Advances in Engineering Research, volume 208
Proceedings of the International Conference on Innovation in Science and Technology (ICIST 2020)

Optimization Biodiesel Production Using CaO Nanocatalyst From Egg Shell Waste

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***Abstract*—Biodiesel is an alternative diesel fuel, made from renewable biological sources such as vegetable oils and animal fats. Used cooking oil is one of the biodiesel raw materials. The development of biodiesel synthesis in this study focuses on production efficiency and reducing negative effects on the environment. In the research carried out, the production of biodiesel from waste cooking oil used variations in the concentration of solid calcium oxide (CaO) catalysts with nano size from chicken egg shells. The steps of this research are catalyst preparation, raw material analysis, esterification reaction, transesterification reaction, and analysis. The results from this research are the chicken eggshell can be used as a CaO-solid catalyst with nano size which can increase the yield of biodiesel and the parameters of density, viscosity, free fatty acids and acid numbers in accordance with the SNI Biodiesel.**

Keywords—egg shell waste, CaO, nanocatalyst, biodiesel, pilot plant

I. INTRODUCTION

Biodiesel is an alternative diesel fuel, made from renewable biological sources such as vegetable oils and animal fats. Biodiesel can be biodegradable and non-toxic, has low emissions and also environmentally friendly. Vegetable fuel in the form of methyl esters from fatty acids (fatty acid methyl esters, FAME) [1,2].

Biodiesel raw materials come from various sources, including oil, one of which is used cooking oil that contains carcinogenic substances which can endanger human health and endanger the environment. Because it is quite dangerous and can be reused, waste cooking oil can be used as raw material for biodiesel. Using waste cooking oil can reduce waste oil waste disposal. Besides cooking oil waste has a high economic value.

The catalyst is a compound that can accelerate the reaction. In the manufacture of a compound generally uses a homogeneous catalyst and heterogeneous catalyst. Heterogeneous catalysts have the advantage of being more environmentally friendly, stable at high temperatures, having large pores and relatively low prices and reducing wasted water and catalysts can be reused for further processing [3].

Calcium oxide (CaO) is an important inorganic material, because it can be used as a catalyst for transesterification reactions because it has many advantages which are high in activity, long-lasting, low cost, and have high base strength [4]. CaO is slightly soluble in methanol compared to other alkaline earth metal oxides or hydroxides such as SrO and Ba (OH)2 which are fully dissolved in the reaction media [5].

Most CaO catalysts used in the transesterification reaction are still micro-sized, as reported by Xin, 2009 [6], which uses CaO crystals with a diameter of 4-8 μm for the transesterification reaction. Therefore, in this research, nano sized CaO synthesis is needed in an effort to obtain a CaO catalyst with higher activity, where the CaO catalyst is obtained from chicken eggshells. From the literature it is known that the CaCO3 content in chicken eggshells is about 94% by weight [7,8]. Therefore, it can be expected that eggshells can be used as a source of high purity CaO so that they can act as a catalyst in the transesterification reaction of oil and methanol into biodiesel. Source of raw material (chicken eggshell) is quite a lot and at the moment it is only discarded (not yet utilized). Therefore, utilizing chicken egg shell as a catalyst is a good step to increase the economic value of chicken eggshells and reduce the environmental burden.

II. MATERIALS AND METHODS

A. Materials and Equipment

The raw material used in this research is used waste cooking oil, the catalyst used is a chicken egg shell which will be carried out before the catalyst preparation to obtain nano-sized catalyst.

B. Procedures

1) Preparation CaO Nanocatalyst from egg shell waste: The catalyst preparation technique uses the wet impregnation method. At first, 500gram chicken egg shells were crushed using a mortar and sieved until a 250mesh nano-sized chicken egg powder was obtained. Then the chicken egg powder is washed thoroughly using aquadest, drained, and dried at 1050C for 24 hours in the oven. Then weigh the nanoparticle catalyst by 20gram, and the catalyst is thermally decomposed (calcined) at 900oC for 2 hours [9]. The resulting calcination is then stored in a desiccator to keep the catalyst condition dry.

2) Raw materials analysis:

a) Filtering: Filtering used cooking oil using filter paper from gauze to free it from dirt.

b) Determination of density: Intake of density using balance sheet and pycnometer. At first the pycnometer empty is weighed and the results recorded. Then do a re-weighing of the sample to find the density. Sampling of the solution is carried out three times in order to obtain the average or tendency of the resulting value. The solution that is inserted in the pycnometer is confirmed to be full and there is no residue outside the pycnometer.

3) Determination of viscosity: Intake of viscosity can be done using the Visward Ostward method. This research was conducted using an Ostward Viscometer with three bubbles. The solution is inserted using a dropper until it meets bubble A (located in a single bubble neck) the solution will fill bubble B (located in the neck of the lower double bubble). The solution that fills bubble B will be sucked with a eyedropper ball to the upper limit of bubble C (located in the upper double bubble neck). After the upper limit of bubble C is reached the pipette ball is released while calculating the duration of the solution drop with a stopwatch. Data is collected three times.

4) Determination of free fatty acid concentration:

- Weigh 14 grams of cooking oil weighed.
- Insert into 250 mL erlenmeyer.
- Add 25 mL of ethanol.
- Add 3 drops of phenolphtalein indicator (PP).
- Titrate with 0,05 N NaOH until a pink solution is formed and does not disappear for 30 seconds.

5) Write the volume of NaOH used: The FFA or Free Fatty Acid (FFA) equation is as follows:

$$FFA = \frac{N\,NaOH\ x\ v\ NaOH\ x\ 200}{w\ x\ 1000}\ x\ 100\% \quad (1)$$

Where :
NNaOH : concentration of NaOH (N)
vNaOH : Titration volume of NaOH (mL)
w : Mass of waste cooking oil (gram)
200 : mass molar of fatty acid (g/mol)

6) Determination of acid numbers: Determination of the acid number value using the following equation:

$$Acid\ Number = \frac{39{,}9\ x\ N\ NaOH\ \ x\ v\ NaOH}{w} \quad (2)$$

Where :
NNaOH : concentration of NaOH (N)
vNaOH : Titration volume of NaOH (mL)
w : Mass of waste cooking oil (gram)
200 : mass molar fatty acid (g/mol)
39,9 : mass molar of NaOH (g/mol)

C. Esterification Reaction

The purpose of the esterification stage using a sulfuric acid catalyst is to reduce the levels of free fatty acids in oil. Free fatty acid levels must be less than 0,5%. The procedures of Esterification Reaction are:

- Mixing 100 mL of used cooking oil with 18 M sulfuric acid catalyst as much as 5% v/w
- Add methanol, where the mole ratio of methanol /oil is 40: 1
- Heat used cooking oil at 60^0C for 60 minutes.
- Leave the used cooking oil for 24 hours, until the triglyceride and glycerin layers are formed.
- Separating the triglyceride and glycerin layers (settling process 1).
- The triglyceride layer will be used at the transesterification stage.

D. Transesterification Reaction

- Mixing the oil derived from the esterification stage with a solution of methanol and nanoparticle catalyst.
- Heat the mixture and stir in a 60ºC tank for 10-15 minutes.
- Precipitating the mixture was carried out until separated by two phases in this study, deposition occurred for 16 hours then glycerol and crude methyl ester formed (settling process 1).
- b. Wash crude methyl esters for 15 minutes with water at 40ºC-50ºC and stir until a normal pH (6,8-7,2) (washing process).
- Sedimentation was repeated to separate the water for 10 hours (settling process 2).
- Heat the result of methyl ester to evaporate the washing water remaining at a temperature of 90ºC - 100ºC (drying process).

E. Analysis

1) Analysis of nanoparticle catalysts

2) Analysis of methyl esters

a) Density of methyl esters

b) Viscosity of methyl esters

c) Free fatty acid levels

d) Acid number

e) Yield of methyl esters

III. Results and Discussion

A. *Nanocatalyst Preparations*

The results of characterization using XRD showed that the compound produced from calcination was CaO. The main compound that makes up almost all parts of a chicken eggshell shell is CaCO3, so heating at high temperatures can react to CaO [10]. This is in accordance with the following reaction [11]:

$$CaCO_3 \rightarrow CaO + CO_2$$

And from the XRF analysis results show that the largest composition contained in the chicken eggshell is 98,9% Ca element, so that the chicken eggshell can be used as an economical source of CaO.

B. *Raw Materials Analysis*

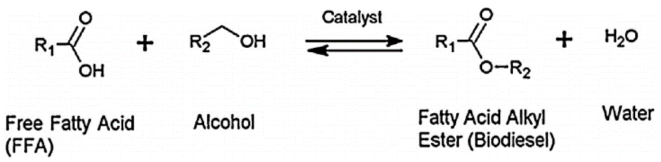
The parameters of raw material analysis are density, viscosity, free fatty acid levels and acid numbers are analyzed, as follows in Table 1.

TABLE I. The Results Analysis of Raw Material

Parameter	Result	Unit
Density	928,9	Kg/m^3
Viscosity	11,85	cSt
Free Fatty Acid	0,7	%
Acid Number	1,954	mg-NaOH/g

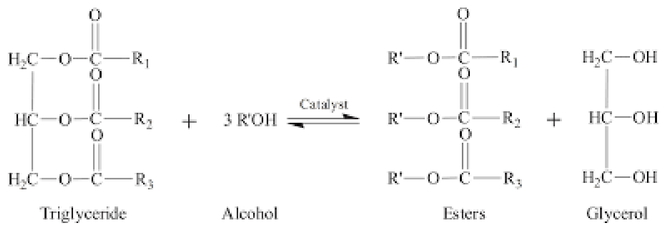
C. *Esterification Reaction*

Esterification reaction is carried out to reduce the levels of free fatty acids in oil by converting free fatty acids into FAME. After the reasterification reaction, the level of free fatty acids in oil was significantly reduced, from 0,7% to 0,2%. The reaction of methanol with free fatty acids is reversible and slow. For the reaction to go to the right and the product produced is high, the reactant molar ratio must be high [12].



D. *Transesterification Reactions*

In the transesterification reaction stage, triglyceride oil is mixed with methanol and catalyzed by CaO nano catalyst. Triglycerides will be converted to di- and mono-glycerides, and then form biodiesel (methyl esters) and glycerol.



1) Density: Density shows the ratio of specific gravity per unit volume. In figure 1 shows the density value of methyl ester tends to increase proportionally with increasing catalyst concentration. The highest density value is 889,1 kg / m^3 at 5% w / w nanocatalyst concentration, while the lowest density value is 868,9 kg / m^3 at 1% w / w nanocatalyst concentration.

Analysis of the increase in density values shows the presence of impurities in the methyl ester. If the catalyst concentration increases, it can cause a saponification reaction which results in varying density values. Factors affecting density include the concentration of basic catalysts and the purification process in washing and drying.

In Figure 1, the range of density values is at 868,9-889,1 kg / m3. This is in accordance with the density limit stated in SNI is 850-890 kg / m^3 [13].

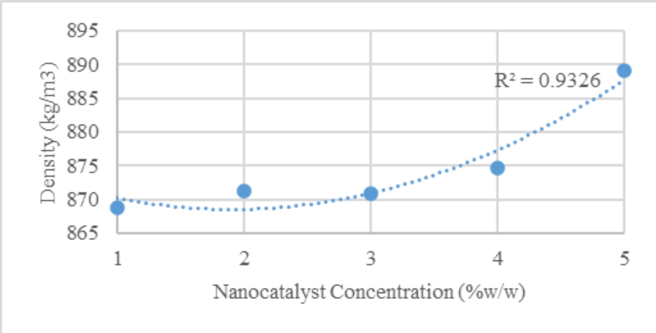


Fig. 1. Effect of nanocatalyst concentration on methyl esther density.

2) Viscosity: Viscosity is a number that states the amount of resistance of a liquid material to flow or the size of the magnitude of the shear resistance of the liquid. Viscosity is the main fuel property because it affects fuel atomization on injection into a diesel engine. It is explained in Fig.2 that the kinematic viscosity of methyl esters towards an increase in base catalyst tends to increase. The lowest viscosity value was 2,37 at 1% w / w catalyst concentration and the highest viscosity value was 3,69 cSt at 5% w / w catalyst concentration.

In figure 2, the range of density values are 2,37 – 3,69 cSt. This is in accordance with the limit of the viscosity value stated in SNI is 2,3-6 cSt [13].

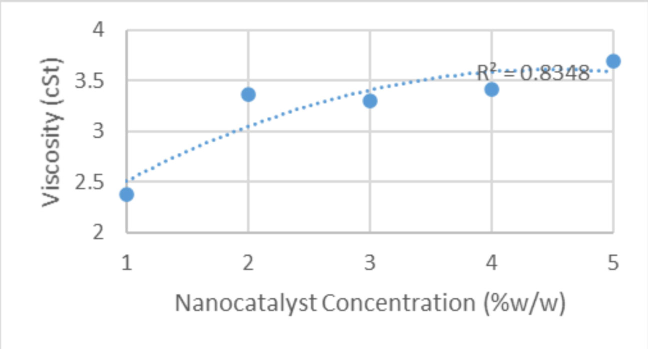


Fig. 2. Effect of Nanocatalyst Concentration on Methyl Esther Viscosity.

3) Free Fatty Acid: In figure 3, as the concentration of the nanocatalyst increases, the value of free fatty acid is decreases. The lowest free fatty acid value is 0,025% at 5% w / w nanocatalyst concentration and the highest free fatty acid value is 0,032% at 1% w / w nanocatalyst concentration. At a concentration of 5% nanocatalyst w/w the oil has not been completely converted into methyl esters, so there are still many free fatty acids. But overall, the value of free fatty acids still meets the 0.02% SNI Biodiesel.

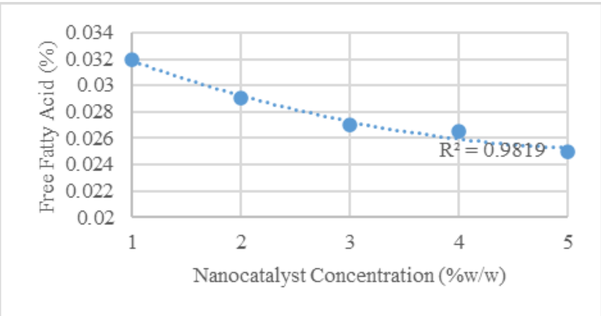


Fig. 3. Effect of Nanocatalyst Concentration on Free Fatty Acid

Acid number: The acid number is the number of milligrams of catalyst needed to neutralize 1 gram of the sample (methyl ester). The acid number shows the acid content still present in the methyl ester. Acid numbers are required to be as small as possible because free fatty acids are corrosive, causing damage to the components of diesel engines, high acid numbers can cause fuel deposits, causing pumps and filters to fail faster. Factors affecting the acid number are the quality of used cooking oil and the concentration of basic catalysts. With a low acid content, the quality of methyl esters increases. This is in accordance with the Arrhenius law where the low activation energy facilitates the rate of reaction, so that the reaction of methyl ester changes will be faster and easier. The acid number has decreased because the NaOH titration volume is the same as the glycerol equation. Figure 4 shows that the lowest acid number is 0,352 mg-NaOH / mg at a 5% w / w nanocatalyst concentration, and the highest acid number is 0,556 mg-NaOH / mg at a concentration of 1% w / w. And the acid number range in this study is in accordance with the SNI Biodiesel acid limit range [13].

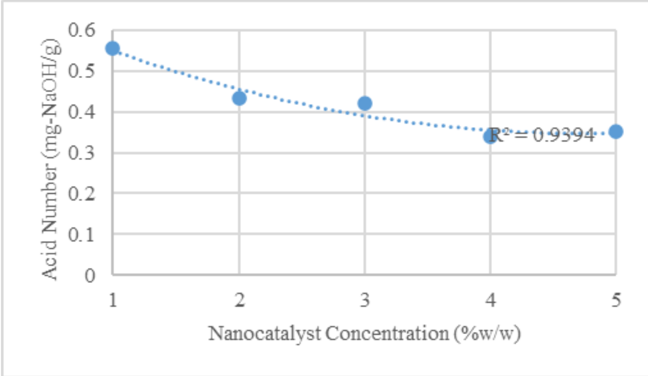


Fig. 4. Effect of Nanocatalyst Concentration on Acid Number.

4) Yield: The catalyst serves to increase the rate of reaction. The more amount of catalyst added will increase the rate of reaction. Increasing the rate of transesterification reaction at a certain time will increase the amount of used cooking oil that is converted to biodiesel. The greater the concentration of catalyst in solution, the smaller the activation energy of a reaction, so that more products will be formed. The increased concentration of catalyst causes an increase in biodiesel yield. The highest yield value is 99,4% at 4% w / w nanocatalyst concentration.

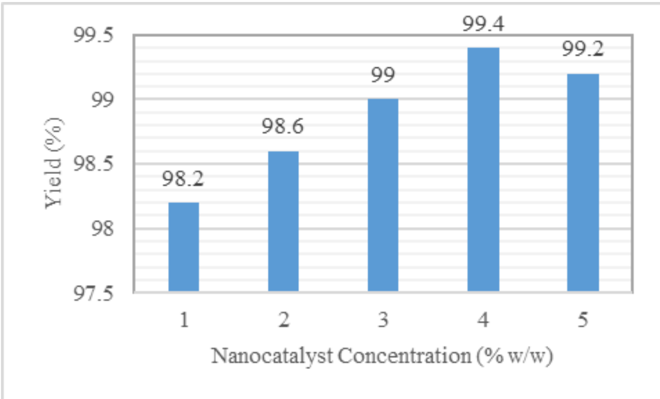


Fig. 5. Yield of methyl ester.

IV. Conclusions

The results of this study consider the current status and promising potential of using nano CaO-based catalysts from eggshell waste as a heterogeneous catalyst in biodiesel production; the value of density, viscosity, free fatty acids, acid numbers meet SNI Biodiesel, and the highest yield of methyl ester is 99.4% at 4% nanocatalyst concentration w / w.

ACKNOWLEDGMENT

This work has been funded by the Local Research, Politeknik Elektronika Negeri Surabaya.

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