Article

Composite Catalyst of Palm Mill Fly Ash-Supported Calcium Oxide Obtained from Eggshells for Transesterification of Off-Grade Palm Oil

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Abstract: This research was designed to synthesize a composite catalyst of palm oil fly ash-impregnated calcium oxide prepared from eggshell waste. Several preparation conditions, such as temperature and time applied to calcination and dehydration processes, were investigated. As a result, the optimum temperature and the length of time of calcination were 900 °C and 3 h, respectively. Meanwhile, the dehydration process was performed optimally at 600 °C for 3 h. The X-ray diffraction (XRD) results indicate that the obtained catalyst mostly contained calcium oxide compounds (CaO and Ca(OH)2) and minor impurities of silica oxides (SiO2 and Ca2SiO4), with a catalyst-specific surface area of 30.24 m2/g. Regarding its catalytic performance, the composite catalyst proved successful for prospective application in transesterification of palm oil off-grade, resulting in methyl palmitate and methyl oleate, which are two biodiesel compounds.

Keywords: biodiesel; calcium oxide; catalysts; fly ash; transesterification

1. Introduction

The unstoppable growing human population, along with the increase in fossil fuel prices and environmental damage, have urged scientific research to focus on finding renewable and eco-friendly energy alternatives. Some renewable energies have been proposed and developed by several countries depending on their available sources, such as wind [1], solar [2,3], geothermal [4–10], biomass [11,12], and hydropower [13] sources. As an agricultural country, Indonesia provides an abundant biomass resource from agriculture products or even waste. This biomass contains energy from carbon compounds, such as cellulose [14], fatty acids [15–17], lignins [18], and pectins [19–21], which can be degraded to obtain fuel materials such as biogas [22], chars [23], or biodiesel [24,25]. Biodiesel consists of mono-alkyl esters obtained from bio-resourced long chain fatty acids (plant- or animal-based), known to be superior, with biodegradable, food microchemical, renewable, and nontoxic properties [26,27]. To produce biodiesel, high-grade vegetable oil is transesterified with methanol with the help of homogeneous base catalysts. Some of the commonly used catalysts are sodium or potassium hydroxides, carbonates, and alkoxides. These catalysts, however, are difficult to separate, producing a huge amount of wastewater, and contributing to emulsification [28].
In the presence of the aforementioned challenges in homogeneous catalytic processes, there has been an intense growth of interest in the improvement and exploration of heterogeneous catalysts for biodiesel production. Some studies on solid acid catalyst preparation have been reported [29,30]. For instance, Peng et al. [31] reported the promising performance of \(\text{SO}_4^{2-}/\text{TiO}_2\text{–SiO}_2\) solid acid catalysts on biodiesel synthesis made of high free fatty acid (FFA) waste oils. Nevertheless, conducting the reaction at a high temperature (200 °C) was required to reach the optimum catalytic activity. Other similar reports on the catalytic performance for transesterification purposes include heterogeneous base catalysts viz. unsupported \(\text{CaO}, \text{Sr(NO}_3)_2/\text{ZnO}, \text{Kl/Al}_2\text{O}_3, \text{Na/NaOH/Al}_2\text{O}_3, \text{KF/MgO, ion-exchange resins, etc.} [32–36]\). Kouzu et al. [37] and Liu et al. [38] used reagent-grade \(\text{CaO}\) catalysts, which are not efficient in terms of the associated cost of biodiesel production. To obtain relatively low-cost alternatives, materials such as chicken eggshells [39,40], oyster shells [41], mud crab shells [42] and mollusk shells [43] have been used as \(\text{CaO}\) resources for biodiesel production. It is worth mentioning that none of the studies reported on the reusability and higher activity of the prepared \(\text{CaO}\) catalysts. Moreover, there are only a few published studies investigating the development of \(\text{Al}_2\text{O}_3/\text{SiO}_2\)-supported \(\text{CaO}\) catalysts (using reagent-grade chemicals) and their application in biodiesel synthesis [36,44–46].

Palm mill fly ash is an inorganic substance from the palm oil mill waste of palm oil refineries, which has a typical chemical composition (on a dry basis) of 55.19% \(\text{SiO}_2\), 30.01% \(\text{Al}_2\text{O}_3\), 4.58% \(\text{Fe}_2\text{O}_3\), 2.12% \(\text{Na}_2\text{O}\), 0.77% \(\text{CaO}\), 1.91% \(\text{MgO}\), 2.74% \(\text{TiO}_2\), 1.28% \(\text{BaO}\), and 1.40% \(\text{K}_2\text{O}\) [47]. The high contents of \(\text{SiO}_2\) and \(\text{Al}_2\text{O}_3\) can be attributed to its potential utilization as an inexpensive catalyst support. Recent research by Jain et al. [48] investigated the application of fly ash to support a calcium oxide catalyst for Knoevenagel condensation, with a good recyclability. Nevertheless, they employed an expensive reagent-grade \(\text{CaCO}_3\) as a feed to obtain the \(\text{CaO}\) catalyst.

As a source of vegetable oil, off-grade palm oil accounts for 7%–10% of the production process in a palm oil mill, where it can reach up to 30 tons production/h. In comparison to high-grade CPO, off-grade palm oil is sold at 30%–40% lower prices [49]. Other than its eminence in terms of its availability and economic factor, the potential of off-grade palm oil as a raw material for biodiesel has scarcely been investigated. This is due to its high FFA content, thus requiring a two-stage reaction (i.e., esterification and transesterification, sequentially) to reduce the levels of FFA, which need to drop to below 5% before transesterification can take place [26].

As reported previously [50], palm oil fly ash-impregnated \(\text{Ca(NO}_3)_2/\text{H}_2\text{O}\) was prepared under experimental conditions as follows: calcination temperature of 800 °C, \(\text{Ca(NO}_3)_2/\text{H}_2\text{O/palm fly ash ratio of 80:20, methanol/oil ratio of 6:1, reaction temperature of 70 °C, and reaction time of 2 h. The prepared catalyst had a surface area of 24.342 m²/g, which had catalytic activity for biodiesel synthesis with a yield value of approximately 71.17%.}

The present work attempted to develop a low-cost and highly efficient supported base catalyst through the utilization of fly ash and \(\text{CaO}\) derived from eggshell waste for the transesterification of off-grade palm oil to yield biodiesel. The effects of various process parameters, including the temperature and the length of time taken for the calcination and dehydration processes, on the yield of fatty acid methyl ester (FAME) were investigated. To understand its catalytic performance, the prepared catalyst was used to catalyze a transesterification reaction to produce biodiesel.

2. Results and Discussion

2.1. Off-Grade Palm Oil Characteristics

To prepare the crude palm oil off-grade, oil palm mesocarp was firstly steamed, mashed, and treated to deactivate the lipase enzyme. This treatment was followed by extraction using a spindle hydraulic press to yield 185 g off-grade palm oil for each kilogram of off-grade palm fruit (18.5% (w/w)). It was then characterized to comprehend the properties of the raw oil, including the following parameters: density, viscosity, water content, and FFA content. The results of the characterization are presented in Table 1.
ASTM D4052 was used to determine the density and ASTM D445 for the kinematic viscosity. From the characterization, it was found that the acid value of the crude oil met the EN 14104 criteria.

Table 1. Physical properties and free fatty acid (FFA) of crude off-grade palm oil compared to palm oil.

| No. | Parameter          | Unit     | Palm Oil Off-Grade | Palm Oil [51] |
|-----|--------------------|----------|-------------------|---------------|
| 1   | Density (40°)      | kg/m³    | 892               | 920           |
| 2   | Viscosity (40°)    | mm²/s    | 29.50             | 31.45         |
| 3   | Water content      | wt.%     | 3.7               | 0.8           |
| 4   | FFA                | mgKOHg⁻¹ | 6.9               | 0.2           |
| 5   | Color              | -        | Orange            | Yellow        |

To provide a comprehensive picture of the off-grade palm oil quality, the parameters were compared to that of standard palm oil, as reported by O’Brien [52] and Barnwal and Sharma [53]. Except for the FFA and water contents, the crude off-grade palm oil samples used in this research shared similarities within the other three parameters with that of standard palm oil. A high amount of FFA (6.9%) was found in the crude palm oil off-grade, where, in comparison, standard palm oil had only 0.2%. This was in line with the higher water content, which can be ascribed to the formation of FFA through hydrolysis. Additionally, the ability of water to react with the catalyst might cause a reduction in catalyst availability in the reaction system. Therefore, homogeneous transesterification is not suitable for biodiesel production using crude off-grade palm oil as the raw material [28]. On the other hand, heterogeneous transesterification methods seemed to be more appropriate.

2.2. Catalyst Characterization

2.2.1. X-ray Diffraction

Figure 1 presents the XRD patterns of the CaO/palm mill fly ash (PMFA) catalysts. According to the analysis, a lower Ca(OH)₂ peak from the CaO/PMFA diffractogram with a higher calcination temperature was observed. This is owing to the fact that a higher calcination temperature leads to more decomposition of Ca(OH)₂, converted into CaO. This is attributed to the modification of the chemical composition of the catalyst through calcination at a high temperature. Hence, as opposed to the Ca(OH)₂ peak, we can observe the higher peak of CaO in the presented diffractogram, which is in a good agreement with the work of Wong et al. [54]. A higher temperature was also expected to improve the mechanical force to avoid leaching [55].

In Figure 1b, representing the XRD pattern of CaO/FA-900 calcinated at 3 h, four peaks of CaO appeared at 2θ: 29.38°, 39.42°, 50.81°, and 64.23° [ICDD 01-077-2376]. In addition, there appeared SiO₂ patterns at 2θ: 26.60° and 36.47° [ICDD 01-075-8320], corresponding to a huge amount of the silica compound, for which fly ash impregnation is responsible. Ca(OH)₂ patterns appeared at 2θ: 34.10°, 47.12°, and 54.35° [ICDD 00-044-1481], ascribed to the intense impregnation of active CaO within the palm oil mill fly ash [56]. The existence of Ca(OH)₂ patterns shows that there remained a few impurities due to the open sample condition during XRD characterization, thus allowing Ca(OH)₂ formation through the absorption of H₂O from the atmosphere during the XRD analysis [44]. In addition, the presence of Ca(OH)₂ compounds indicates that not all of the Ca(OH)₂ was transformed into CaO during the calcination process. The compound Ca(OH)₂ is formed from the reaction of CaO with distilled water during the wet impregnation process [57]. Dicalcium silicate (Ca₂SiO₄) is also observable at 2θ: 29.62°, 39.38°, and 41.51°.
The synthesized CaO/PMFA catalyst samples appear to have the same peak, which indicates that the three samples had the same phase but only a slightly higher CaO peak intensity, as the calcination temperature of the CaO/FA catalyst was spread evenly on the catalyst surface [58]. Meanwhile, the XRD pattern comparison of CaO/PMFA-900 prepared for 2, 2.5, and 3 h and dehydrated at 600 °C is presented in Figure 2.

Figure 2. XRD diffractograms of CaO/PMFA calcinated at 900 °C at various calcination times of (a) 2, (b) 2.5, and (c) 3 h.

Figure 2a shows the XRD pattern of CaO/FA-900 at a calcination time of 2 h. CaO peaks appeared at 2θ: 54.25°, dominated by the highest peak at 2θ: 54.25° with a relative intensity of 100%, which indicates...
the formation of CaO. Meanwhile, the crystalline phase of Ca$_2$SiO$_4$ appeared at 20: 28.67°, 71.65°, and 84.75°, which indicates that the fly ash had been impregnated at the CaO pore. The Ca(OH)$_2$ phase was also detected at 20: 18.00°, 34.0878°, 47.1097°, 48.80°, 54.8404°, and 62.17° (ICDD 00-044-1481).

The three diffractograms appear to have similar peaks, except for that of the several newly formed CaO crystalline substances, where the increase can be associated with CaCO$_3$ decomposition into CaO at a lower calcination time and a higher calcination temperature, as also reported by Wong et al. [58]. This is in accordance with the calcination objective for modifying the chemical composition of CaO/PMFA catalysts using high temperatures.

Meanwhile, the catalyst, which was calcinated at 900 °C for 3 h (CaO/FA-900) was dehydrated at 600 °C for 2 and 4 h. The products of the procedure were then characterized by XRD, and their diffractograms can be observed in Figure 3.

Figure 3. XRD diffractogram of CaO/PMFA calcinated at 900 °C for 3 h at different dehydration times of (a) 2, (b) 3, and (c) 4 h.

Figure 3a indicates peaks at 2θ of 86.238° and 94.990°, which could be assumed to show the existence of CaO in the catalyst samples. In addition, a SiO$_2$ peak appeared at 26.609° and 39.376°, suggesting the abundance of silica, originating from the impregnated fly ash. Dicalcium silicate (Ca$_2$SiO$_4$) was also observable at 2θ: 29.351°, 43.126°, 47.416°, 48.438°, 57.316°, and 65.520°. Figure 3b exhibits the lowest CaO content at 2θ: 48.410° with an intensity of 647.77 (JCPDS File No. 37-1497). A dicalcium silicate peak (Ca$_2$SiO$_4$) appeared at 2θ: 17.944°, 34.018°, 50.756°, and 54.376°. The diffractogram also shows the presence of calcium hydroxide (Ca(OH)$_2$), observable at 2θ: 26.596°, 29.334°, 35.956°, 39.366°, 43.114°, 47.431°, 64.093°, and 64.660°. Figure 3c shows the XRD pattern of SiO$_2$, which appeared at 2θ: 26.608°. The lower intensity observed in the diffractograms can be ascribed to the lower content of fly ash in the samples. The Ca(OH)$_2$ peak can be seen at 2θ: 17.988°, 34.038°, 48.408°, 50.802°, 54.320°, 59.586°, 62.586°, and 83.839°. The combination of CaO and SiO$_2$ (from the PMFA) in the impregnation process may form a reaction, resulting in dicalcium silicate (Ca$_2$SiO$_4$), as suggested by the decrease in the peak intensity of CaO. Consequentially, a higher intensity of Ca$_2$SiO$_4$ was observed at 2θ: 23.0144°, 29.339°, 35.954°, 39.382°, 43.111°, 48.408°, 64.727°, 86.346°, and 93.055°. Due to the water molecules present in
the system, the reaction between CaO and SiO₂ yielded the formation of dicalcium silicate hydrate (Ca₂SiO₄H₂O), as described in the following equation:

\[
2\text{CaO} + \text{SiO}_2 + \text{H}_2\text{O} \rightarrow (\text{CaO})_2(\text{SiO}_2)(\text{H}_2\text{O})
\]  

(1)

However, when the calcination temperature was adjusted to 800–900 °C, the water content was removed. Thus, the reaction only yielded Ca₂SiO₄ [59]. It seems that an increase in the active site on the catalyst results in more products [54]. Meanwhile, according to Soleimani et al., the CaO particles will be impregnated in the SiO₂ pores that exist in the fly ash matrix [60].

Based on the higher Ca₂SiO₄ peak observed in the diffractogram of CaO/FA-900 dehydrated at a higher temperature (Figure 4), it can be concluded that higher temperatures may contribute to yielding more Ca₂SiO₄. This means that not only were the CaO particles impregnated in the SiO₂ pores, but also some CaO reacted with SiO₂ from the palm mill fly ash to produce Ca₂SiO₄.

As presented in Figure 4b, a calcination temperature of 500 °C for 3 h triggered SiO₂ to become more reactive to the CaO compounds, thus forming Ca₂SiO₄, observed at 2θ: 29.360°, 39.376°, 57.3338°, and 83.816°. Peaks for SiO₂ appeared at 2θ: 26.641° and 47.449° only, whereas, according to the [60] dehyation process, SiO₂ caused tenuous Si–O–Si bonds; thus, while the number of SiO₂ reduced during the dehydration process, other new crystals were formed.

2.2.2. Brunauer–Emmett–Teller (BET) and Basic Strength

The BET method was used to determine the specific area of the CaO/PMFA catalysts obtained through calcination with different temperatures of 850, 900, and 950 °C for 3 h, and then dehydration at 600 °C.

The different temperatures used in the calcination process produced catalysts with significantly different surface area values (4.55–30.24 m²g⁻¹). This suggests that pore formation is greatly affected by the calcination temperature. As can be seen in Table 2, a higher calcination temperature tends to increase the surface area. Nevertheless, higher temperatures (950–600 °C) reduced the catalyst surface area; thus, it can be assumed that subsequent blocking of some catalyst pores occurred. This resulted in lower surface areas, although their morphological sizes remained the same as before.

**Figure 4.** XRD pattern of catalyst CaO/PMFA calcinated at 900 °C with various dehydration temperatures of (a) 500, (b) 600, and (c) 700 °C for 3 h.
Table 2. Surface area and basic strength of the obtained CaO/PMFA catalysts.

| Calcination Temperature (°C) | Calcination Time (h) | Surface Area (m²/g) | Basic Strength (H₉) |
|-----------------------------|----------------------|---------------------|---------------------|
| 850–600                     | 3                    | 4.55                | 9.8 < H₉ < 12.2     |
| 900                         | 3                    | 9.31                | 12.2 < H₉ < 15.0    |
| 900–600                     | 3                    | 30.24               | 15.0 < H₉ < 18.4    |
| 950–600                     | 3                    | 14.55               | 9.8 < H₉ < 12.2     |

In addition, a BET summary of the catalysts calcinated at 900 °C for 3 h and dehydrated at 500, 600, and 700 °C for 2, 3, and 4 h, respectively, is shown in Table 3. As previously reported, the surface area of a catalyst has a great influence on its catalytic activity, where a higher surface area can result in higher catalytic activity [61]. Therefore, the treatment proposed in this research was expected to be capable of increasing the surface area of the prepared CaO/PMFA catalysts. As presented in Tables 2 and 3, we can compare the surface area of the prepared catalysts with and without the hydration and dehydration treatment, respectively. A plain distinction can be observed on the surface area of CaO/PMFA-900 (9.31 m²/g), which was lower than that of CaO/FA-900-600 (30.24 m²/g). These results are in good agreement with those of Yoosuk et al. [62], where they found the hydration coupled with dehydration treatment on CaO could yield a twice as high surface area.

Table 3. Surface area and basic strength of the obtained CaO/PMFA-900/3 h catalyst.

| Dehydration Temperature (°C) | Dehydration Time (h) | Surface Area (m²/g) | Basic Strength (H₉) |
|-------------------------------|----------------------|---------------------|---------------------|
| 500                           | 3                    | 17.55               | 9.8 < H₉ < 12.2     |
| 600                           | 3                    | 30.24               | 15.0 < H₉ < 18.4    |
| 700                           | 4                    | 18.39               | 9.8 < H₉ < 12.2     |

As can be seen in Table 3, CaO/PMFA-900/3 h dehydrated at 600 °C had a surface area as high as 30.24 m²/g. By increasing the temperature, the catalyst can undergo crystallization, followed by an increase in the surface area [63]. The presence of CaO crystals may close the pores of the fly ash, resulting in a decrease in the surface area [64]. Hence, the enormity of the surface area found from the BET analysis can be attributed to an uneven distribution of the CaO crystals in the catalyst support pores, which occurred during the impregnation.

2.2.3. Hammett Indicator Titration

The appearance of a pink color in the colorless phenolphthalein was observed after the addition of the CaO/PMFA catalysts. However, the color change due to the addition of CaO/PMFA catalysts was not observed in 4-nitroaniline. These results reveal that the basic strength of the CaO/PMFA catalysts was within 9.3 < H₉ < 18. Therefore, our catalysts were comparable to reagent-grade CaO, owing to the similar basic strength value (approximately 15.5 < H₉ < 18.4) [42,65]. Based on the results of this investigation, CaO/FA calcinated at 900 °C and dehydrated at 600 °C (CaO/FA-900-600) generated the strongest basic strength, as can be seen in Tables 2 and 3.

2.3. Yield and Biodiesel Characterization

To obtain a scientific description of how temperature and calcination time influence the catalytic activity of CaO/PMFA catalysts in the transesterification reaction, the catalysts were employed in the transesterification reaction, in which the mol ratio of methanol to oil was around 10:1, the catalyst concentration was 1 wt.%, and the reaction temperature was at 70 °C for 2 h. As a result of the reaction process, Figure 5 shows the yield of biodiesel obtained from the CaO/PMFA catalysts.
The yield of the obtained biodiesel was higher than using the CaO catalyst, which was synthesized from Ca(NO$_3$)$_2$ calcinated at 850 °C, and the surface area was 909 m$^2$/g [50]. A calcination temperature of 850 °C could not change the chemical structure of the catalyst, which eventually deactivated the catalyst. On the contrary, a temperature of 900 °C allowed for a greater formation of surface area, stemming from high active sites distributed throughout the pores and the surface of the catalyst. Hence, the self-reaction among the catalyst’s particles could be avoided [67]. Meanwhile, according to Liu et al. [68], the insufficient amount of CaO was responsible for the lower yield of FAME. These results further suggest that the catalytic activity of CaO/PMFA does not greatly correspond to the surface area (BET).

A different phenomenon can be seen in Figure 6. Because the CaO/FA-900/3 h catalyst resulted from a temperature of 600 °C and a 3-h-long dehydration, it possessed higher Ca$_2$SiO$_4$ and CaO contents than the other catalysts. Moreover, it had the strongest basic strength. This result is in line with the work of Kesica et al. [63], who stated that the stronger the base, the higher the catalytic activity. The optimum yield obtained was 86.2% at 600 °C for 3 h. As the temperature and dehydration time of the catalyst increase, the catalyst gradually changed into a stable crystal and increased its specific area. However, the biodiesel yield decreased after passing the optimum conditions at a temperature of 600 °C for 3 h.

**Figure 5.** The influence of the temperature and time of the calcination process on the activity of the obtained CaO/FA catalyst for fatty acid methyl ester (FAME) production.
2.4. Characteristics of the Biodiesel

In order to ensure that a machine has optimal working ability and strong durability, any biodiesel that is to be used for said machine should firstly 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 4.

The highest biodiesel, methyl ester, was produced from the transesterification process by using the CaO/PMFA catalyst calcinated at 600 °C for 3 h. The results of the GC–MS fragmentation pattern analysis of the transesterification product are shown in Figure 7, indicating a large peak of methyl esters with specific retention times of 35.39 and 37.42 min.
As can be seen in Figure 7, the major component of the biodiesel in this research was found to be methyl palmitate (46.62%), whilst methyl stearate presented a smaller percentage (3.65 wt.%). The total amount of saturated fatty acids in the product was 51.12%, consisting of myristic acid, palmitic acid, and stearic acid. Meanwhile, the total amount of unsaturated fatty acids was 48.84%, consisting of oleic acid and linoleic acid. The composition of this biodiesel product met the standards issued by the Ministry of Energy and Mineral Resources Republic of Indonesia No. 189 / K / 10 / DJE / 2019 concerning the standards and quality (specifications) of biofuel as a type of other fuel. Impurities in the biodiesel are acceptable, as suggested by the 96% biodiesel yield, where the other 4% can be comprised of catalyst residue, glycerol, methanol, and water. The level of methyl ester was 96.5%, and based on the stipulated biodiesel quality standard (SNI 7182: 2015), the biodiesel product passed the SNI requirements.

2.5. The Catalyst’s Reusability, Stability, and Regeneration

Figure 8 presents the percentage of the yielded FAME for five cycles of CaO/PMFA-900-600 usage to evaluate the reusability of the catalyst. Note that in order to begin each new run, the liquid was removed, leaving the catalyst deposition to be retrieved later. After the first cycle, the catalyst experienced a significant deactivation (from 86.20% to 75.47%). The catalytic activity continued to decrease afterward; even after the fifth cycle, saturation was not observed. These results simply suggest continuous deactivation of the catalyst following the reaction cycle.

Catalyst deactivation is widely attributed to the heterogeneity of the basicity on the catalyst’s surface. Weakened Lewis basic sites (O²⁻) on the catalyst’s surface were observable, whereas medium and low basic sites dominated the catalytic activity due to their maintained stability. The weakening can be associated with the adsorption of massive amounts of triglycerides onto the CaO/PMFA catalyst’s surface. Other than the weakening of the Lewis basic sites (O²⁻), leaching could also be responsible for the decrease in catalytic activity. For this purpose, we carried out a simple experimental procedure to investigate whether leaching occurred in the CaO/PMFA-900-600 catalyst during the transesterification. The fresh catalyst was submerged in methanol for 24 h, after which it was removed from the methanol and then used in the transesterification process. A lower yield percentage of FAME was expected if leaching occurred. Nevertheless, the same yield was observed, suggesting the absence of leaching in the CaO/PMFA-900-600 catalyst. Therefore, it is safe to conclude that the weakened Lewis basic
sites caused by massive adsorption of triglycerides on the catalyst’s surface is the primary reason for deactivation.

Figure 8. The decreasing activity of the CaO/PMFA-900-600 catalyst observed after each cycle of the 3-h transesterification (at 70 °C, methanol to oil molar ratio of 6:11, and catalyst weight of 6 wt.%).

Figure 9 shows a comparison of the performance of the CaO/PMFA catalysts after various regeneration treatments. As can be seen, catalytic activity was still observable during the second cycle, where the yield percentage of FAME was comparable to the one obtained using the fresh catalyst. On the other hand, recalcination carried out in air completely restored the catalyst’s activity after the second cycle deactivation. These results indicate that the washing process using methanol is not able to completely remove the accumulated triglycerides from the catalyst’s surface, which might form coke when heated at high temperatures in a nitrogen environment.

Figure 9. Effect of the regeneration of the CaO/PMFA-900-600 catalyst 0–8-h transesterification (at 70 °C, methanol to oil molar ratio of 6:11 and catalyst loading of 6 wt.%).
3. Experimental Procedure

3.1. Materials

Off-grade palm oil purchased from the local factory in Riau, Indonesia, was used as feedstock raw material in this present work, while fly ash was obtained from a palm oil refinery. The palm mill fly ash was further denoted as PMFA. The chicken eggshell waste was collected from a local bakery. Methanol, sulfuric acid (H\(_2\)SO\(_4\)), ethanol, potassium oxide (KOH), and oxalic acid were purchased from R & M Marketing, Essex, UK, and Merck (Darmstadt, Germany), respectively.

3.2. Preparation of the CaO/PMFA Catalyst

Firstly, the CaO particle was derived from chicken eggshell waste through a combination method of the calcination, hydration, and dehydration methods as described above. The biomass was cleaned with distilled water, and then dried at 105 °C overnight using an oven. The next steps of the procedure involved mechanical grounding and sieving to obtain a homogeneous powder 150 µm in size. The fine eggshell powder was then treated at various calcination temperatures from 850 to 900 °C, respectively, for 2–3 h.

In order to obtain aqueous Ca(OH)\(_2\), a three-neck flask was filled with 250 mL of pure deionized H\(_2\)O, followed by the addition of 18 g of the calcined eggshells, and then stirred at 700 rpm. The temperature was set at 70 °C in a closed system to minimize water loss. Then, 12 g of PMFA was added dropwise and stirred rapidly for the next 4 h to reach homogeneity. The solution was left for 18 h to obtain Ca(OH)\(_2\) precipitation on the PMFA. The water content was removed from the mixture by setting the temperature to 105 °C in an oven for 24 h. This step produced the dried catalyst, followed by a recalcination at 500, 600, and 700 °C, respectively, in a muffle furnace for three different durations of between 2 and 4 h. The obtained catalysts were referred to as CaO/PMFA catalysts, in which each obtained CaO/PMFA catalyst, prepared at different dehydration temperatures of 500, 600, and 700 °C, were characterized using Hammett indicators, X-ray diffraction (XRD), and Brunauer–Emmett–Teller (BET), and were then applied for catalytic study in the transesterification process.

3.3. Characterization

The base strength of the catalyst (H\(_\text{b}\)) was determined using the following Hammett indicators: bromothymol blue (H\(_\text{b}\) > 7.2), phenolphthalein (H\(_\text{b}\) > 9.8), alizarine yellow (H\(_\text{b}\) > 11.0), 2,4-dinitroaniline (H\(_\text{b}\) = 15), and 4-nitroaniline (H\(_\text{b}\) = 18.4). The procedure was initiated by diluting the Hammett indicators in 10 mL methanol, where color changes were observed after the addition of ± 300 mg of the catalyst, and equilibrium was reached [40,51]. Other characterizations included in this study were XRD (Shimadzu XRD 600 X-ray Diffractometer, 30 kV, 30 mA, Kyoto, Japan) and total surface area determined by BET method using N2 adsorption at 77.3 K (Quantachrome Instruments, FL, USA). FAME was calculated following the SNI 7182: 2015 application note.

3.4. Study of the Catalytic Performance on the Transesterification Process

The catalytic study in this experiment was referred to in our previous work [40]. The esterification procedure was initiated by adding 60 g of crude off-grade palm oil into a three-neck flask at 60 °C. Methanol was added with a mole ratio of 12:1 (methanol/oil), followed by the addition of 1% (w/w) H\(_2\)SO\(_4\) as a catalyst. The mixture was left at 400 rpm for 1 h to allow the reaction to take place. The catalyst (H\(_2\)SO\(_4\)), along with the residual methanol, was removed using a separating funnel. The FFA of the lower layer was determined, followed by the transesterification reaction. The next steps of the procedure were carried out in a transesterification reactor, where 50 g of the earlier esterification product was added and heated at 70 °C. To the reactor, methanol was added with a mole ratio of 10:1 (methanol/oil), followed by 6% (w/w) prepared CaO/PMFA, and then stirred at 400 rpm. Once the reaction was completed, a rotary evaporator was used to retrieve the methanol in a vacuum (at 45 °C). The catalyst separation was conducted through filtration; meanwhile, the glycerol layer was removed with the help of a separating funnel. For FAME content analysis, a dilution with n-hexane took place right after the upper layer was
separated from the bottom layer. The yielded FAME content was calculated according to the Indonesian standard (SNI 7182: 2015).

4. Conclusions

A calcium oxide base catalyst, obtained from eggshell waste, supported by palm mill fly ash (CaO/PMFA), was developed and applied successfully for transesterification in biodiesel production, made of off-grade palm oil. It produced the best yield of biodiesel of 86.2% by using the obtained CaO/PMFA catalyst, which was treated for the calcination process at 900 °C for 3 h at a dehydration temperature of 600 °C for 3 h. The biodiesel yield strongly tends towards CaO particles on the CaO/PMFA catalyst’s surface.

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