CaO from chicken eggshell supported on activated carbon and KOH (CaO/C/KOH) as catalyst for biodiesel production from off grade palm oil

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Abstract. This study carried out the catalyst synthesis of calcium oxide (CaO) from chicken eggshells supported on activated carbon (C) and activated by KOH solution (CaO/C/KOH). The effects of variation of KOH concentration and the CaO:C mass ratio to catalyst performance were also investigated. The catalyst was used in the biodiesel production from off-grade palm oil. The catalyst with the highest catalytic activity was obtained at the CaO:C mass ratio of 12:6 and the KOH concentration of 25%. The transesterification that was performed under the conditions of the oil: methanol molar ratio of 1:10, the catalyst concentration of 1% -b oil, the reaction temperature of 65 °C, and reaction time of 3 hours produced a biodiesel yield of 85.74%. The catalyst characterization by using XRD, Hammet indicator, and Brunauer-Emmet-Teller (BET) showed the product was in the crystalline phase of CaO, K2CO3, K2O Ca(OH)2, and CaCO3, the base strength of H_ > 12.2, and the specific surface area of 17.890 m²/g, respectively. The results showed that the KOH concentration in the catalyst activation process was directly proportional to the biodiesel yield. Several methyl esters such as methyl palmitate and methyl oleate were found in biodiesel through Gas Chromatography-Mass Spectrometry (GC-MS) analysis.

1. Introduction
After using fossil energy has caused many negative impacts, and its resource is decreasing, alternative energy becomes a popular subject in both scientific and engineering. Many countries explore and develop the new energy according to the available energy resources they have, such as wind, hydro, solar [1], geothermal [2–8], and even biomass [9,10]. Especially for the agricultural country, biomass conversion to be energy resources is highly interesting. Besides solving agricultural waste, it also increases the value of some less valuable agricultural products, such as off-grade palm oil.
Off-grade palm oil is a product from the residual sorting in the Palm Oil Mill that has not been fully utilized. The amount of available off-grade palm oil is quite large, around 7-10% of the product. This oil is usually sold 30-40% cheaper than CPO [11]. Off-grade palm oil can be used as an alternative raw material for biodiesel production. As a palm family, it contains high FFA content [12]. Transesterification is the most common method used to convert this content to biodiesel.

A homogeneous alkaline catalyst is one of the catalysts that is usually used in transesterification because it has high catalytic activity, high biodiesel conversion, and relatively short reaction time (± 1 hour) [13]. However, this catalyst has some disadvantages: it cannot be re-used or regenerated, difficult to separate from the product, require more equipment for separation and purification, so that production costs increased [14]. The heterogeneous solid base catalysts can be used as an alternative because it has advantages, including environmentally friendly, easy to separate, providing high selectivity, low cost, sustainable processes, and less waste [15].

CaO catalysts are one of a heterogeneous solid base catalyst. It is usually obtained from limestone, calcium carbonate, and calcium hydroxide. This catalyst is easily provided from chicken eggshell waste or synthesized from fine material. Chicken eggshells contain 94% CaCO3, 1% MgCO3, 1% Ca3(PO4)2 and 4% organic ingredients. According to [16], the use of CaO directly as a catalyst causes oxygen ions on the CaO surface to form hydrogen bonds with glycerin. So that the viscosity of glycerin increases and forms a suspension. The formation of the suspension makes it difficult for CaO and glycerin to be separated from the product. To overcome this problem, CaO must be impregnated with catalyst support or metal oxide. Previous research has reported the use of CaO from Ca(NO3)2-H2O and eggshells as a source and provide well catalytic activities in biodiesel production [17–20].

As reported previously, the performance of CaO catalysts supported on activated carbon was influenced by the CaO: C mass ratio, temperature, and calcination time [21,22]. The more significant the amount of CaO used the more increase the biodiesel yield. Different things were obtained from the effect of calcination temperature, which indicates that the increase in calcination temperature reduced product yield [23]. In this study, CaO was impregnated on activated carbon and KOH (CaO/C/KOH). Activated carbon has the advantage of increasing the surface area. Its composition is higher and easily separated from the product [21]. It is expected that the synthesis of the CaO/C/KOH catalyst will increase the catalyst product's performance so that it increases the yield of biodiesel.

2. Materials and methods
The chicken eggshell wastes were collected from the local bakery, KOH, aquadest, off-grade palm fruits were obtained from PTPN V, H2SO4, methanol, and Hammet indicators were obtained from PT. Bratachem. The tools used were spindle hydraulic press, condenser, three-neck boiling flask, thermometer, magnetic stirrer, and heating mantle.

2.1. Synthesis of CaO/C/KOH Solid base catalyst
Chicken eggshells were cleaned and dried at 110 °C for 12 hours, mashed using a shaker mill and sieved with 100-200 mesh sizes to homogenize the size, and calcined at 900 °C for 3 hours to get calcium oxide (CaO) [21]. The activated carbon was uniformed in size using the 100-200 mesh sieves. Furthermore, CaO and activated carbon were weighed according to the variation of mass ratio, 12 gr CaO each with a variation of 6 gr, 8 gr, and 10 gr of activated carbon. Each of the mixtures was dissolved in KOH with the concentration variation of 15, 20, and 25% each as much as 100 ml. Then it was stirred until homogeneous to have the Ca(OH)2 solution. The process condition was carried out at room temperature for 24 hours with a stirring speed of 400 rpm. The slurry formed was dried in the oven at 110 °C for 5 hours and calcined for 5 hours at 500 °C.

The study of the catalytic performance was studied on the transesterification process using the same method reported in the previous research by [19,20].
2.2. Characterization of catalysts and biodiesel product
The crystalline phase, basicity, and specific surface area of catalysts were characterized by using X-Ray Diffraction (XRD), Hammet Indicators, and Brunauer-Emmet-Teller (BET) methods, respectively. The characteristics of biodiesel tested included the acid number, flash point, cetane number, and viscosity (kinematic viscosity). The composition of biodiesel was analyzed using GC-MS.

3. Result and discussion

| Parameter          | Off grade palm oil | Standard CPO SNI 01-2901-2006 |
|--------------------|--------------------|-------------------------------|
| Colour             | Orange             | Yellow                        |
| Density 40°C (kg/m³) | 892.11             | -                             |
| Viscosity 40°C (mm²/s) | 29.47             | -                             |
| Water content (%)  | 3.5                | Max 0.5                       |
| FFA (%)            | 9.28               | Max 0.5                       |

It can be seen in Table 1 that off-grade palm oils have high water content, which can cause the hydrolysis process to occur so that the FFA level increased [24]. Also, water can react with the catalyst, so that the catalytic activity will decrease [25,26]. Water also causes form soap during the transesterification process[27]. Therefore, water needs to be removed by heating the oil above the boiling point of the water. High FFA levels are carried out through an esterification process to reduce FFA levels from 9.28% to 1.38 [28].

3.1. Hammet indicator titration of CaO/C/KOH catalyst
All CaO/C/KOH catalysts that made from the variation of CaO:C mass ratio, that are (12:6), (12:8), and (12:10) and the variation of KOH concentrations, that are 15, 20, and 25 (% w) calcined at a temperature of 500 °C were tested the basic strength using the Hammet indicator. The results showed that the catalyst alkalinity ranged from H₃ > 9.3 - 12.2. The basic nature of the catalyst increases with increasing KOH concentration and CaO:C ratio. Catalysts with an H₃ > 9.3 basicity are relatively strong catalysts for the transesterification process [29].

3.2. Characterization of CaO/C/KOH catalyst using x-ray diffraction (XRD)
The effect of calcination temperature and KOH concentration on the crystalline phase of the catalyst was studied by comparing each XRD pattern of the catalysts. The XRD pattern showed that the amount of CaO was very small because the percentage of CaO content has reacted with KOH and activated carbon in the catalyst in the impregnation process to form K₂CO₃. So that K₂CO₃ has a greater composition than CaO, that is 52.18% with a peak of 2θ: 34.74°, 28.18°, 41.44°, 58.15°, and 55.68°with the peak of 34.74°as the highest peak, as shown in Figure 1.

The carbonate compound formed on activated carbon after impregnation with KOH, which was thought of as K₂CO₃, where potassium binds to a carbonate group. When activated carbon was modified with KOH, acidity neutralization occurred at the carbon surface. KOH also reacted with carbon as follows:

\[
\text{CaO + C + 4KOH} \rightarrow \text{K}_2\text{CO}_3 + \text{Ca(OH)}_2 + 2\text{K} + \text{H}_2 \tag{1}
\]

\[
4\text{KOH} + \text{C} \rightarrow \text{K}_2\text{CO}_3 + \text{K}_2\text{O} + 2\text{H}_2 \tag{2}
\]
In these reactions, there are K and H ions which will release due to the calcination process at high temperatures, so that the K$_2$CO$_3$ compound was produced. The three XRD patterns of the synthesized CaO/C/KOH catalysts, shown in Figure 2, reveals that there was still a few impurities of Ca(OH)$_2$ and CaCO$_3$. These were caused by the sample contamination with air to form Ca(OH)$_2$ through H$_2$O absorption from the atmosphere [30]. Besides, these impurities’ presence indicated that Ca(OH)$_2$ and CaCO$_3$ have not been converted to CaO during the calcination. The presence of the CaCO$_3$ peaks was due to the imperfect decomposition of CaCO$_3$ into CaO and CO$_2$, so that it formed CaCO$_3$ in the calcite phase. The XRD pattern of the three samples of CaO/C/KOH catalyst also appeared to have a peak that tended to be the same. This indicated that the three samples have the same phase except for the peak intensity of the K$_2$CO$_3$ compound, which was slightly larger as the KOH concentration increased [22].

3.3. The surface area of CaO/C/KOH catalyst using Brunauer-Emmet-Teller (BET)

The CaO/C/KOH catalyst with CaO:C mass ratio of 12:6 and KOH concentration of 25%, which gave the highest yield, was characterized using BET. It resulted in the catalyst surface area of 17.980 m$^2$/g. There was an increase of surface area caused by activation by KOH on CaO/C/KOH catalyst compare
to research by [23] that reported the surface area of the CaO/C catalyst without activation by KOH was 15.890 m$^2$/g. This suggests that the activation by KOH increased the outer surface of the catalyst.

3.4. Yield and biodiesel characterization

The effect of the variation of CaO mass ratio and KOH concentration on biodiesel yield is shown in Figure 3. The highest yield of 85.74% was obtained at the CaO mass ratio of 12:6 and KOH concentration of 25%. Biodiesel yield decreased with increasing the amount of CaO, but it increased with increasing KOH concentration. This is caused by CaO accumulation to form clumps (agglomeration) on the surface of the catalyst so that it prevented contact between the active side of the catalyst and the reactants [16]. Also, agglomeration covered the micropore of the catalyst, so that the surface area became small, and the active base side is reduced [13,16,31]. Meanwhile, the KOH concentration is directly proportional to the biodiesel yield. The presence of KOH increased the alkaline catalyst that increased the activity of the catalyst [31]. However, The excess KOH concentration also reduced the activity of the catalyst. If the KOH concentration is too high, CaO will dissolve, thereby reducing the number of the active side of the catalysts [22].

![Figure 3. Effect of CaO:C mass ratio and KOH concentration on biodiesel yield.](image)

The effect of activated carbon as the support for CaO catalyst was studied by comparing the biodiesel yield obtained from transesterification by using CaO/C, CaO/C/KOH, and without a catalyst. The higher biodiesel yield was obtained by using CaO/C/KOH (85.7%), followed by CaO/C (61.96%) and without catalyst (31.55%) as Figure 4 portrays. This is because the CaO/C/KOH catalyst has a larger surface area of 17.890 m$^2$/g than the surface area of the CaO catalyst without metal oxide of 1.963 m$^2$/g. According to [14], the loading of CaO into an alkaline or metal oxide increased the number of base sides and the surface area of the catalystsso that the catalytic activity of the CaO catalyst increased.
In Figure 5, it can be seen the two highest peaks of methyl esters, which are methyl oleate with a biodiesel composition of 60.32% (peak number 4) and methyl palmitate with a biodiesel composition of 34.52% (peak number 3). The conversion result from carboxylic acid groups to methyl esters in the biodiesel production process reached 100%. This methyl ester content was included in the predetermined biodiesel quality standards (SNI 7182: 2015), which is 96.5%. This indicates that the biodiesel product produced was pure. Based on the results of the GC-MS analysis, CaO/C/KOH catalyst can be used as a catalyst in biodiesel production.

To ensure a machine has optimal work and strong durability, the biodiesel that is about to be used for the machine should first meet a certain quality standard. Hence, in this research, the obtained biodiesel was characterized, in which the characteristics were later compared with the Indonesian standard (SNI 7182: 2015), as presented in Table 2.
Table 2. Characteristics of the obtained biodiesel.

| No | Characteristic         | Unit       | Result       | SNI 7182:2015 |
|----|------------------------|------------|--------------|---------------|
| 1  | Density                | kg/m³      | 860-880      | 850-890       |
| 2  | Kinematic viscosity    | mm²/s      | 3.17-5.64    | 2.3-6.0       |
| 3  | Acid number            | mg-KOH/g   | 0.35         | Max. 0.5      |
| 4  | Cetane number          | -          | 52           | Min. 51       |

4. Conclusion

The catalyst characterization showed that the CaO/C/KOH catalyst calcined at a temperature of 500 °C for 5 hours was in the crystalline phase of CaO, K₂CO₃, K₂O Ca(OH)₂, and CaCO₃, the base strength of H₃O⁺ > 12.2, and the specific surface area of 17.890 m²/g, respectively. The best catalytic activity of the CaO/C/KOH catalyst was obtained at the addition of a KOH concentration of 25% and CaO:C mass ratio of 12:6 with a biodiesel yield of 85.74%.

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