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Eco-Friendly Approach to Palm Oil Biodiesel Production: Torrefied Palm Frond Carbon as a Source for CaO/C/NaOH Catalysts

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Abstract

Biomass-based sources for energy generation have attracted much attention recently due to its environmental benefits. These days, using edible oils and alkali catalysts, such as CaO, is standard practice for the transesterification step of the biodiesel synthesis process. Glycerine and methanol will form hydrogen bonds with the oxygen ions on the CaO surface, increasing the viscosity of the glycerine and causing CaO to suspend. Even though CaO was utilized directly as a catalyst in the transesterification process, extracting the CaO and glycerine from the final product will be challenging. To solve this issue, any extra metal oxides or catalyst supports ought to be impregnated into the CaO. This work has investigated the possible use of eggshells and palm fronds in developing bifunctional catalysts for biodiesel production. A series makes the processes' catalyst, including impregnation, calcination, and torrefaction. To assess the catalyst's performance, the esterification and transesterification of palm oil with a 2.9% free fatty acid content were investigated at a methanol/oil ratio of 6:1, catalyst concentration of 1-3% by weight, reaction temperature of 70 °C, and duration of 3 hours. The catalyst was found to have a specific surface area of 8.266 m^2/g. There was an 89.4% yield of biodiesel produced. A viable, economical, and ecologically friendly method of producing biodiesel is to use eggshells and palm fronds in catalyst synthesis.

1. Introduction

Calcium stands out as one of the most abundant metals on Earth, with its highest concentration found in seawater as an ion. Limestone and fossilized remnant sites also contain it as an oxide [1]. However, natural resource exploitation is necessary to extract calcium from these resources, which frequently has a detrimental effect on the ecosystem. A different method of producing calcium sources has been employed in light of environmental safety. This method involves using abundant renewable resources found in nature, such as eggshell material wastes, as eggshells contain high levels of calcium oxide [2]. In actuality, eggshell waste from the food industry or egg consumption has been a plentiful waste in the environment. It's intriguing to employ waste materials to create environmentally friendly calcium oxide (CaO) [3].

One heterogeneous base catalyst that can be used to trans-esterify vegetable oils is CaO. Surface area and basicity are two of the CaO catalyst's properties that

impact yield production and determine its performance [4]. CaO is produced by calcining $CaCO_3$, which can be readily obtained from various sources, including animal bones and eggshells. Eggshells are one readily available source of $CaCO_3$, primarily derived from food processing waste. According to reports, the chemical makeup of eggshells is composed of 94% calcium carbonate, 1% magnesium carbonate, 1% calcium phosphate, and 4% other organic matter. Eggshells can create active heterogeneous catalysts because they have high and abundant $CaCO_3$ levels [5, 6].

It is common practice to use alkali catalysts, such as CaO, in the transesterification process of biodiesel synthesis using edible oils like Jatropha curcas oil [7]. However, in actual use, even though CaO was used directly as a catalyst in the transesterification process, the oxygen ions on the CaO surface will bond with methanol and glycerine to form hydrogen bonds, which will increase the viscosity of the glycerine and cause CaO to suspend; as a result, it will be challenging to separate the CaO and glycerine from the product [8]. Any catalyst supports, or additional metal oxides should be impregnated into the CaO to solve this issue [8, 9]. Previous studies have drawn attention to the use of metal oxide-supported solid base catalysts (CaO). Several published articles have addressed the modification of CaO catalyst, such as those that KF/CaO-Fe_3O_4 [10], CaO/Al/Fe_3O_4 [11], CaO/ZnO [9], CaO/$CoFe_2O_4$ [12], K_2O/CaO-ZnO [13], $MgFe_2O_4$-CaO [14] and CaO/Biochar [15]. These investigations aimed to determine which heterogeneous solid base catalysts are suitable for product separation. In addition, the catalysts demonstrated the highest biodiesel yields and good catalytic properties [11]. Furthermore, using a catalyst allows for a higher biodiesel yield from commercial edible sunflower oil.

Glycerin and oxygen ions (O_2) on the surface of CaO will form hydrogen bonds when CaO is used directly as a catalyst, increasing glycerin's viscosity and forming a suspension [8]. Extracting CaO and glycerin from the product becomes challenging due to the suspension's formation. To solve these issues, metal oxide or catalyst support must be impregnated into CaO. Eggshells and CaO from $Ca(NO_3)_2.H_2O$ have been used as sources and have been shown to have good catalytic activities in the synthesis of biodiesel in earlier studies [5, 16, 17]. Because they are a rich source of cellulose, palm fronds are utilized. A product with a high carbon content that is produced by heating biomass is called biochar. Liu et al. [18] state that biochar has a carbon content of 45–60% by weight, which is less than that of activated carbon made from coal (80–95%) and carbon black (> 95%). Furthermore, biochar contains significant amounts of oxygen and hydrogen. Small amounts of chemical elements like K, Na, Ca, Mg, Si, Al, Fe, and others are another feature of biochar. Activated biochar is a good way to support CaO catalyst because of its weakness and because it has elements and benefits of its own. The research aims to produce CaO/C/NaOH catalysts from palm fronds by pyrolysis and torrefaction, which will produce activated biochar. Additionally, the study aims to explore the effects of temperature and duration during pyrolysis on the catalyst quality, which is then used in the transesterification process to produce biodiesel from palm oil.

2. Materials and Methods

2.1. Materials

The experiment's raw materials, waste chicken eggshell and palm oil, were gathered from an Indonesian palm oil production facility in the province of Riau. Aldrich products were the source of some chemicals, such as methanol, ethanol, sulfuric acid (H_2SO_4), sodium oxide (NaOH), and oxalic acid. An apparatus comprising a heating mantel, condenser, thermometer, and magnetic stirrer was employed in this experiment to conduct a transesterification reaction in a 500 mL three-neck flask batch reactor. The catalysts were prepared using an oven, a furnace, a filter with holes between 100 and 200 mesh, and analytic weights.

2.2. Preparation of CaO/C/NaOH Base Catalyst

In the first step, chicken eggshells are cleaned and dried at 110 °C to prepare the precursor of calcium oxide (CaO). The dried chicken eggshells were then crushed in a shaker mill and sieved through a mesh size of 100–200 to homogenize the size. To extract calcium oxide (CaO), sifted chicken eggshells are then calcined for three hours at 900 °C [19].

The preparation of activated biochar is the second stage. The palm frond is used as the raw material, which is chopped into one cm-long pieces. Then, the palm frond pieces are dried until the raw material moisture content test results are less than 10%. Nitrogen gas (N_2), flowing at a constant flow rate of 150 ml/minute for 45 minutes at a temperature of 275 °C, will be used to undergo a torrefaction process on the palm fronds in a horizontal fixed-bed reactor. The process of pyrolysis, the first step in producing biochar, had to be finished. The solid torrefaction product is weighed first. The pyrolysis process in the torrefaction process is carried out in a horizontal fixed-bed reactor at 550 °C. The entire pyrolysis process takes five minutes. When the process is complete, the pyrolysis products are removed and weighed. The final sample was designated as CaO-X, with

X denoting the calcination temperature. This pyrolysis process uses a horizontal fixed bed reactor in a torrefaction process conducted at temperatures between 400 °C (X1) and 450 °C (X2). It takes 15 (Y1), 20 (Y2), and 25 (Y3) minutes to finish the pyrolysis process.

After the process, the pyrolysis products are removed, and their weight can be determined. CaO-XY was the design of the final sample, where Y is the calcination time. The next step is to make the CaO/biochar catalyst. The size at which biochar is sieved is between 100 and 200 mesh. CaO/Biochar/NaOH catalyst preparation was carried out by sifting the biochar with a 100-200 mesh size. Calcium oxide (CaO) and biochar are weighed according to the variable mass-to-weight ratio of the catalyst. The CaO that has been weighed is mixed with biochar, dissolved with NaOH in a beaker, and stirred until homogeneous to form a $Ca(OH)_2$ solution. The result of this mixing will form a slurry. The slurry was dried in an oven at 105°C for 5 hours. The slurry that had been calcined was kept at 500°C in the furnace for five hours.

2.3. Catalyst Characterization

Some characterization methods, including X-ray diffraction (Shimadzu XRD 600 X-ray Diffractometer, 30 kV, 30 mA) and BET surface area, were used in this experiment. A prepared sample was filled through gold sputtering on the surface of CaO/C/NaOH. Pictures were gained through scanning electron microscope pictures gained at 15 kV with 10,000 times enlargement. For these calcium compounds, basic properties were determined by the indicator method.

2.4. Esterification Reaction

The production of biodiesel will involve the addition of a catalyst at a concentration of 1 - 3% by weight of oil after the cooking oil has been evaluated for density, water content, and free fatty acid content. An esterification reaction will be used to produce biodiesel. The methanol and oil reactant mixture will be mixed in a 10:1 ratio for three hours at a temperature of 65 °C and a stirring speed of 600 rpm. The esterification product is left to stand after the reaction is finished until the glycerol and crude biodiesel layer form. Once the layer has formed, 60 °C-heated distilled water is used to wash the crude biodiesel to purify it. The residual methanol and water were then evaporated by heating it to 105°C. Additionally, an analysis was conducted on the properties of the biodiesel generated.

3. Results and Discussion

There were two phases to this investigation. To obtain a CaO/C/NaOH catalyst impregnated with NaOH, the first step involves calcining eggshells to create a CaO catalyst. This is followed by producing biochar from palm fronds to act as a supporting catalyst for the torrefaction and pyrolysis processes. Eggshells can generally be cleaned of air and organic compounds below 600 °C, but they can also produce carbon dioxide between 700 and 800 °C. Therefore, the calcination temperature must exceed 800 °C to obtain CaO catalyst from eggshells. The second step involves using the CaO/C/NaOH catalyst to produce biodiesel based on palm oil.

Using x-ray diffraction (XRD), the CaO/C/NaOH catalyst is characterized to ascertain its structure, crystallinity, and the presence or absence of CaO material formation. XRD patterns were observed at 2θ angles ranging from 10° to 70°. The CaO/C/NaOH catalyst was tested using the XRD method in six different variations: CaO-X1Y1, CaO-X1Y2, CaO-X1Y3, CaO-X2Y1, CaO-X2Y2, and CaO-X2Y3. The XRD comparison uses temperature and time variations, adding NaOH at a 20%-b concentration, and the corresponding CaO: C catalyst mass of (12:6) gr. Figure 1 displays the catalyst's XRD pattern.

A CaO-X1Y1 XRD pattern was obtained using a catalyst ratio of 12:6 at 400 °C for 15 minutes. Five CaO peaks were visible at angles 2θ: 32,187, 37,337, 53,829, 64,119, and 67,340, with angle 2θ: 67,340° having the highest peak. A carbon pattern is present at angle 2θ, with the following positions: 26.228°, 42.213°, 44.365°, 50.381°, 53.973°, and 59.405°. It was noted that none of the six samples of the artificial CaO/C/NaOH catalyst had any $CaCO_3$ or $Ca(OH)_2$ composition, suggesting that the catalyst was suitable for use as an activator.

The similarity of the peaks across the six samples suggests that they are all from the same phase. CaO's peak intensity rises as a result of its increased composition. Table 1 shows the peaks contained in the six catalysts.

The surface area of a solid catalyst has a direct impact on its catalytic activity. To characterize the CaO/NaOH/C catalyst, six samples with a mass ratio of 12:6 and a 20% concentration of NaOH were used and the results can be seen in Table 2.

The biochar catalyst (CaO-X2Y1) produced the maximum surface area (8.733 m^2/g). Egg shells can be used as a CaO catalyst to make biodiesel impregnated with fly ash, according to research by Niju et al. [20]. The test results showed that the catalyst had a surface area of 8.6401 m^2/g, a basicity of 12.2<H_<15.0, and a biodiesel yield of 94.52%. The investigation results were then compared to those of other studies that produced catalysts without using the calcination process. The CaO/C/NaOH catalyst's surface area obtained from this study is similar to that of

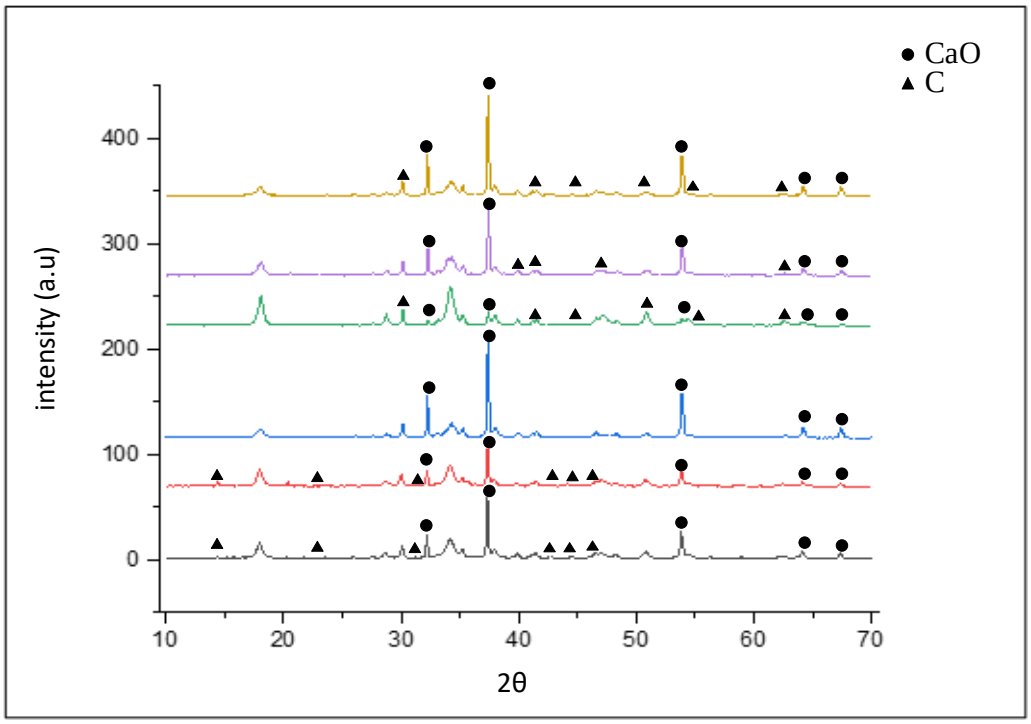

Figure 1. XRD pattern of CaO/Biochar Catalyst: (a) CaO-X1Y1; (b) CaO-X1Y2; (c)CaO-X1Y3; (d)CaO-X2Y1; (e) CaO-X2Y2; and (f)CaO-X2Y3.

Table 1. CaO/NaOH/C catalysts' XRD peaks.

Sample	% NaOH	Compound	2θ (°)					
JCPDS Data	-	CaO	32.2	37.3	58.3	64.1	67.3	-
		$CaCO_3$	29.4	39.4	43.2	47.4	46.5	-
		$Ca(OH)_2$	28.6	34.1	47.1	50.8	-	-
CaO-X1Y1	20	CaO	32.18	37.33	53.82	64.11	67.34	
		C	26.22	42.21	44.36	50.38	53.97	59.40
CaO-X1Y2	20	CaO	32.19	37.34	53.84	64.13	67.36	-
		C	41.33	43.91	47.08	61.89	-	-
CaO-X1Y3	20	CaO	32.20	37.35	53.86	64.15	67.37	-
		C	26.22	42.21	44.36	50.38	53.97	59.40
CaO-X2Y1	20	CaO	32.24	37.40	53.93	64.23	67.46	-
		C	-	-	-	-	-	-
CaO-X2Y2	20	CaO	32.24	37.40	53.93	64.23	67.46	
		C	15.88	23.92	32.08	42.84	43.81	44.60
CaO-X2Y3	20	CaO	32.24	37.40	53.92	64.23	67.46	-
		C	15.88	23.92	32.08	42.84	43.81	44.60

Fanny et al. [21], who synthesized CaO with a surface area of 7.7 m^2/g without any modifications.

Additionally, the data indicates that the sample's surface area has shrunk. This goes against the theory that the catalyst surface area increases with the width of the XRD peak. Generally, the catalyst increases surface area and gradually solidifies into stable crystals. However, the catalyst's surface area decreases as the calcination temperature rises above the optimal temperature limit. This leads to agglomeration, or clumping together of the catalyst's surface, which reduces the catalyst's surface area [17]. Numerous events, including those that happened during the catalyst's preparation before calcination, could be to blame for its small surface area because the calcination temperature in this study was fixed [22].

In a study by Lee et al. [23], active metal oxide catalysts like CaO, MgO, and Al_2O_3 decreased surface area following their impregnation with NaOH. This indicates that the catalyst's pore volume penetrated by Na^+ ions has significantly decreased. Putra's research shows that the CaO/zeolite catalyst's surface area decreased [24]. CaO particles partially obstruct the zeolite network during the impregnation process. CaO particles

Table 2. BET surface area of the obtained CaO/C/NaOH catalyst.

Sample	Pyrolysis Temperature (°C)	Pyrolysis Time (min)	Surface area (m^2/g)
CaO-X1Y1	400	15	4.472
CaO-X1Y2		20	7.946
CaO-X1Y3		25	6.192
CaO-X2Y1	450	15	8.733
CaO-X2Y2		20	7.900
CaO-X2Y3		25	5.926

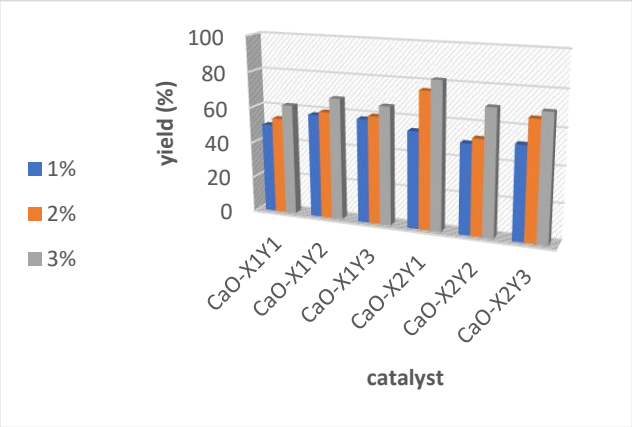

Figure 2. The yield of biodiesel produced from palm oil using CaO/C/NaOH catalyst prepared at various pyrolysis temperatures, pyrolysis time and catalyst concentration.

fill the zeolite pores that function as active carbon; therefore, the more CaO absorbed into the zeolite, the smaller the catalyst's surface area. The specific surface area of the zeolite will decrease due to the CaO-filled zeolite pores spreading out in a particular way. The causes of the decrease in surface area in both studies may have contributed to the findings of this investigation. The data in Table 2 clearly show that the catalyst's surface area is prone to decrease when using a CaO/C/NaOH catalyst with high CaO purity. This is because CaO reduces the specific surface area of carbon by filling its pores.

Numerous research studies have been conducted on the synthesis of CaO catalysts. For example, Oko et al. [25] synthesized CaO catalysts from eggshells impregnated with NaOH and technical activated carbon; they obtained the following surface area results for calcination temperatures: 1.4 m^2/g, 1.3 m^2/g, and 1.1 m^2/g. To produce catalysts with a surface area of 0.720 m^2/g, 1.963 m^2/g, and 0.088 m^2/g, Helwani et al. [17] studied the production of CaO catalysts impregnated with fly ash that was synthesized using varying calcination temperatures of 800, 850, and 900°C, respectively. A CaO/KOH catalyst with a surface area of 5.471 m^2/g was produced by Kusyanto et al. [26] using KOH-impregnated rice husks without a calcination process. Using CaO impregnated with synthetic activated carbon and NaOH, Rahayu et al. [27] produced biodiesel with a catalyst surface area of 18.880 m^2/g. The findings of this investigation demonstrate that the activated carbon-impregnated CaO has a greater surface area. Helwani et al. [28] prepared CaO/C/KOH catalysts by impregnation with KOH, followed by calcination at 500°C, resulting in a catalyst surface area of 7.890 m^2/g. The CaO/NaOH catalyst surface area values measured in this study from palm fronds are comparatively close to those from previous studies. This shows that converting palm fronds into active carbon can enhance the surface area of the CaO catalyst.

Numerous investigations concerning the calcination procedure following impregnation typically yield a comparatively greater surface area. The surface area of the catalyst produced will increase as the temperature is raised during the calcination process. However, a higher relative calcination temperature may accelerate the Na ion acceleration, covering a larger surface area with excessive potassium. This can potentially increase the pore volume and destroy the formed catalyst pores. According to several studies, 600 °C is the ideal calcination temperature for producing the maximum surface area [17].

To understand how the temperature and pyrolysis time influence the activity of the CaO/C/NaOH catalyst, the transesterification process was designed in this experiment with the experimental conditions consisting of 6:1 for the methanol oil molar ratio, the catalyst weight of 1 - 3% (wt.), the reaction temperature of 70 °C, and the reaction time of 3 hours. Figure 2 shows the yield of biodiesel resulting from this experiment.

The biodiesel yield ranges from 50% to 89.4%, based on Figure 2. The largest yield was obtained at the ratio of the mass ratio of the CaO/C/NaOH catalyst to 12:10 and the concentration of NaOH 20%, a calcination temperature of 450 °C, pyrolysis time of 20 min, and catalyst loading of 3 wt%. According to Liu et al. [8], the amount of CaO carried influences the yield produced; if it is too little, then the active side of the catalyst is less, so 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.

As mentioned, the chicken eggshell has been modified via calcination-torrefaction-pyrolysis followed by a wet impregnation process with NaOH. Specifically, the catalysts (CaO/C/NaOH) were treated at different

pyrolysis temperatures of 400 and 450 °C and pyrolysis times of 15, 20, and 25 mins, respectively. The optimal yield of biodiesel obtained was around 89.4%. These results are very different from previous research, as reported by Helwani et al. [15], where a yield of 75.1% was obtained using KOH as the impregnation solution.

4. Conclusions

According to this study, a solid catalyst made from eggshell waste can increase its activity through the torrefaction, pyrolysis, and calcination process, which is a suitable way to produce biodiesel through a transesterification reaction from palm oil. The transesterification experiment's ideal parameters were determined to be a calcination temperature of 450 °C, a pyrolysis time of 20 min, and a catalyst loading of 3% wt. The findings indicated that the primary component of the biodiesel produced was methyl ester, with a yield of 62% when using CaO as a catalyst and a yield of 75.1% when using CaO/C/NaOH as a catalyst in place of CaO. This experiment also revealed that a crucial factor in the catalyst treatment process was the catalyst's calcination temperature; however, a high calcination temperature was needed to obtain mechanical strength and stop the leaching process during their application.

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Conflicts of Interest: All the authors declare no conflicts of interest.

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