Original Article

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Heca Journal of Applied Sciences

Vol. 1, No. 1, 2023

Palm Frond Waste as a Carbon Source in the Synthesis of CaO/Biochar Catalysts for the Biodiesel Production Process

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Article History

Received 30 April 2023
Revised 23 May 2023
Accepted 1 June 2023
Available Online 7 June 2023

Keywords:
Biochar
Palm frond
Pyrolysis
Torrefaction

Abstract

This study aims to synthesize and determine the characterization of activated CaO/Biochar and identify the effect of the mass ratio of CaO/Biochar and KOH concentration on the activity of CaO/Biochar catalysts for the synthesis of CPO-based biodiesel. CaO was obtained from eggshell waste. Biochar is obtained from palm fronds through a torrefaction process. CaO/Biochar catalyst was synthesized by impregnation process using KOH solution. The biodiesel transesterification process using CaO/Biochar catalysts. XRD analysis results obtained CaO and $Ca(OH)_2$ compounds in the catalyst, and the basicity value of the catalyst was >9.3. The best catalytic activity of the CaO/biochar catalyst was obtained at a mass ratio of 12:10 and a concentration of 20% KOH catalyst, with a biodiesel yield of 75.1%.

1. Introduction

The ever-growing population causes an increase in energy demand worldwide. It is reported that today's consumption of petroleum is 105 times faster than nature could create. These facts, together with the limited resources of oil reserves and their use, contribute to the increase in atmospheric carbon dioxide causing global warming, which is recognized as a major threat to mankind [1].

Indonesia, as one of the largest producers of crude palm oil (CPO) in the world, has the opportunity to develop large-scale biodiesel production. This is because the total production of crude palm oil in Indonesia in 2017 reached 35,359,384 tons and covered an area of 12,307,677 hectares of oil palm plantations. Meanwhile, the province that has produced the largest CPO palm oil since 2016 is Riau, with a production output of 23.58% of the total palm oil production in Indonesia [2].

Biodiesel is a renewable and environmentally friendly energy source developed as a result of the depletion of petroleum reserves and global warming, biodegradable, non-toxic, and produces fewer harmful exhaust gases than diesel, such as sulfur dioxide (SO_2), carbon monoxide (CO), carbon dioxide (CO_2), non-toxic hydrocarbons, combustibles, and other carbon particles. Another advantage of biodiesel is that it has a high cetane number and flash point, so it is easy to handle and has good lubrication properties that can extend engine life. Biodiesel can be used directly without the need to modify existing engines [3].

Calcium oxide (CaO) is a heterogeneous base catalyst that can be used for the transesterification of vegetable oils.

The performance of the CaO catalyst is influenced by its characteristics, such as surface area and basicity, which affect the yield produced [4]. CaO is obtained from calcination from $CaCO_3$, whose sources are easily obtained, such as eggshells, animal bones, and others. One source of $CaCO_3$ that is easily obtained is from eggshells, which are mostly produced from food processing waste. The chemical composition of eggshell has been reported as follows: calcium carbonate (94%), magnesium carbonate (1%), calcium phosphate (1%), and other organic matter (4%). $CaCO_3$ levels are high and present in abundance, so it is possible to make active heterogeneous catalysts from eggshells [5, 6].

The use of CaO directly as a catalyst will cause oxygen ions (O_2) on the surface of CaO to form hydrogen bonds with glycerin so that the viscosity of glycerin increases and forms a suspension [7]. The formation of suspension causes CaO and glycerin to be difficult to separate from the product. To overcome these problems, CaO must be impregnated with a catalyst support or metal oxide. Previous research has reported the use of CaO from $Ca(NO_3)_2$. H_2O and eggshells as a source and provide well catalytic activities in biodiesel production [5, 8–13]. Palm fronds are used because they contain a lot of cellulose as a carbon source. Biochar is a carbon-rich product obtained from the heating process of biomass. According to Liu et al. [14], the carbon content of biochar is in the range of 45–60% by weight, lower than carbon black (> 95%) and activated carbon derived from coal (80–95%). Large amounts of hydrogen and oxygen are also present in biochar. Another characteristic of biochar is that it contains small amounts of chemical elements such as K, Na, Ca, Mg, Si, Al, Fe, and others. Due to the weakness of CaO catalyst and supported by the advantages and elements of biochar, activated biochar is suitable to support CaO catalyst.

2. Materials and Methods

Waste chicken eggshell and palm oil used as raw materials in this experiment were collected from a palm oil production in Riau province, Indonesia. Some of the chemicals used, including methanol, sulfuric acid (H_2SO_4), ethanol, potassium oxide (KOH), and oxalic acid, were purchased from Aldrich products. The equipment used for this experiment was a three-neck flask with a capacity of 500 mL as a batch reactor for a transesterification reaction, which was equipped with a heating mantel, condenser, thermometer, and magnetic stirrer. A strainer with a hole size of around 100 and 200 mesh, an oven, a furnace, and analytic weights were used to prepare the catalysts. A spindle press was used to collect palm oil and XRD characterization equipment were used to characterize the catalysts.

2.1. Preparation of CaO

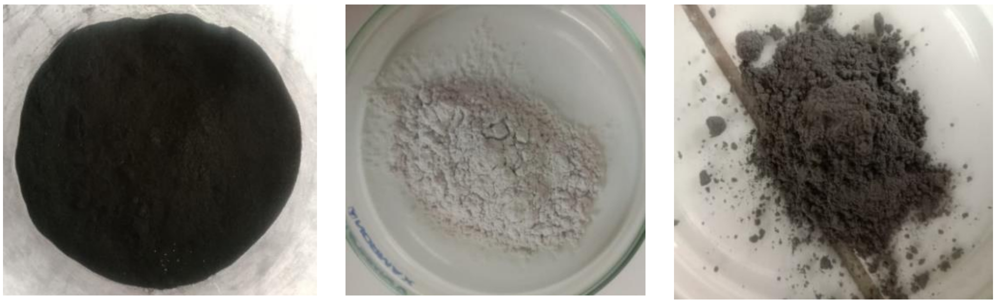
In the first step, the chicken eggshells are cleaned and dried at 110 °C for 24 hours. The dried chicken eggshells were mashed using a shaker mill and sieved with a size of 100–200 mesh to homogenize the size. Chicken eggshells that have been sifted, then calcined at a temperature of 900 °C for 3 hours to get calcium oxide (CaO) [15].

2.2. Preparation of Biochar

The second step is the preparation of activated biochar. The raw material from the palm frond is cut into small pieces with a size of 1 cm. After that, the pieces of palm midrib are dried in the sun so that the raw material of this palm midrib has a water content test result below 10%. The palm fronds will go through a torrefaction process that uses a torrefaction temperature of 275°C for 45 minutes with nitrogen gas (N_2) flowing at a constant flow rate of 150 ml/minute in a horizontal fixed-bed reactor. The next step was to carry out the pyrolysis process, which is the main process in the formation of biochar. This pyrolysis process is carried out using a horizontal fixed-bed reactor in the torrefaction process, which is operated at a temperature of 550°C. The pyrolysis process lasts for 5 minutes. When the pyrolysis process is complete, the pyrolysis products are removed and weighed.

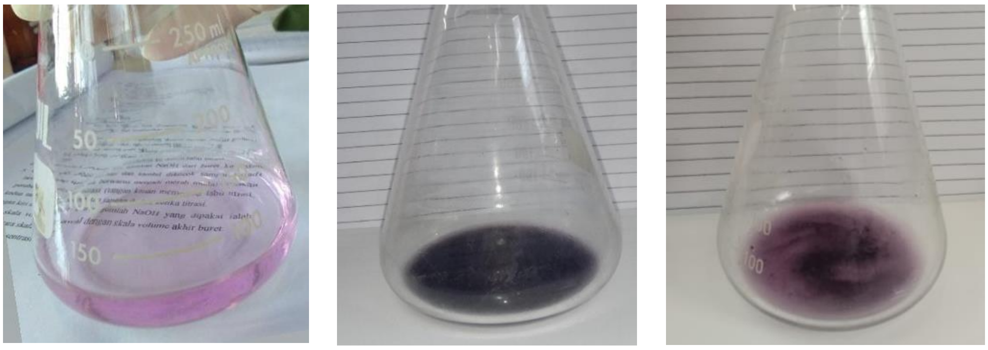
2.3. Preparation of CaO/Biochar Solid Base Catalyst

Next is the preparation of the CaO/biochar catalyst. Biochar is sieved at a size of 100–200 mesh. Furthermore, calcium oxide (CaO) and biochar were weighed according to the variable mass ratio to the weight of the catalyst. Based on the research variables, the catalyst weighed 6 g, 8 g, and 10 g, respectively. CaO that has been weighed is mixed with biochar, dissolved with 25 ml of KOH in a beaker, and stirred until homogeneous to form a solution of $Ca(OH)_2$. The process conditions were carried out at room temperature for 24 hours with a stirring speed of 400 rpm. The slurry was dried in an oven at 105°C for 5 hours. The dried slurry was calcined in the furnace for 5 hours at 500°C. Then the activated CaO/biochar catalyst was tested for XRD characterization. The strength of the basic site was expressed by an acidity function ($H\_$). The indicators used were bromothymol blue (pKBH = 7.2), phenolphthalein (pKBH = 9.3), indigo carmine (pKa = 12.2), and 2,4-dinitroaniline (pKBH = 15.0).



(a) (b) (c)

Figure 1. (a) Biochar catalyst (b) CaO catalyst (c) Catalyst CaO/Biochar.



(a) (b) (c)

Figure 2. Basicity test: (a) CaO (b) Biochar (c) CaO/Biochar 12:8 with KOH 20%.

2.4. Esterification Reaction

A catalyst with a concentration of 1% by weight of oil will be added to the manufacture of biodiesel, which is first characterized by palm oil in the form of density, water content, and free fatty acid content. Biodiesel production will be carried out using an esterification reaction. The mixture of methanol and oil reactants will be carried out in a ratio of 10:1 under conditions of a process temperature of 65°C and a stirring speed of 600 rpm for 3 hours. After the reaction is complete, the esterification product is allowed to stand until two layers are formed, the crude biodiesel is purified by washing it with distilled water that has been heated to 60°C. Then it was heated to 105°C to evaporate the remaining methanol and water. Furthermore, the characteristics of the biodiesel produced were analyzed.

3. Results and Discussions

The steps of this research are divided into two steps. The first step is the preparation of CaO catalyst from eggshells by the calcination process. While the second step is making biochar from palm fronds as a catalyst support for torrefaction and pyrolysis processes, Air and organic compounds can generally be removed from eggshells at temperatures below 600 °C, while carbon dioxide can be produced from eggshells at temperatures around 700–800 °C. Therefore, to obtain CaO catalyst from eggshell, the calcination temperature used must be above 800 °C [6].

Figure 1 shows the biochar catalyst, CaO catalyst, and CaO/biochar catalyst. The use of CaO/biochar catalysts in the transesterification process of palm oil into biodiesel will affect the quality, amount of product, and process conditions. The catalyst was synthesized by the calcination-hydration method (impregnation-dehydration). According to Liu et al. [16], the nature of CaO, which easily reacts with CO_2 and H_2O, will result in a decrease in the selectivity of the catalyst, which also affects the resulting product. Glycerol and methanol will form an emulsion with CaO, which will complicate the separation process. In the hydration stage, biochar was impregnated by the adsorption of the alkali metal CaO with distilled water as a solvent. The alkali metal CaO is obtained from the calcination of $CaCO_3$ obtained from chicken skin, while biochar is obtained from torrefaction and rapid pyrolysis processes.

Based on the results of the basicity test using a phenolphthalein indicator, each variable CaO/biochar showed a color change to a more concentrated purple. as seen from Figure 2. The results obtained form a purple color, this identifies that the catalyst has an alkalinity of $H\_ > 9.3$ and proves that the catalyst obtained is basic.

CaO/Biochar catalyst characterization using x-ray diffraction (XRD) at 2θ between 10° - 70°. Comparison of

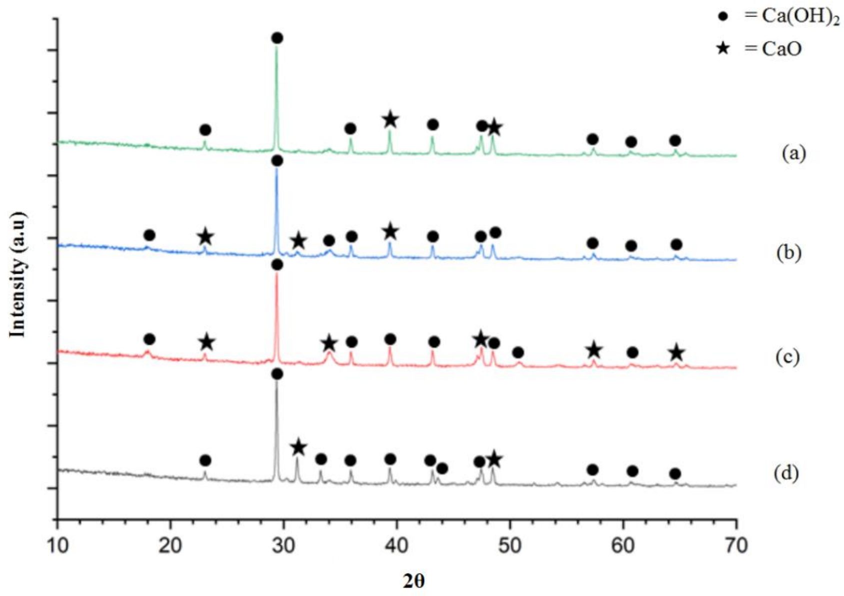


Figure 3. XRD Pattern of CaO/Biochar Catalyst: (a) CaO/Biochar Catalyst 12:6, KOH 15%. (b) CaO/Biochar catalyst 12:6, KOH 20%, (c) CaO/Biochar catalyst 12:10, KOH 20% (d) CaO/Biochar catalyst 12:8, KOH 20%.

Table 1. Characteristics of biodiesel product.

Sample	Variable		Characteristic			
	CaO: Biochar ratio	KOH (%)	Density (kg/m³)	Kinematic viscosity (mm²/s)	Acid Number (mg KOH/g)	Yield (%)
1	12 : 6	15	882.7	4.61	0.31	56.2
2	12 : 8	15	852.9	4.59	0.34	27.5
3	12 : 10	15	869.2	4.56	0.29	57.9
4	12 : 6	20	883.2	4.35	0.25	70,.1
5	12 : 8	20	883.5	4.33	0.23	55.8
6	12 : 10	20	879.7	4.31	0.25	75.1
7	12 : 6	25	877.9	4.19	0.33	49.3
8	12 : 8	25	870.5	4.18	0.34	49.9
9	12 : 10	25	965.4	4.16	0.29	40.6

XRD patterns of CaO/Biochar catalysts prepared using variations in the mass ratio of catalyst weight and KOH concentration are shown in Figure 3. The presence of a peak in the test results indicates the crystallinity of the catalyst; the higher the intensity, the greater the crystallinity. During calcination, $CaCO_3$ is oxidized to CaO and CO_2 with air flowing continuously into the furnace, where the CO_2 formed will go out of the furnace along with air access. From Figure 3, the results of the XRD test can be seen that there is a peak of CaO at an angle of 2: 23.0209°, 29.3672°, 39.3861°, 48.5285o, and 54.2877°. This indicates that not all are converted to CaO. In addition, the test results indicate that $CaCO_3$ has been successfully impregnated with biochar. While the pattern of $Ca(OH)_2$ shows that the CaO/biochar synthesized catalyst still contains a small amount of impurities due to the condition of the sample being exposed during XRD characterization, thus allowing the formation of $Ca(OH)_2$ through absorption of H_2O from the atmosphere during XRD analysis [17], In addition, the presence of $Ca(OH)_2$ indicates that not all $Ca(OH)_2$ has been converted to CaO during the calcination process.

Based on the characteristics obtained from Table 1, it can be seen that the higher mass ratio of CaO:biochar, the resulting density tends to decrease. But a high concentration of KOH results in a higher density. This is because excess KOH causes a saponification reaction to form glycerol with a higher density. In the transesterification process, where fatty acids react with a KOH catalyst to form soap. With the soap produced in the manufacture of biodiesel, it causes the surface tension of biodiesel to be high, and if the surface tension is high, it is difficult to break down the molecules of the compound. This is related to the viscosity of the biodiesel compound.

The yield of biodiesel produced ranges from 27.5% to 75.1%. based on Figure 4. The largest yield was obtained at the ratio of the mass ratio of the CaO/Biochar catalyst

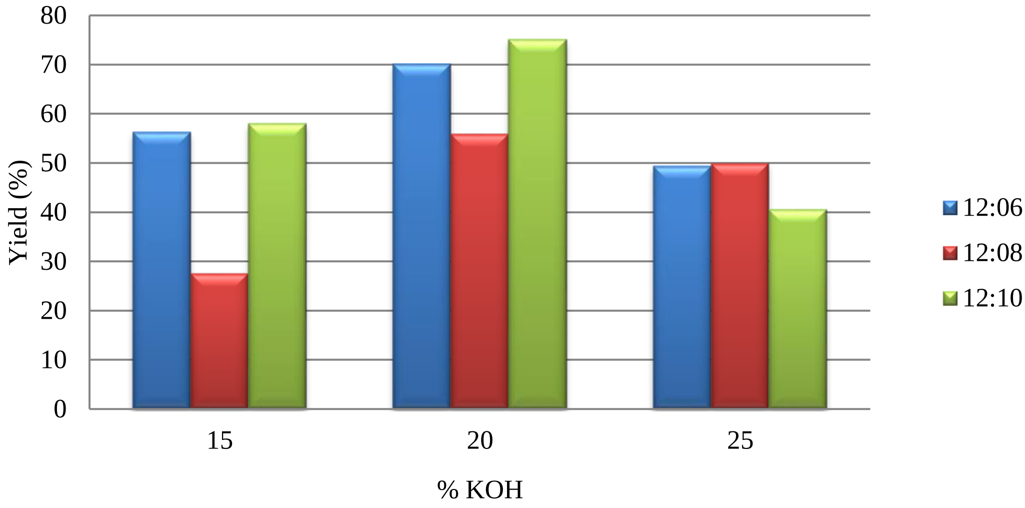


Figure 4. Yield comparison with KOH concentration.

to 12:10 and the concentration of KOH 20%. According to Liu et al [7], the amount of CaO carried has an influence on the yield produced, if it is too little then the active side of the catalyst is less so that the resulting yield is small. The greater the concentration of the catalyst in the solution, the lower the activation energy of a reaction, so that more products will be formed. Increasing the concentration of catalyst causes an increase in biodiesel yield.

4. Conclusions

CaO and biochar catalysts can be synthesized and used in the transesterification process of biodiesel production from palm oil. The higher the CaO/biochar ratio and KOH concentration, the higher the biodiesel yield. The highest catalytic activity of CaO/biochar of 75.1% was obtained at the catalyst's mass ratio 12:10, KOH concentration of 20%, has an acid number of 0.25 mg-KOH/g, density of 879.7 kg/m^3, and viscosity in accordance with SNI biodiesel standard 7182:2015.

Author Contributions: The following statements should be used "Conceptualization, Z.H. and S.Z.A.; methodology, Z.H.; software, T.N.S.; validation, Z.H., S.Z.A. and V.E.T.; formal analysis, T.N.S.; investigation, V.E.T.; resources, T.N.S.; data curation, T.N.S.; writing—original draft preparation, Z.H.; writing—review and editing, S.Z.A.; visualization, J.A.; supervision, J.A.; project administration, S.Z.A.; funding acquisition, Z.H. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by University of Riau under International Collaboration Grant with grant number: 8004/UN19.5.1.3/AL.04/2023.

Ethical Clearance: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data is available by request.

Acknowledgments: The authors express their gratitude to their individual institutions and universities.

Conflicts of interest: All the authors declare that there are no conflicts of interest.

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