Advances in science, engineering and technology in combating pollution for a sustainable future

Novel iron sand-derived α-Fe₂O₃/CaO₂ bifunctional catalyst for waste cooking oil-based biodiesel production

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Abstract

The main aim of this work was to develop a heterogeneous Fe₂O₃/CaO₂ bifunctional catalyst prepared from iron sand and 3 different CaO₂ sources (CaCO₃, Ca(OH)₂, and limestone) using wet impregnation and calcination methods for biodiesel production. The effects of different CaO₂ sources and Fe/Ca ratio in the catalyst were investigated to provide insight into the catalyst character and biodiesel yield. X-ray diffraction, X-ray fluorescence, and scanning electron microscopy analyses were used to characterize the catalyst. CaCO₃ was concluded as the best CaO₂ source, while the best Fe/Ca configuration was found to be 1:4, giving the highest biodiesel yield (97.0401%) with no diglycerides. Greater addition of Fe loading would result in an amorphous structure, and all catalysts were relatively crystalline. Fe was concluded to favor the esterification reaction and biodiesel formation, while CaO₂ was seen to favor the transesterification reaction and fatty acid methyl ester (FAME) formation. The catalyst mechanism was also established in this study, where esterification of free fatty acid (FFA) and glycerol took place on the acid site to produce diglyceride and transesterification of triglyceride by methanol occurred on the basic site.

Keywords: Biodiesel · Bifunctional catalyst · Diglycerides · Fe₂O₃/CaO₂ · Iron sand · Simultaneous esterification-transesterification · Waste cooking oil

Nomenclature

FAME Fatty acid methyl ester
FFA Free fatty acid
GCMS Gas chromatography mass spectrometry
PEG-4000 Polyethylene glycol 4000
SEM Scanning electron microscopy
XRD X-ray diffraction
XRF X-ray fluorescence
WCO Waste cooking oil
ρ Density

Introduction

Energy is not only one of the major aspects of the national economy, but also an important aspect of life. According to BP Statistical Review of World Energy (2021), world energy consumption fell by 4.5% on 2020 due to the COVID-19 pandemic affecting the economy output and activity. Despite the fall, the renewable energy demand rose to 9.7% that indicates the world’s commitment to reduce emission as established on The Paris Agreement and the opportunity to further develop the area. Biofuel, particularly biodiesel, is one of the most used energies in Indonesia with numerous advantages, such as renewable, biodegradable, and lower emission level, and promotes complete combustion in engines. It is commonly produced through a transesterification process using an acid or base catalyst and has strict restrictions on the free fatty acid (FFA) and water content (<2%) to avoid saponification (de Araújo et al. 2013). It is known that esterification process has helped with these problems, but alas the 2 different steps require different catalysts, are complex, and would inevitably raise the production cost (Pruszko 2020; Pan et al. 2017). To overcome these concerns, a heterogeneous bifunctional
catalyst that could facilitate a simultaneous esterification-transesterification reaction could be used. Past researches on the bifunctional catalysts were SO₄/Mg-Al-Fe₂O₃ prepared from FeCl₂.4H₂O, FeCl₃.6H₂O precursors via co-precipitation method and followed by encapsulation and sulfation for transesterification of waste cooking oil on 95°C and 300-min operation conditions (Gardy et al. 2019); CaO/Ag for transesterification of soybean oil on 72°C and 90-min operation conditions prepared by impregnation of calcium methacrylate to AgNO₃ solution (Zhu et al. 2021); and CaO/La₂O₃ prepared from Ca(NO₃)₂.4H₂O and La(NO₃)₃.6H₂O via co-precipitation method for transesterification of jatropha oil with 160°C and 3-h reaction temperature and time (Lee et al. 2015) where all those catalysts showed 97-99% biodiesel conversion. However, the complex catalyst preparation and synthetic precursors used hindered the possibility of the catalyst for sustainable biodiesel production. Hence, sustainable and suitable compounds are needed to ensure sustainability.

A heterogeneous base catalyst such as CaO is one of the best and most used catalysts in biodiesel production due to its high catalytic and basicity levels, moderate condition operability, and high biodiesel conversion (Faruque et al. 2020). Numerous studies had reported excellent CaO catalyst activity, including Kouzu et al. (2008) who conducted transesterification of biodiesel from soybean oil and obtaining a 99% conversion with 120 min and 65°C reaction time and temperature; Viola et al. (2012) obtaining a 93% biodiesel conversion in 80 min and 65°C from transesterification of used cooking oil; Colombo et al. (2017) who conducted transesterification of soybean oil in a recycling reactor and achieved a 100% biodiesel conversion with 75-min reaction time and 3%w/w catalyst mass; Huang et al. (2021) achieving 97.8% biodiesel yield with 2 h and 65°C reaction time and temperature from transesterification of soybean oil. However, the possible suspension formation and high glycerin viscosity in the product consequently made CaO to be mostly used as a support catalyst (Helwani et al. 2020). CaO₂ could be synthesized from many resources, namely CaCO₃, Ca(OH)₂, waste (eggsheells, fish bones), or natural rocks (limestone) that guaranteed raw material sustainability. On the other hand, Fe₂O₃ also has the potential to be developed along with CaO₂ as a bifunctional catalyst. Zhang et al. (2021) have investigated the effects of Fe₂O₃ catalyst on the combustion and emission characteristics in diesel engine and noted a significant NO and NOₓ conversions of 72.3% and 76.1% respectively in a diesel fueled engine. The NO emission is an important aspect in supporting an environmentally friendly fuel alternative. It has been strictly regulated in the Euro VI standard, requiring NOₓ emission reduction by 95% in heavy-duty diesel engines (Zhang et al. 2022a) since 90% of the NO emission was known to originate from fossil fuel combustion (70% caused from diesel engines), further highlighting the potential of Fe₂O₃ as a catalyst (Zhang et al. 2022b). Fe₂O₃ could be synthesized from iron sand which is an abundant natural resource in Indonesia. Chemical co-precipitation using an acid and base solution, followed by calcination, was the commonly used methods for synthesis. Widayat et al. (2019) have successfully obtained the best surface area and pore volume of Fe₂O₃ at 700°C calcination temperature. Fatmaliana et al. (2020) have also successfully obtained a 96.58% Fe₂O₃ content using these methods, which was further supported by Widodo et al. (2020) whom obtained 100% Fe₂O₃ phase after calcination at 900°C temperature. In addition to its sustainability and cheap price, the utilization of iron sand is still limited to metal industries and buildings’ raw material (Ardiani et al. 2020) that allows a room for further development. Moreover, there has been no research that studied and compared iron sand-derived bifunctional catalyst Fe₂O₃/CaO₂ with different CaO₂ sources (CaCO₃, Ca(OH)₂, and limestone) for biodiesel production. This research aims to develop a Fe₂O₃/CaO₂ bifunctional catalyst using wet impregnation method and calcination for biodiesel production with waste cooking oil (WCO) raw material through simultaneous esterification-transesterification process.

Materials and methods

This study followed the research method by Widayat et al. (2019) with several modifications. In particular, modifications in the preparation of α-Fe₂O₃/CaO₂ bifunctional catalyst, simultaneous esterification-transesterification method in biodiesel production, and the centrifugation of biodiesel product to separate the impurities.

Preparation of α-Fe₂O₃ and CaO₂

Figure 1 presents the preparation steps of α-Fe₂O₃/CaO₂ bifunctional catalyst. α-Fe₂O₃ was prepared using iron sand (obtained from Adipala Beach, Cilacap, Central Java, Indonesia) by chemical co-precipitation and calcination methods. Iron sand was subjected to magnetic separation pre-treatment to separate the iron ores (Fe₂O₄) from the impurities. The chemical co-precipitation began with adding Fe₃O₄ to 12 M HCl (37%, Merck, Germany), stirred using a magnetic stirrer (MS7-H550-S, DLAB, China) at 70°C for 50 min. Afterward, the mixture was filtered and added with polyethylene glycol 4000 (PEG 4000) with a 5:1 volume ratio before stirred for 1 h at 70°C. NH₄OH (25%, Merck, Germany) was added next, and the mixture was stirred again until a precipitate was formed. The precipitate was then washed and vacuum filtered to obtain the filtrate. The filtrate was dried in the vacuum oven (DZF-6020, MTI Corporation, USA) for 2 h at 120°C before calcined using a tube furnace (STF54454C, Lindberg/
Blue M, Asheville NC, USA) at 700°C for 2 h to change the Fe₃O₄ phase into α-Fe₂O₃ and remove the remaining unwashed impurities.

To prepare CaO₂, CaCO₃ (99%, Merck, Germany) was first ground to homogenize the particle size using mortar and pestle. The homogenized powder was then calcined using a tube furnace (STF54454C, Lindberg/Blue M, Asheville NC, USA) at 950°C for 2 h to obtain CaO₂. These steps were repeated with Ca(OH)₂ (96%, Merck, Germany), and limestone (obtained from Padalarang, Bandung, West Java, Indonesia).

**Preparation and characterization of α-Fe₂O₃/CaO₂ bifunctional catalyst**

The α-Fe₂O₃/CaO₂ bifunctional catalyst was prepared by wet impregnation and calcination methods. First, the previously prepared α-Fe₂O₃ powder was mixed to each of the CaO₂ powder obtained from CaCO₃, Ca(OH)₂, and limestone with varying weight ratios (2:1, 1:1, 1:2, 1:3, 1:4, and 1:5 %w/w). The mixture was diluted with demineralized water (100 %w/w CaO) and stirred using a magnetic stirrer (MS7-H550-S, DLAB, China) at 60°C for 13 h. The mixture was then filtered to obtain the filtrate, and later dried in the vacuum oven (DZF-6020, MTI Corporation, USA) at 120°C for 2 h before calcined in a tube furnace (STF54454C, Lindberg/Blue M, Asheville NC, USA) at 700°C for 2 h.

X-ray diffraction (XRD), X-ray fluorescence (XRF), and scanning electron microscopy (SEM) characterizations were carried out to determine the surface morphology, composition, and crystallinity of the prepared catalysts. The XRD analysis was performed using the Shimadzu XRD-7000 equipment with patterns measured at 30 mA and 40 kV under Cu-Kα radiation at k = 1.54 Å. The diffraction pattern was observed at 2θ angles from 10 to 90° with a 0.5-s step time. The X’Pert HighScore software (PANalytical copyright 2022) was used to determine the components through the obtained peak intensities. The XRD analysis was carried out using the Rigaku Supermini 200 equipped with a Benchtop tube under a sequential wavelength-dispersive XRF (WDXRF) spectrometer. Meanwhile, the SEM analysis was carried out using the SEM JEOL JSM6510LA equipment at 20 kV and 1.00000 nA probe current. A detailed
specification of equipment used in the catalyst preparation is shown in Table 1.

**Catalytic performance test**

The catalytic performance of the prepared catalysts was tested by biodiesel production. Waste cooking oil (WCO) obtained from household and restaurant wastes in Tembalang, Central Java, Indonesia was used as the raw material. Prior to the biodiesel production, WCO was pre-treated to remove the water and impurities by heating it to 100°C for 40 min and filtering. The filtrate was then determined its %FFA content using the acid-base titration. First, 5 ml of methanol (99.98%, Merck, Germany) was added to 5 ml of WCO and added with 2 drops of Phenolphthalein indicator. The mixture was titrated with 0.1 N NaOH until a pink color persisted. The following equation was used to calculate the FFA content:

\[
\% \text{FFA} = \frac{\text{NaOH volume (ml)} \times \text{NaOH normality (N)} \times \text{fatty acid molecular weight}}{\rho_{\text{WCO}} \times \text{Sample volume (ml)} \times 1000} \times 100
\]

The simultaneous esterification-transesterification process was carried out to produce biodiesel. The pre-treated WCO and methanol (1:15 molar ratio) was poured into a three-necked flask. A 1 %w/w catalyst was also added to the mixture, then stirred at 65°C for 3 h. A Liebig condenser was set into the three-necked flask and was connected to a cooler (CCP5-15, DLAB, China) to maintain the cooling water at 19-20°C. The mixture was taken 10 ml every 15 min and centrifuged (3500 rpm, 15 min) to determine the formation mechanism of the biodiesel, with 5 ml subjected to gas chromatography mass spectrometry (GCMS) analysis and the other 5 ml subjected to FFA titration. After the simultaneous esterification-transesterification process ended, the remaining product was poured into a separating funnel and left for 12 h where the methanol would rise to the top layer, biodiesel in the middle layer, and the catalyst settling on the bottom layer. The middle layer was collected and washed in the separating funnel with warm water (60-70°C) until the spent water was transparent, indicating no impurities left. The product was centrifuged (DMO 412, Scilogex, USA) at 3500 rpm.

### Table 1 Specification of equipment used in α-Fe₂O₃/ CaO₂ bifunctional catalyst preparation

| Equipment                             | Specification                                                                 |
|---------------------------------------|-------------------------------------------------------------------------------|
| Magnetic stirrer (MS7-H550-S, DLAB, China) | Speed range 0-1500 rpm                                                       |
|                                       | Heating temperature range 25-550°C, increment 5°C                             |
|                                       | Temperature control, display accuracy ±10°C, ±1°C                              |
| Vacuum oven (DZF-6020, MTI Corporation, USA) | Vacuum level < 50 mTorr (at 200°C)                                           |
|                                       | Temperature range 30-200°C                                                    |
|                                       | Temperature control accuracy ±1°C                                             |
|                                       | Temperature uniformity ±5°C at 100°C                                          |
| Tube furnace (STF54454C, Lindberg/Blue M, Asheville NC, USA) | Heating temperature range 25-1700°C                                           |
|                                       | Process tube diameter 3" (76.2 mm)                                           |
|                                       | Heated length 24" (609.6 mm)                                                  |
|                                       | Controller accuracy ±0.1%                                                    |
| XRD (Shimadzu XRD-7000S, Japan)        | Goniometer radius 200-275 mm                                                  |
|                                       | Operation angle range −12 to 164° (2q), −6 to 82° (cs), −6 to 132° (qd)     |
|                                       | Operating speed 0.1-50°/min (qs, qd), 0.1-100° (2q)                           |
|                                       | Detector preset time 0.1-1000 s                                               |
| XRF (Rigaku Supermini 200, Japan)      | Sample rotation 60 rpm (50/60 Hz)                                             |
|                                       | 20 scanning speed Max. 1200°/min                                              |
|                                       | Step scanning 0.002-1.0°                                                     |
|                                       | Temperature control 35°C ± 0.3°C                                              |
| SEM (JEOL JSM6510LA, Japan)            | Magnification ×5 to ×300,000                                                   |
|                                       | Electron gun accelerating voltage 0.5-30 kV (55 steps)                        |
|                                       | Maximum specimen size 150 mm                                                  |
for 15 min as the final separation process and biodiesel were collected.

**Characterization of biodiesel product**

The biodiesel product obtained in this study was subjected to yield, density, viscosity, %FFA, and GCMS analyses to determine its properties and suitability to both the Indonesian and European standards. The density and viscosity were measured using 25 ml pycnometer and Ostwald viscometer respectively. The GCMS analysis to determine the biodiesel components was carried out using the QP 2010S Shimadzu, DB-1 column equipment, while the yield of the biodiesel and fatty acid methyl ester content (%FAME) were calculated using the following equation:

\[
\% \text{Yield} = \frac{\text{Biodiesel weight (g)}}{\text{Feed weight (g)}} \times 100
\]

\[
\% \text{FAME} = \frac{\text{Area FAME based on GCMS} \times \text{biodiesel weight (g)}}{\text{Feed weight (g)}} \times 100
\]

**Results and discussion**

**Characterization of α-Fe₂O₃/CaO₂ bifunctional catalyst**

**Effect of different CaO₂ sources to α-Fe₂O₃/CaO₂ catalyst**

Based on Fig. 2, it could be seen that the α-Fe₂O₃/CaO₂ catalyst synthesized from all 3 CaO sources (CaCO₃, Ca(OH)₂, and limestone) have common peaks of CaO₂ (portlandite) and Fe₂O₃ phases. The CaO₂ peaks were detected at 2θ = 18.228°, 34.358°, 47.547°, 51.161°, and 54.764°, while peaks belonging to Fe₂O₃ were detected at 2θ = 29.726°, 33.963°, 50.988°, 51.226°, and 54.869°. The presence of both the CaO₂ and Fe₂O₃ peaks on all of the synthesized α-Fe₂O₃/CaO₂ catalysts indicated that the α-Fe₂O₃ metal dopant has been successfully impregnated to the CaO₂ catalyst. Both the CaCO₃ and Ca(OH)₂-derived catalysts have a monoclinic crystal structure, while the limestone-derived catalyst has a cubic crystal structure. The peak intensity correlates with the degree of crystallinity of the catalyst. The higher the peak intensity, the higher the degree of crystallinity is. This was reflected in Fig. 2, and the Ca(OH)₂-derived catalyst has the highest...
degree of crystallinity (68.8628%) that indicates it being the most crystalline, while the CaCO3-derived catalyst has the lowest (54.1226%). The low crystallinity in the CaCO3-derived catalyst could be explained by the high Fe2O3 phase present that acted as defects in the structure, hence disrupting the order of the crystal system and consequently lowering the crystallinity. Nevertheless, all the three catalysts were concluded to be relatively crystalline judged by the relatively high degree of crystallinity.

The CaO2 phase formed in this study was due to the presence of water vapor during the calcination of CaCO3, Ca(OH)2, and limestone (mainly composed of CaCO3) as an open tube furnace was used, allowing ambient air to flow through. The presence of water vapor would form an intermediate (CaHCO3.OH) that later decomposes as Ca(OH)2 and finally forming CaO2. Giammaria and Lefferts (2019) that had studied this pathway also noted that the formation of the intermediate from CaCO3 was faster than the formation of CaO, explaining the favorable formation of CaO2. The pathway is illustrated in Fig. 3. Another factor affecting the formation of this CaO2 phase was the calcination temperature of the catalyst, which was only 700°C. Numerous studies have stated that the CaO phase was formed on calcination temperatures higher than 900°C (Mohadi et al. 2016; Malau and Adinugraha 2020). At the temperature of 700°C, the decomposition of CaCO3, Ca(OH)2, and limestone (composed mainly of CaCO3) was incomplete, hence forming the CaO2 phase as there was insufficient energy to break the oxygen bond.

The phases detected on the XRD results were cross-checked with XRF analysis to accurately determine the composition of each α-Fe2O3/CaO2 catalysts. Based on Table 2, Ca(OH)2-derived α-Fe2O3/CaO2 catalyst has the highest Fe2O3 composition, followed with limestone-derived and lastly CaCO3-derived catalyst with very small differences (±0.1 to 0.5). These findings were in line with the peak intensities shown from the XRD results: Ca(OH)2 showed the highest intensity, followed by limestone and lastly CaCO3. The presence of MgO as an impurity in limestone-derived α-Fe2O3/CaO2 catalyst was not an unusual phenomenon as limestones were known to have impurities of magnesium carbonates and dolomites (CaMg(CO3)2) (Fairbridge et al. 1967).

The synthesized α-Fe2O3/CaO2 catalyst surface morphology was also analyzed via SEM characterization as shown in Fig. 4. Based on the XRD and XRF results, it was gathered that impregnation has been successfully carried out in the catalyst. Impregnation process would deposit the metal load on the surface of the catalyst instead of the catalyst pore, and this phenomenon could be observed in the SEM results (Fig. 4), where well-distributed small circular particles spread on the surface of the larger irregular shaped bulk, proving that the metal load (α-Fe2O3) has been successfully deposited and simultaneously supported the conclusion gathered from the previous XRD and XRF results. It could also be seen that the Ca(OH)2-derived α-Fe2O3/CaO2 catalyst has the most defined shape of a monoclinic structure, while the limestone-derived catalyst has a relatively defined cubic shape, supporting the XRD results that conclude Ca(OH)2 has the highest crystallinity.

Similarly, the least defined shape on CaCO3-derived catalyst shown in Fig. 4(A) also supported the XRD result previously mentioned. The CaCO3-derived catalyst gave the lowest peak intensity (Fig. 2) consequently giving lower crystallinity and structure arrangement. Agglomeration on the limestone-derived catalyst could also be seen on Fig. 4(C) which could be explained by the presence of water vapor.
during the calcination process (Fig. 3) that inevitably bind the catalyst particles together by Van der Waals forces on the catalyst surface, known as the sintering effect commonly found in heterogeneous catalysts (Forzatti and Lietti 1999). The high amount of α-Fe₂O₃ metal dopant detected by the XRF analysis (Table 2) in the limestone-derived catalyst also contributed to the big particle size, as metal dopants will promote the crystal growth rate (Kasim et al. 2014).

Effect of Fe/Ca ratio to α-Fe₂O₃/CaO₂ catalyst

Based on Fig. 5, the 2 major peaks detected were CaO₂ and Fe₂O₃ that indicates a successful impregnation. The CaO₂ peaks were detected at 2θ = 18.228°, 34.358°, 47.547°, and 51.161°, while the Fe₂O₃ peaks were detected at 2θ = 33.963°, 51.226°, and 54.869°. It could also be clearly observed that greater addition of α-Fe₂O₃ to the catalyst (Fe/Ca ratio 2:1) will give a very amorphous structure, as indicated by the lack of distinguishable sharp peaks in the diffractogram. There was also no Fe₂O₃ phase and peaks detected on this variable, even though the α-Fe₂O₃/CaO₂ was added twice the amount of CaO. Mos et al. (2018) stated that copper (Cu) radiation in XRD analysis is not suitable to be used in characterizing Fe₂O₃ peaks, although majority of studies nowadays still used it to characterize iron oxides containing samples and could provide a decent analysis. This incompatibility resulted in a high background noise that could mask the low intensity peaks given by the Fe₂O₃ phase. Moreover, the fact that the addition of α-Fe₂O₃ gave an amorphous structure to the catalyst also further hid the possible α-Fe₂O₃ peaks present, since the weak peaks could be easily masked by the broad hump of the amorphous pattern. Mardwita et al. (2020) had also obtained similar condition in their alumina-supported cobalt and chromium catalyst, and explained that these undetected peaks were due to the metal particles highly dispersed in the catalyst surface, consequently pushing alumina to be dominant and the only phase able to be detected by the XRD radiation.

Based on Fig. 6, it could be observed that the α-Fe₂O₃ particles were present in all of the catalyst surfaces,
corroborating the XRD and XRF results presented in Fig. 5 and Table 3 respectively that the impregnation process has been successful. Sintering effect was clearly observed in the results, starting from the Fe/Ca ratio 1:2 (Fig. 6(C)) to the most prevalent agglomerate formed in Fe/Ca ratio 1:5 (Fig. 6(F)). It was established that CaO could readily absorb water in ambient atmosphere; hence, with higher CaO composition, there would be a higher chance of sintering effect taking place.

**Characterization of the biodiesel product**

**Effect of different CaO 2 sources to the biodiesel and FAME yield**

The successfully synthesized α-Fe 2O 3/CaO 2 catalysts from CaCO 3, Ca(OH) 2, and limestone sources were subjected to biodiesel production to determine their catalytic performance. Based on Fig. 7, the limestone-derived α-Fe 2O 3/CaO 2 catalyst has the highest biodiesel yield (77.1672%), followed by the Ca(OH) 2 source (68.7972%), and lastly the CaCO 3 source (62.3761%). In this study, biodiesel yield referred to the yield of product containing FAME, diglycerides, and monoglycerides; hence, to determine the pure FAME content (without the incompletely converted triglycerides), the FAME yield was also calculated. The limestone-derived catalyst gave the highest FAME yield (62.0656%), followed closely by CaCO 3 (61.5902%) and lastly Ca(OH) 2 (32.7062%). Based on the XRF result (Table 2), limestone-derived catalyst has the lowest CaO composition but a high α-Fe 2O 3 composition with only a very small difference (±0.1) with the Ca(OH) 2-derived catalyst. This indicates that the limestone-derived catalyst favored the esterification reaction catalyzed by α-Fe 2O 3 rather than the transesterification reaction catalyzed by the CaO component to form biodiesel. Similarly, the Ca(OH) 2-derived catalyst that has the highest CaO composition (Table 2) has a lower biodiesel yield due to the dominant transesterification reaction led by the CaO component. The transesterification reaction caused soap formation since the waste cooking oil used as the raw material contained high FFA, further explaining the very low FAME yield. Likewise, the CaCO 3-derived catalyst that has the lowest α-Fe 2O 3 component (Table 2) has the lowest biodiesel yield (62.3761%) since there would be less available active metal species for the esterification reaction to form biodiesel.

**Table 3** XRF result of CaCO 3-derived α-Fe 2O 3/CaO 2 catalyst with different Fe/Ca ratio

| Component | Composition (% mass) |
|-----------|---------------------|
|           | 2:1 1:1 1:2 1:3 1:4 1:5 |
| Fe 2O 3   | 46.5210 37.6119 17.3153 14.7596 14.0586 11.6086 |
| CaO       | 34.0959 40.2651 57.5325 57.5465 57.5688 60.4373 |
| Al 2O 3   | 0.9191 0.5194 0.5190 0.3843 0.3916 0.4364 |
| SiO 2     | 1.0155 0.8946 0.9950 0.9464 0.9205 0.9223 |
| TiO 2     | 3.6866 2.9273 1.3199 1.1800 0.9737 1.0770 |
| V 2O 5    | 0.4386 0.3648 0.1995 0.1282 n.d n.d |
| MnO       | 0.3395 0.2545 0.1296 0.1065 0.0892 0.0760 |

* n.d not detected

![Fig. 5 XRD result of CaCO 3-derived α-Fe 2O 3/CaO 2 catalyst with different Fe/Ca ratio](image-url)
Based on Table 4, the only biodiesel product that has met both the Indonesian and European standards (SNI 7182:2015 and EN 1421:2008) respectively was the biodiesel produced using the CaCO₃-derived catalyst. This catalyst also gave biodiesel with the lowest FFA content (2.2534%), indicating that the catalyst was the most successful in converting the FFA in the waste cooking oil to biodiesel. Therefore, it could be concluded that among the 3 CaO sources investigated in this study, CaCO₃ was the best CaO source to be combined with the metal dopant α-Fe₂O₃ in giving the best catalytic performance in biodiesel production despite it giving the lowest biodiesel yield (Fig. 7).

The trend of FAME formation was investigated using GCMS analysis in this study (Fig. 8). Based on Fig. 9, the Ca(OH)₂-derived α-Fe₂O₃/CaO₂ catalyst formed the highest FAME (hexadecanoic acid, methyl ester and 9-octadecenoic acid, methyl ester) on the 60th min mark, which was the fastest among the catalysts. It was followed by the limestone-derived α-Fe₂O₃/CaO₂ catalyst which experienced the highest FAME formation on the 90th min mark. Meanwhile, the CaCO₃-derived α-Fe₂O₃/CaO₂ catalyst gave the highest FAME formation on the 180th min mark.

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The CaCO₃ and limestone-derived catalyst showed higher levels of the diglyceride hexadecanoic acid, 2-hydroxy-1,3-propanediyl ester (an incomplete form of FAME), which meant that these catalysts have lower selectivity and thus...
favored the formation of biodiesel instead of FAME. Meanwhile, the Ca(OH)\textsubscript{2}-derived catalyst showed a complete formation of the 9-octadecenoic acid methyl ester and only a small amount of diglyceride formed, indicating that this catalyst was more selective towards FAME formation and thus more suitable in biodiesel conversion. Nevertheless, all the catalysts showed good conversion of the free fatty acid 9-octadecenoic acid to the FAME 9-octadecenoic acid methyl ester as shown on their higher yield compared to the other components.

### Table 4 Effect of different CaO\textsubscript{2} sources to the physicochemical characteristics of biodiesel

| Parameters          | CaO\textsubscript{2} sources | WCO Indonesian standard (SNI 7182:2015) | European standard (EN 1421:2008) |
|---------------------|-----------------------------|----------------------------------------|----------------------------------|
| Density (g/ml)      | CaCO\textsubscript{3}  | 0.8830                                  | 0.85-0.89                        | 0.86-0.90                       |
|                     | Ca(OH)\textsubscript{2} | 0.9448                                  | 4.3830                           | 5.4330                          |
|                     | Limestone                 | 0.9144                                  | 4.3870                           | 3.7-6.0                         |
| Kinematic viscosity (cSt) | CaCO\textsubscript{3}  | 4.3880                                  | -                                | -                               |
|                     | Ca(OH)\textsubscript{2} | 4.3790                                  | -                                | -                               |
|                     | Limestone                 | 4.3870                                  | -                                | -                               |
| FFA (%)             | CaCO\textsubscript{3}  | 2.2534                                  | -                                | -                               |
|                     | Ca(OH)\textsubscript{2} | 4.2817                                  | -                                | -                               |
|                     | Limestone                 | 2.7699                                  | -                                | -                               |

**Fig. 8** GCMS results of biodiesel product from different CaO\textsubscript{2} sources
Simultaneous esterification-transesterification of the bifunctional $\alpha$-Fe$_2$O$_3$/CaO$_2$ catalyst

To justify the role of esterification in the synthesized bifunctional $\alpha$-Fe$_2$O$_3$/CaO$_2$ catalyst, the trend of FFA conversion through the course of reaction time is investigated and depicted in Fig. 10. The bifunctional $\alpha$-Fe$_2$O$_3$/CaO$_2$ catalysts from 3 different CaO sources were shown to successfully convert the FFA in the WCO feedstock, as seen by the decreasing FFA trend from 6.8164 to 2.2534% (CaCO$_3$), 4.2871% (Ca(OH)$_2$), and 2.7699% (limestone). The CaCO$_3$-derived catalyst has the lowest FFA content left by the end of the 3-h reaction time, indicating a higher conversion rate than the other catalysts. Despite the generally downwards trend of the conversion, there was still an increase in the FFA content; which could be attributed to the reaction between the triglycerides and water that was the byproduct of the FFA esterification by the acid site of the bifunctional catalyst.

Meanwhile, the bifunctional catalyst was already proven able to carry out the transesterification reaction by the formation of FAME and diglycerides as seen in the GCMS results (Fig. 9). The FFA conversion trend in Fig. 9 was shown to correlate with the FAME formation in Fig. 8 where decreasing FFA gave increasing FAME yield, which was congruent with the esterification and transesterification reactions. The raise in diglycerides was also consistent with the raise in the FFA, thus giving evidence to the reaction between the triglyceride and water that yield not only FFA, but also diglycerides. In conclusion, the bifunctional $\alpha$-Fe$_2$O$_3$/CaO$_2$ catalyst synthesized in this study was capable of carrying the simultaneous esterification-transesterification reaction as seen by the evidences.

Fig. 9 Formation of FAME components through the course of reaction time
Effect of Fe/Ca ratio to the biodiesel and FAME yield

Based on Fig. 11, the highest biodiesel yield (97.0401\%) was achieved on Fe/Ca ratio 1:4. It was established that the synthesized catalyst favored the esterification reaction and that the Fe$_2$O$_3$ component was more dominant than the CaO$_2$. This conclusion was corroborated by the very low biodiesel yield (54.3709\%) given when the Fe ratio was the lowest (1:5), as there was not enough Fe active species to carry out the esterification of the relatively high FFA content in the WCO, thus giving a low yield. The Ca leaching to the methanol phase of the biodiesel system could also contribute to this low yield, which has been proven by numerous studies including Mansir et al. (2017) and Colombo et al. (2017). It was also noteworthy that when the Fe ratio was double (2:1), the FAME yield was lower than the Fe/Ca ratio 1:5, indicating that despite the catalyst favoring the esterification reaction, the CaO$_2$ component that was responsible for the transesterification reaction was also important and created a synergistic effect in the biodiesel conversion.

To further understand the phenomena, the FAME components and physicochemical characteristics of the biodiesel are investigated and shown in Tables 5 and 6 respectively. Based on Table 5, the 1:4 Fe/Ca ratio that gave the best biodiesel and FAME yield was shown to only have the complete methyl ester components (hexadecanoic acid methyl ester and 9-octadecenoic acid methyl ester) with no diglycerides, indicating that this ratio was the best configuration. Meanwhile, the small number of diglycerides and high number of complete FAME in the 1:5 Fe/Ca ratio explained that the Fe$_2$O$_3$ component in the catalyst favored the formation of diglycerides, while the CaO component favored the formation of methyl esters. This phenomenon could be seen in the other ratios, including the 2:1 Fe/Ca ratio which gave the highest diglyceride components among the other.
The favorable formation of diglycerides instead of methyl esters in the biodiesel affected the kinematic viscosity property. Diglyceride is an incomplete methyl ester with 2 unbroken triglyceride chains that would have a heavier molecular weight, raising the kinematic viscosity of the biodiesel. Based on Table 6, all Fe/Ca ratios except 1:3 and 1:4 have higher viscosities as there was the diglyceride component. Nevertheless, the viscosities of all the biodiesel still passed the European and Indonesian standards. The diglyceride content is also regulated and included in the total glycerol parameter, and per the standards only the 1:3 and 1:4 Fe/Ca ratio had passed. Meanwhile, the densities of all the ratios had passed both standards, except the 1:3 Fe/Ca ratio; and the lowest FFA content of the 1:4 Fe/Ca ratio showed the best conversion of FFA to methyl esters among the variables. In conclusion, the physicochemical results (Table 6) supported the conclusion that 1:4 Fe/Ca ratio was the best catalyst configuration.

Predicted mechanism of the bifunctional α-Fe₂O₃/CaO₂ catalyst

Based on the GCMS results and physicochemical properties of the synthesized CaCO₃-derived bifunctional α-Fe₂O₃/CaO₂ catalyst, it was concluded that the catalyst was able to catalyze simultaneous esterification-transesterification reaction, with α-Fe₂O₃ component as the acid site favoring diglyceride formation and the CaO₂ component as the basic site favoring the formation of methyl esters. It was known that the diglyceride compound could be formed due to the esterification between FFA and glycerol with an acid catalyst (Kong et al. 2019). Considering that there was no glycerol layer present on the decantation process, the mechanism

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**Table 5** Major FAME components in biodiesel produced from varying Fe/Ca ratios

| FAME component                                      | Fe/Ca ratio | 2:1    | 1:1    | 1:2    | 1:3    | 1:4    | 1:5    |
|-----------------------------------------------------|-------------|--------|--------|--------|--------|--------|--------|
| Hexadecanoic acid, methyl ester                     | 7.75%       | 34.56% | 32.09% | 31.16% | 31.78% | 31.71% |
| 9-Octadecenoic acid, methyl ester                   | 12.17%      | 60.67% | 47.32% | 63.38% | 63.65% | 45.72% |
| Hexadecanoic acid, 2-hydroxy-1,3-propanediyl ester  | 13.39%      | 0.64%  | 13.58% | n.d    | n.d    | 3.53%  |
| 9-octadecenoic acid, 2-hydroxy-1,3-propanediyl ester| 1.94%       | n.d    | 3.01%  | n.d    | n.d    | 0.41%  |

*n.d not detected

**Table 6** Effect of Fe/Ca ratio to the physicochemical characteristics of biodiesel

| Parameters                | Fe/Ca ratio | 2:1    | 1:1    | 1:2    | 1:3    | 1:4    | 1:5    | Indonesian standard (SNI 7182:2015) | European standard (EN 1421:2008) |
|---------------------------|-------------|--------|--------|--------|--------|--------|--------|-------------------------------------|----------------------------------|
| Density (g/ml)            | 0.8788      | 0.8747 | 0.8830 | 0.8420 | 0.8805 | 0.8815 | 0.85-0.89                          | 0.86-0.90                        |
| Kinematic viscosity (cSt) | 4.7387      | 4.6331 | 4.3882 | 4.2076 | 4.4318 | 4.7027 | 2.3-6.0                           | 3.5-5.0                           |
| FFA (%)                   | 1.4084      | 0.8450 | 2.2534 | 1.1267 | 0.4131 | 2.8167 | -                                 | -                                 |
| Diglycerides (%)          | 15.33       | 0.64%  | 16.59% | -      | -      | 3.94%  | <0.24                             | <0.2                             |
| Methyl ester (%)          | 34.29       | 95.89% | 79.41% | 98.20% | 99.73% | 82.08% | >96.5                             | >96.5                             |
of the bifunctional α-Fe₂O₃/CaO₂ catalyst was predicted with the assumption that the glycerol formed in the transesterification reaction was completely converted (Fig. 12). The mechanism started with the adsorption of the carbonyl group in the FFA to the acid site and the adsorption of the methanol to the basic site of the catalyst. These adsorptions would produce carbocation and oxygen anion respectively. Next, nucleophilic attack will happen on the surface of the...
catalyst: the carbocation with the second hydroxyl group in glycerol (due to the GCMS result detecting the component fatty acid-2-hydroxy-1,3-propanediyl ester) on the acid site while the oxygen anion in the hydroxyl group of methanol with the carbonyl group in the triglyceride on the basic site. The breaking down of the 3 fatty acid chains of the triglyceride (transesterification reaction) in the basic site will yield 3 FAME molecules and glycerol as the byproduct. Meanwhile, the esterification of glycerol with FFA on the acid site will produce water and the diglyceride compound. Finally, desorption of the products will take place and the catalytic cycle will begin again.

Conclusion

The bifunctional α-Fe₂O₃/CaO₂ catalysts were successfully synthesized from 3 different CaO₂ sources, with Ca(OH)₂-derived catalyst having the highest crystallinity (68.8628%) and CaCO₃-derived catalyst the lowest (54.1226%). It was observed that the greater addition of α-Fe₂O₃ component to the CaO₂-derived catalyst would give a very amorphous structure. Meanwhile, the limestone-derived α-Fe₂O₃/CaO₂ catalyst gave the highest biodiesel yield (77.1672%), but biodiesel obtained from CaCO₃-derived catalyst was the only product that met the Indonesian and European standards. The best Fe/Ca configuration was concluded to be 1:4 as it gave the highest biodiesel yield (97.0401%) with complete methyl ester conversion and no diglycerides, indicating high purity biodiesel with negligible impurities which would help reduce the wear and tear in engines. It was also discovered that the α-Fe₂O₃ component favored the esterification reaction and formation of diglycerides, while the CaO₂ favored the transesterification reaction and formation of methyl esters (FAME). Based on these discoveries, the catalyst mechanism was predicted that esterification of FFA and glycerol taking place on the acid site will produce diglyceride, while transesterification of triglyceride by methanol took place on the basic site. These discoveries would significantly increase the efficiency in biodiesel production process as the cause for incomplete methyl ester conversion was identified, consequently giving insight to industries for a way to produce biodiesel without any by-products and impurities. Moreover, the elimination of glycerol or diglyceride separation process would also save the cost of water and electricity, hence improving the economics of production in biodiesel industries.

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References

Ardiani NR, Setianto S, Santosa B, Wibawa BM, Panatarani C, Joni IM (2020) Quantitative analysis of iron sand mineral content from the south coast of Cidahu, West Java using rietveld refinement method. AIP Conf Proc 2219:040003

BP Statistical Review of World Energy (2021) (online) London: BP Statistical Review of World Energy. https://www.bp.com/content/dam/bp/business-sites/en/global/corporate/pdfs/energy-economics/statistical-review/bp-stats-review-2021-full-report.pdf. Accessed 29 Apr 2022

Colombo K, Ender L, Barros AAC (2017) The study of biodiesel production using CaO as a heterogeneous catalytic reaction. Egypt J Pet 26:341–349

De Araújo CDM, de Andrade CC, e Silva, E. d. S. and Dupas, F. A. (2013) Biodiesel production from used cooking oil: A review. Renew Sust Energ Rev 27:445–452

Fairbridge RW, Chilingar GV, Bissell HJ (1967) Chapter 1 introduction. In: Chilingar GV, Bissell HJ, Fairbridge RW (eds) Development in sedimentology. Elsevier, Amsterdam

Faruque MO, Razzak SA, Hossain MM (2020) Application of heterogeneous catalysts for biodiesel production from microalgal oil - a review. Catalysts 10:1025

Fatmaliana A, Maulindra, Sari N (2020) Synthesis and characterization of hematite (Fe₂O₃) of iron ore and magnetite (Fe₃O₄) from iron sand through precipitation method for industrial raw materials. J Neutrino: J Fisika dan Aplikasinya 12:37–42

Forzatti P, Lietti L (1999) Catalyst deactivation. Catal Today 52:165–181

Gardy J, Nourafkan E, Osatiashtiani A, Lee AF, Wilson K, Hassanpour A, Lai X (2019) A core-shell SO₄/Mg-Al-Fe₃O₄ catalyst for biodiesel production. Appl Catal B Environ 259:118093

Giammaria G, Lefferts L (1999) Catalyst deactivation. Catal Today 52:165–181

Huang J, Zou Y, Yaseen M, Qu H, He R, Tong Z (2021) Fabrication of hollow cage-like CaO catalyst for the enhanced biodiesel production via transesterification of soybean oil and methanol. Fuel 290:119799

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Springer
Kasim MF, Kamarulzaman N, Kamil SA (2014) Investigation of phase, purity, morphology and particle size of \( \text{Zn}_{1-x}\text{Cu}_x\text{O} \) materials via X-ray diffraction (XRD) and microscopic techniques. Adv Mater Res 895:343–346

Kong PS, Pérès Y, Wan Daud WMA, Cognet P, Aroua MK (2019) Esterification of glycerol with oleic acid over hydrophobic zirconia-silica acid catalyst and commercial acid catalyst: optimization and influence of catalyst acidity. Front Chem 7:205

Kouzu M, Kasuno T, Tajika M, Sugimoto Y, Yamanaka S, Hidaka J (2008) Calcium oxide as a solid base catalyst for transesterification of soybean oil and its application to biodiesel production. Fuel 87:2789–2806

Lee HV, Juan JC, Taufiq-Yap YH (2015) Preparation and application of binary acid-base \( \text{CaO-La}_2\text{O}_3 \) catalyst for biodiesel production. Renew Energy 74:124–132

Malau ND, Adinugraha F (2020) Penentuan suhu kalsinasi optimum \( \text{CaO} \) dari cangkang telur bebek dan cangkang telur burung puyuh. J Edu Mat Sains 4:193–202

Mansir N, Teo SH, Ibrahim ML, Taufiq-Yap YH (2017) Synthesis and application of waste egg shell derived \( \text{CaO} \) supported \( \text{W-Mo} \) mixed oxide catalysts for FAME production from waste cooking oil: Effect of stoichiometry. Energy Convers Manag 151:216–226

Mardwita M, Yusmartini ES, Wisudawati N (2020) Effects of cobalt and chromium loadings to the catalytic activity of supported metal catalysts in methane oxidation. Bull Chem React Eng Catal 15:213–220

Mohadi R, Anggraini K, Riyanti F, Lesbani A (2016) Preparation calcium oxide (\( \text{CaO} \)) from chicken eggshells. Srijiwijaya J Environ 1:32–35

Mos YM, Vermeulen AC, Buismen CJN, Weijma J (2018) X-ray diffraction of iron containing samples: the importance of a suitable configuration. Geomicrobiol J 35:511–517

Pan H, Zhang H, Yang S (2017) Production of biodiesel via simultaneous esterification and transesterification. In: Fang Z, Smith R Jr., Li H (eds) Production of biofuels and chemicals with bifunctional catalysts. Biofuels and Biorefineries vol. 8., 1st edn. Springer, Singapore

Pruszko R (2020) Chapter 23 – biodiesel production. In: Dahiya A (ed) Bioenergy: biomass to biofuels and waste to energy, 2nd edn. Academic Press, London

Viola E, Blasi A, Valerio V, Guidi I, Zimbardi F, Braccio G, Giodarno G (2012) Biodiesel from fried vegetable oils via transesterification by heterogeneous catalysis. Catal Today 179:185–190

Widayat, Putra DA, Nursafitri I (2019) Synthesis and catalytic evaluation of hematite (\( \alpha\text{-Fe}_2\text{O}_3 \)) magnetic nanoparticles from iron sand for waste cooking oil conversion to produce biodiesel through esterification-transesterification method. IOP Conf. Series. Mater Sci Eng 509:012035

Widodo RD, Priyono R, Anis S, Ichwani AA, Setiawan B, Fitrriyana DF, Rochman L (2020) Synthesis and characterization of iron (III) oxide from natural iron sand of the south coastal area, Purworejo Central Java. J Phys Conf Ser 1444:012043

Zhang Z, Ye J, Tan D, Feng Z, Luo J, Tan Y, Huang Y (2021) The effects of \( \text{Fe}_2\text{O}_3 \) based DOC and SCR catalyst on the combustion and emission characteristics of a diesel engine fueled with biodiesel. Fuel 290:120039

Zhang Z, Tian J, Li J, Cao C, Wang S, Lv J, Zheng W, Tan D (2022a) The development of diesel oxidation catalysts and the effect of sulfur dioxide on catalysts of metal-based diesel oxidation catalysts: a review. Fuel Process Technol 233:107317

Zhang Z, Li J, Tian J, Zhong Y, Zou Z, Dong R, Gao S, Xu W, Tan D (2022b) The effects of Mn-based catalysts on the selective catalytic reduction with \( \text{NH}_3 \) at low temperature: a review. Fuel Process Technol 230:107213

Zhu Z, Liu Y, Cong W, Zhao X, Janaun J, Wei T, Fang Z (2021) Soybean biodiesel production using synergistic CaO/Ag nano catalyst: process optimization, kinetic study, and economic evaluation. Ind Crop Prod 166:113479

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