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Research Article

Utilization of Chicken Eggshells as Catalyst in Biodiesel Synthesis from Waste Cooking Oil

Lizda Johar Mawarani[1*], Thomas Andherson Sihombing[1], Doty Dewi Risanti[1], Muhannad Illayan Massadeh[2], and Dwi Prananto[3]

[1]Department of Engineering Physics, Institut Teknologi Sepuluh Nopember, Kampus ITS Sukolilo Surabaya, Indonesia 60111
[2]Department of Biological Science and Biotechnology, Faculty of Science, The Hashemite University 13133, Zarqa, Jordan
[3]Materials Science Program, Faculty of Engineering, Niigata University, Niigata City, Niigata 950-2181, Japan

Abstract: Solid oxides are the most used catalyst for the synthesis of biodiesel, one of which is calcium oxide (CaO). This research reports the synthesis of CaO catalysts sourced from chicken eggshells through the calcination process. Chicken eggshells were cleaned and dried for 24 h at 120 °C. The eggshells were then calcined at temperatures varying from 600 °C to 900 °C for 6 h and the resulted sample were characterized by FTIR and XRD. The biodiesel synthesis was conducted at 65 ºC with a reaction time of 2 h and the concentration of catalyst was varied at 3 wt%, 6 wt%, and 9 wt%. The optimal biodiesel synthesis was obtained at a concentration of CaO catalyst formed at a calcination temperature of 900 ºC at 9 wt%. The yield of biodiesel conversion was obtained at 81.43 % and glycerol was produced as a by-product.

Keywords: Alternate Feedstock, Calcination, Environmentally Friendly Catalyst, Reduce Production Cost, Renewable Energy, Reuse Waste Material

1. INTRODUCTION

Sustainable biodiesels are usually made from vegetable oils, inedible oils, fats, algae, and waste cooking oil. The vegetable oil is more efficient for biodiesel production due to the low content of free fatty acids (FFA) [1–3]. The high content of FFA in biodiesel synthesis can trigger a saponification reaction and reduces the quality of biodiesel [4]. Biodiesel synthesis from vegetable oil requires more expensive production costs than waste cooking oil since waste cooking oil is easy to obtain [5]. Thus, waste cooking oil is more attractive for biodiesel synthesis [6].

A calcium oxide (CaO) catalyst is a heterogeneous base catalyst that can be used as an accelerator in biodiesel synthesis reactions. One of the CaO catalysts can be synthesized through the calcination process of $CaCO_3$. One of the many wastes containing $CaCO_3$ is chicken eggshells. Chicken eggs are widely consumed in Indonesia, so chicken eggshells are quite abundant. Eggshells have many advantages, among them are biodegradable, recyclable, and biocompatible [7]. Eggshells consist of 94 % $CaCO_3$, 1 % $Ca_3(PO_4)_2$, 1 % $MgCO_3$, and 4 % of organic ingredients [8]. The solid waste of chicken eggshells is harmless to the environment, it is generally disposed of in landfills without any pretreatment.

2. MATERIALS AND METHODS

This research used the waste of chicken eggshells as feed stock to produce CaO catalysts. The eggshells were cleaned then dried at 100 ºC for 24 h and

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*Corresponding Author: Lizda Johar Mawarani <lizda@ep.its.ac.id>

crushed to reduce their particle size up to 60 mesh.

CaO catalysts were made through the calcination process of sieved eggshell particles. The process is intended to remove carbon dioxide compounds through the decomposition reaction of calcium carbonate ($CaCO_3$) contained in eggshells so that calcium oxide compounds are obtained. Equation (1) shows the reaction during the calcination process [9]:

$$CaCO_3 \quad CaO + CO_2 \qquad (1)$$

The chicken eggshell powder was then calcined for 6 h at a varied temperature of 600 °C, 700 °C, 800 °C, and 900 °C. The resulted sample was analyzed and characterized using X-ray Diffractometer (XRD) and the Fourier Transform Infra-Red (FT-IR) spectroscopy.

The next step was the pretreatment process to reduces the content of FFA in the waste cooking oil sample. In this study, the desired FFA content is < 1 %. The process was started by heating waste cooking oil (300 mL) at a temperature of about 55 °C to 65 ºC. Then a mixed solution of methanol (15% of the mass waste cooking oil) and H_2SO_4 catalyst (1% of the mass waste cooking oil) was put into the waste cooking oil sample at 60 ºC for 2 h. After the reaction finished, the waste cooking oil was washed using distilled water. The waste cooking oil was then reheated at 120 ºC for 10 min. Then to prepare a lye solution, the CaO catalyst from chicken eggshells was mixed with methanol with a molar ratio of 6:1. The added lye solution to the pretreated waste cooking oil with a varied concentration of 0 wt%, 3 wt%, 6 wt%, and 9 wt% and heated at 65 ºC for 2 h for transesterification reaction. After the transesterification reaction was completed, the biodiesel sample was left for one night to separate the upper layer containing biodiesel. Glycerol in the lower layer must be washed to neutralize the biodiesel from glycerol.

3. RESULTS AND DISCUSSION

The physical formation of CaO can be seen from the color change of the eggshell after the calcination process. Calcination at 600 °C produced a dark gray powder, at 700 °C produced a pale gray powder, at 800 °C produced a pale gray with a little white, and at 900 °C produced a white powder with a little gray. The higher the calcination temperature, the more metal oxides formed which is indicated by the color change of the chicken eggshells powder to white [9].

The results of XRD for the chicken eggshells powder after calcination at a temperature of 600 ºC to 900ºC, are shown in Figure 1. The XRD pattern for calcination at 900 °C shows the successful formation of the crystalline CaO structure as indicated by the appearance of a sharp peak at 2θ = 32.2°, 37.4°, 53.9°, 64.2°, and 67.4° that indicate an increase in the resulting CaO digitality. Commercial CaO also has the same peaks on the XRD pattern. However, there are still peaks associated with the $CaCO_3$ phase which appeared at 2θ = 29.4° and 47.3° also the $Ca(OH)_2$ which appeared at 2θ = 28.6°, 34.2°, 47.2°, and 50.9°.

The compound fraction is calculated using the Reference Intensity Ratio (PERR) shown in Equation (2) [10]:

$$Fraction\ R\ (\%) = \frac{\sum \frac{I_i}{I_{max}}}{\sum \frac{I_p}{I_{max}}} x\ 100\ \% \qquad (2)$$

Figure 1 shows that at calcination temperature of 600 ºC, 700 ºC, and 800 ºC high composition of $CaCO_3$ was formed with compound fraction around 68 % to 86 % along with the minor composition of CaO, $Ca(OH)_2$, and impurity with respective compound fraction around 7 % to 8 %, 3 % to 5 %, and 11 % to 19 %. This indicates that at calcination temperatures of 600 ºC, 700 ºC, 800 °C only a small amount of $CaCO_3$ is converted to CaO. For 900 ºC calcination temperature, the composition of CaO was optimally formed with a fraction compound of 85.02 % with 3.73 % of $CaCO_3$, 11.24 % of $Ca(OH)_2$, and is already clean from impurity.

FTIR analysis of the CaO catalyst was carried out at 4 000 cm^{-1} to 400 cm^{-1} wave numbers as shown in Figure 2 [11]. The OH band appeared at a wave number of 3 639.06 cm^{-1} to 3 760.21 cm^{-1} for the calcination temperature of 800 ºC and appeared very sharply at 900 ºC, but did not appear at temperatures of 600 ºC and 700 ºC. The OH band is considered as a CaO characteristic [12] so that the appearance of the OH group indicates a peak fit between the three samples. However, the emergence of these OH groups cannot merely be used to justify that the sample analyzed is CaO because the presence of $Ca(OH)_2$ also causing the emergence of a dip in the area of about 3 643 cm^{-1} as shown by previous research [13]. The presence of such dip may be due to the adsorbent of water on the CaO surface because of its nature as an absorber of water from the air [13].

The CaO is detected by referring to the wave number at the area around 400 cm^{-1} in the sample. Referring to the standard CaO, $CaCO_3$, and $Ca(OH)_2$ spectrum, the CaO spectrum appeared to broaden at that wave number. Dips in the region of about 400 cm^{-1} to 500 cm^{-1} are connected with the stretching of Ca-O bonds. The sample with a calcination temperature of 900 ºC indicates more CaO formation, due to the broadened dip at the wave number.

The calcination temperature greatly influences the structure of the catalyst and its catalytic properties. Therefore, the catalytic activity of the sample of eggshell powder was then tested through a process of transesterification to convert triglycerides to biodiesel (free acid methyl esters/ FAME). The FFA level of the waste cooking oil is reduced from 4.045 % to 0.775 % by the CaO catalyst; a significant reduction of 80.84 %.

This research found that only eggshell powder produced by calcination at 900 ºC can form glycerol after the transesterification reaction with the waste cooking oil. This is mainly because eggshell powder with calcination temperatures of 600 ºC, 700 ºC, and 800 ºC was not producing enough CaO and was mainly dominated by $CaCO_3$ or calcite. Previous studies also found that if the eggshell powder is dominated by $CaCO_3$, it was not able to catalyze and eliminate energy during the transesterification reaction [14].

The CaO catalyst from eggshell Powder with calcination temperatures of 900 ºC produced a fraction of biodiesel of about 66.76 %. This can prove that a higher calcination temperature increases the catalytic properties of the transesterification process. In addition, the formation of glycerol after the transesterification process also justifies the presence of biodiesel because it has fulfilled the transesterification reaction. This is also confirmed by previous research which discussed its calcination temperature at 900 ºC and found that the catalyst that was very active in the transesterification reaction process [15].

In biodiesel synthesis, the concentration of catalyst is also very much influences the transesterification process. Figure 3 shows the biodiesel yield at different catalyst concentrations.

Figure 3 shows that the biodiesel yield increases monotonically with increasing calcium oxide (CaO) catalyst concentration. This increase is consistently occurring in all samples of chicken eggshell powder. From the results, it was found that the CaO catalyst produced at 900 ºC calcination temperature gave the largest contribution in converting triglycerides to biodiesel by 81.43 % with a concentration of 9 wt%. The synthesis of biodiesel with a commercial catalyst was also carried out to compare the biodiesel produced with a catalyst from the eggshell. The highest biodiesel production was obtained on the 9 % catalyst concentration which was 83.59 %. This yield is higher than the catalyst from eggshells at the same concentration. However, for the 3 wt% and 6 wt% eggshell catalysts, the biodiesel yield was higher than the commercial CaO catalyst. This is caused by the increase in the reaction rate at a high concentration of catalyst which reduces the activation energy [12].

The yield of biodiesel is higher than the results of Muhammad et. al. [16] that synthesized biodiesel from used cooking oil using a microwave and CaO catalyst from chicken eggshells and duck eggshells. The catalyst composition varied from 1 % to 10 % and showed the maximum amount of yield of biodiesel at a composition of 5 % CaO from chicken and duck eggshells, respectively 40.74 % and 67.07 %. From this known that used cooking oil biodiesel with CaO catalyst from chicken eggshells and through common transesterification in this study gives better results.

The biodiesel produced in the experiment was then tested to determine whether it is suitable with the available standards for use. The tests carried out were among others to determine the kinematic viscosity, density, pour point, flash point, and fog point. The biodiesel characteristics are shown

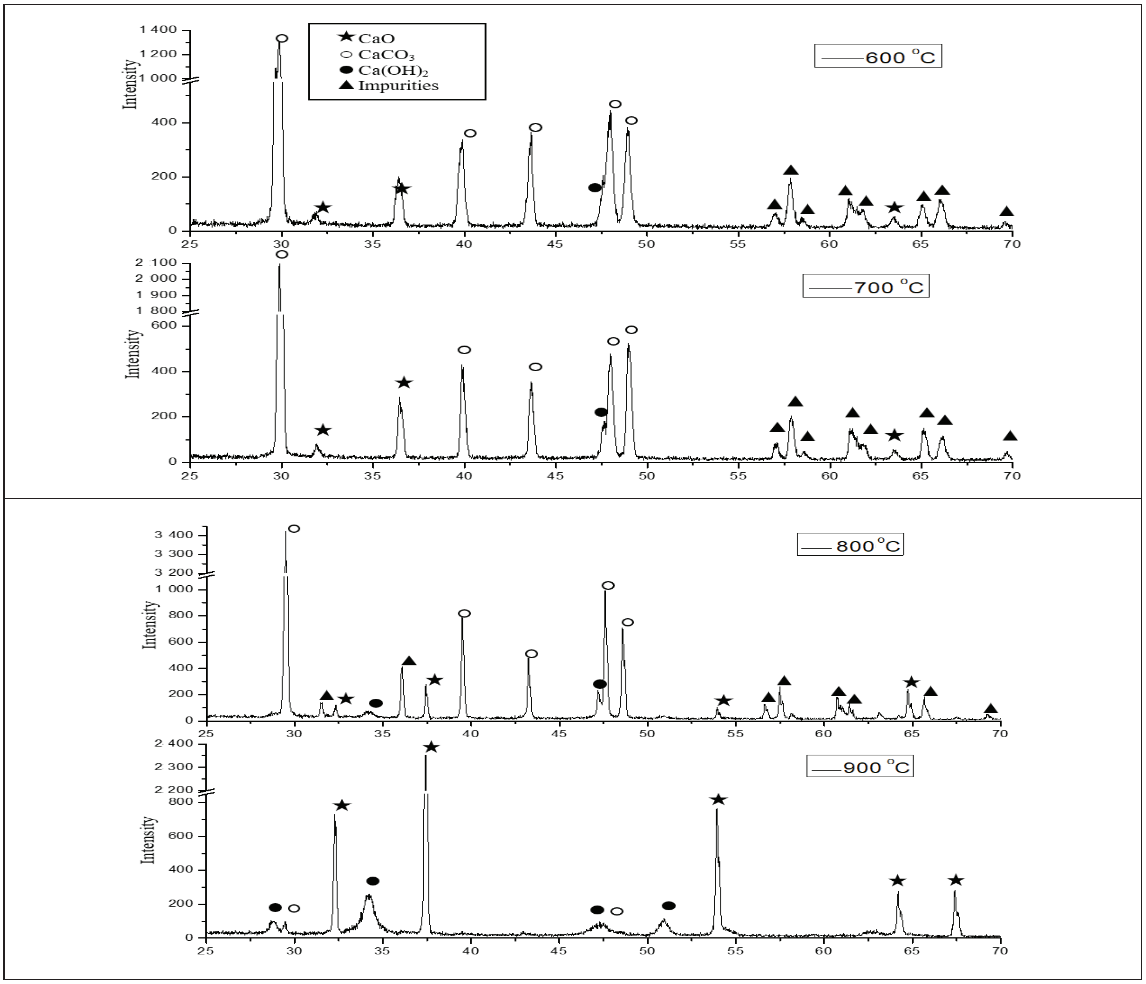

Fig. 1. XRD diffraction pattern of 6 h calcined eggshells

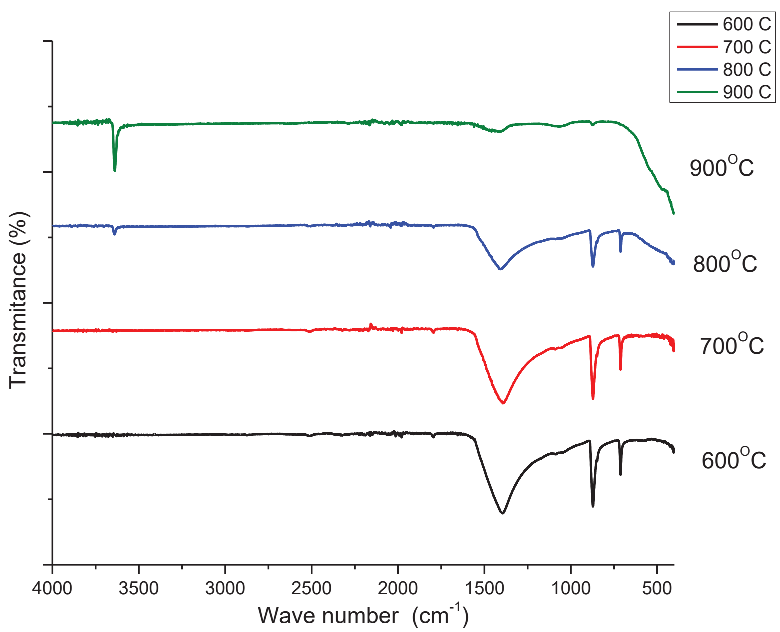

Fig. 2. Graph of FTIR results of chicken eggshells powder with 6 h calcination

in Table 1. Density test of the biodiesel samples produced with CaO catalyst formed by calcination temperatures at 800 ºC and 900 ºC, commercial CaO, and without catalyst were met with SNI and ASTM standards for all concentrations. But for the samples produced with CaO formed by calcination temperature at 600 ºC and 700 ºC the density of the biodiesel of which has not met with the standard for all catalyst concentrations.

The results of the kinematic viscosity test of the biodiesel samples with CaO catalyst formed at 900 ºC calcination temperature and commercial CaO catalysts were met with the SNI and ASTM standards and were characterized by a rather thin physical property. When compared to conventional diesel the kinematic viscosity value of the biodiesel samples that met the standard is not much different, which is around 4.6 $mm^2 s^{-1}$. This means that CaO catalyst formed with calcination temperature of 900 ºC and commercial CaO can reduce the kinematic viscosity of biodiesel.

Flashpoint of all the biodiesel samples was met with SNI standards (minimum 100 ºC) and ASTM (minimum 130 ºC) so that all biodiesel samples were within safe limits of fire hazards during storage, handling, and transportation. But the flashpoint value of the biodiesel samples produced by CaO catalyst formed at a calcination temperature of 900 ºC and commercial CaO and CaO catalyst formed at 600 ºC, 700 ºC, 800 ºC, for the same process. The case without catalyst has a very significant difference with a ratio of about 1: 2. It should be noted that the flashpoint that is too high is also not good to be used because biodiesel will be difficult to light itself [17].

The test results of the cloud points of all biodiesel samples were met with the two standards. For the pour points, test CaO catalyst formed at calcination temperatures of 800 ºC and 900 ºC and

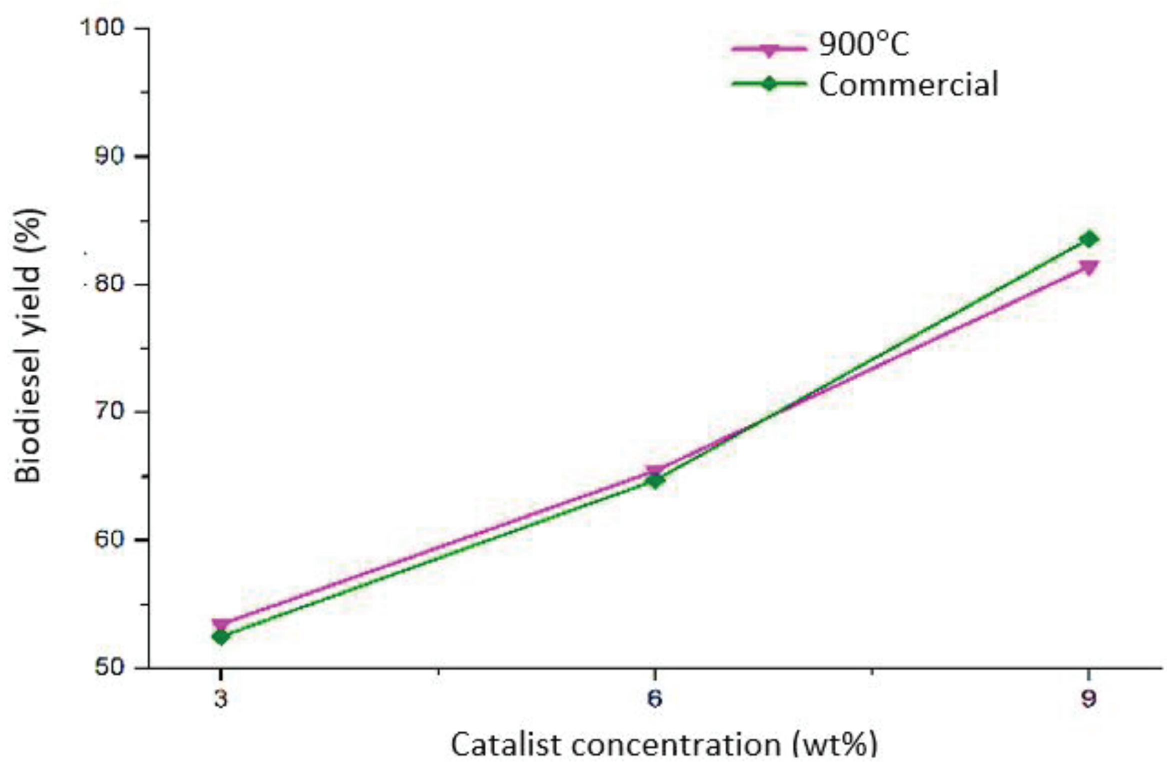

Fig. 3. Graph of the yield of biodiesel at a different catalyst concentration

Table 1. Biodiesel sample characteristics based on SNI and ASTM

Characteristics			Density ($kg\ m^{-3}$)	Kinematic viscosity ($mm^2\ s^{-1}$)	Point (°C)		
					flash	pour	cloud
ASTM D6751			800 to 880	1.90 to 6.00	Min. 100	Max. 18	Max. 18
SNI-04-7182:2015			850 to 890	2.30 to 6.00	Min. 120	Max. 18	Max. 18
Without catalist		**0**	880	25.02	326.5	18.3	15.1
CaO catalist concentration (wt%)	**600 °C**	**3**	910	34.39	328.3	21.6	17.6
		6	900	34.23	336.8	20.8	16.5
		9	900	34.22	327.7	21.4	16.3
	700 °C	**3**	910	36.37	334.7	20.1	16.4
		6	900	33.72	330.9	18.9	16.6
		9	890	32.96	327.2	18.3	16.7
	800 °C	**3**	870	33.6	332.6	16.1	14.8
		6	850	34.32	326.7	17.7	14.6
		9	850	33.9	318.7	17.1	13.7
	900 °C	**3**	870	3.88	175.5	15.4	11.3
		6	860	4.41	178.3	16.7	11.7
		9	870	4.58	175.8	17.8	10.7
	Commercial	**3**	860	3.99	185.4	16.1	11.8
		6	870	4.39	186.7	17.5	11.5
		9	860	4.53	184.6	17.7	11.6

commercial CaO were met with SNI (maximum 18 ºC) and ASTM (maximum 18 ºC). Whereas for the CaO catalyst formed at a calcination temperature of 600 ºC and 700 ºC, and without catalyst were not meet with the standards so it is not recommended.

4. CONCLUSION

Based on the results of the characterization and analysis carried out on the CaO catalyst and biodiesel samples, this article concluded that the CaO catalyst formed with calcination at a temperature of 900 ºC can be used as a reference for the production of biodiesel where the concentration of 9 wt% yields the highest biodiesel formation of about 81.43 %. The results of the test to characterize the biodiesel samples that met with the qualifications of SNI-04-7182: 2015 and ASTM D6751 were obtained from the biodiesel samples Synthesized by CaO catalyst form chicken eggshell with calcination temperature of 900 ºC and commercial CaO with 3 wt%, 6 wt%, and 9 wt% catalyst concentration.

5. CONFLICT OF INTEREST

The authors declare no conflict of interest.

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