waste cooking oil. Waste cooking oil, methanol and duck eggshell catalyst were put into a three-neck flask equipped with a cooled reflux condenser. Stirred the mixture at 500 rpm and heated at 45ºC, 55ºC and 65ºC, for 1, 2, and 3 hours. The results were filtered to separate the catalyst and product and put into a separatory funnel to stand for one day. The layer will be formed into two; the top layer is biodiesel, and the bottom layer is glycerol.

The biodiesel product is separated from the glycerol through the bottom of the separatory funnel and then collected. The purification process is carried out by heating the biodiesel for 15 minutes at 115°C to remove residual methanol and water. The reaction results were analyzed, including density, viscosity, flash point, acid number test, cetane number, FFA, and total ester.

3 Result and Discussion

The activation stage of the CaO catalyst begins with the preparation of duck eggshells impregnated with KOH which aims to obtain duck eggshell that have the ability as an alkaline catalyst. Eggshells obtained from sifting were calcined at 800ºC for 4 hours to decompose $CaCO_3$ into CaO. Duck eggshells were reheated at 110ºC for 24 hours, then were impregnated with KOH at 60°C for 2 hours. At this stage, various KOH/100 mL aquadest were given (10 g; 15 g; 20 g; and 25 g). The impregnation product was heated using an oven at 60 °C for 8 hours, separated with filter paper, and dried at 110 °C for 24 hours. The next stage is duck eggshell calcination at 450°C for 4 hours to keep the catalyst relatively stable at high temperatures (Peng et al., 2018).

Cooking Oil Sample Preparation

25 L of waste cooking oil were obtained from catering in the Cilegon area. The samples were tested for initial quality before being treated. The samples were tested for initial quality before treated are shown in Table 1.

Table 1. Quality of waste cooking oil samples before purifying

Characteristics	Result
Density at 25°C (kg/L)	9.125
Kinematic Viscosity at 40°C (Cst)	40.3
Fatty Acid Content (%)	0.14
Acid Number (mg KOH/g)	3.07
Water Content (%)	0.13

Based on Table 1, it was shown that the waste cooking oil sample has a very high acid number. The sample must be purified using 6% NaOH with a ratio of 4 mL NaOH in 100 mL waste cooking oil sample. The quality of used cooking oil after being treated is shown in Table 2.

Table 2. Quality of waste cooking oil samples after purification

Characteristics	Result
Density at 25°C (kg/L)	9.125
Kinematic Viscosity at 40°C (Cst)	408
Fatty Acid Content (%)	0.04
Acid Number (mg KOH/g)	0.12
Water Content (%)	0.13

The results showed that the acid number decreased after purification. The acid number with a value of 0.12 mg KOH/g has met the standard to be used as raw material for biodiesel synthesis following SNI 7182:2015 (maximum of 0.5 mgKOH/g). The results of this purification are also following the research of Wiyata & Broto [9].

Table 3. Ester Compounds contained in Biodiesel Samples

No	Retention Time	% Area	Compound Name
1	14.322	0.66	Dodecanoic acid, methyl ester (CAS) Methyl laurate
2	17.265	1.42	Tetradecanoic acid, methyl ester (CAS) Methyl myristate
3	19.698	0.59	9-Hexadecenoic acid, methyl ester, (Z)- (CAS) Methyl palmitolea
4	19.971	33.30	Hexadecanoic acid, methyl ester (CAS) Methyl palmitate
5	21.174	0.14	Heptadecanoic acid, methyl ester (CAS) Methyl heptadecanoate
6	22.059	13.67	9,12-Octadecadienoic acid (Z,Z)-, methyl ester (CAS) Methyl lino
7	22.145	39.30	9-Octadecenoic acid, methyl ester (CAS) methyl octadec-9-eno
8	22.370	6.12	Octadecanoic acid, methyl ester (CAS) Methyl stearate
9	24.349	0.24	11-Eicosenoic acid, methyl ester (CAS) methyl 11-eicosenoat
10	24.593	0.58	Eicosanoic acid, methyl ester (CAS) Arachidic acid methyl ester

Biodiesel Synthesis

Biodiesel synthesis was carried out with a ratio of oil: methanol molar ratio of 1:7. The CaO catalyst concentration used was 2% of the amount of waste cooking oil. Waste cooking oil, methanol and duck eggshell catalyst were put into a three-neck flask equipped with a cooled reflux condenser. The mixture was stirred at 500 rpm and heated at 45ºC, 55ºC and 65ºC, for 1, 2, and 3 hours. The stirring time was following the research of Ardiansah et al [3].

The results were filtered to separate the catalyst and product and put into a separatory funnel to stand for one day. The layer was formed into two phases where the top layer is biodiesel and the bottom layer are glycerol. The purification process was carried out by heating the biodiesel for 15 minutes at 115°C to removing residual methanol and water. The results of the biodiesel quality test are shown in Table 3 below.

Based on Table 3, the total value of methyl esters in the biodiesel sample is 96.02%. The minimum standard set by SNI: 7182:2015 is 96.5%. It is shows that the total ester parameter has not met the requirement.

4 Conclusion

The transesterification reaction of waste cooking oil can be produced using a heterogeneous catalyst (CaO) from duck eggshells. The best biodiesel quality was shown at a reaction time of 2 hours. The parameters of acid number, density, FFA, viscosity, and flash point of the product made meet the standards of SNI: 7182: 2015, except for the cetane number parameter, and the total methyl ester does not met the requirements.

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