Hybrid CaO/ZnFe₂O₄ Modified with Al₂O₃ as a Green Catalyst for Biodiesel Production from Waste Cooking Oil

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Abstract
In this work, biodiesel was produced from waste cooking oil (WCO) via a green catalyst of CaO-ZnFe₂O₄ modified Al₂O₃. The catalyst was characterized using Fourier-transform infrared spectroscopy (FTIR), X-ray powder diffraction (XRD), scanning electron microscopy (SEM), energy dispersive x-ray (EDX), SEM-mapping, Brunauer-Emmet-Teller (BET), transmission electron microscopy (TEM) analyses. The catalytic activity increased with the combination of nanoparticles effect and support catalysts obtained biodiesel yield of nano-Al₂O₃, nano-CaO, ZnFe₂O₄, CaO-ZnFe₂O₄, and CaO-ZnFe₂O₄/Al₂O₃ is 36.86%, 67.16%, 74.83%, 86.54%, and 93.41%, respectively. The best biodiesel yield was 93.41% with a mass ratio of Al₂O₃ to CaO-ZnFe₂O₄ (2:1). The physicochemical properties (acid number, density, kinematic viscosity, flash point, and cetane number) of biodiesel under the optimal conditions agreed with the ASTM standard. These results show that the developed nanocomposite has great potential to reduce biodiesel production costs because derived from WCO. In conclusion, CaO-ZnFe₂O₄ modified Al₂O₃ as a catalyst has a high potential for biodiesel production on a large scale.

Keywords: Biodiesel; catalyst; nanocomposite; transesterification; waste cooking oil

1. INTRODUCTION
In the last few years, energy issues have grown due to global demand worldwide. The depletion of fossil energy sources and the growth of environmental pollution were the main contributing factors to renewable energy development. Biodiesel is a renewable alternative energy substitute for fossil fuels, it reduces greenhouse gasses and is non-toxic, and biodegradable. Biodiesel is obtained through the triglyceride transesterification reaction from fatty acids such as edible feedstocks, non-edible feedstocks, and waste feedstocks such as waste cooking oils (WCO) with low-chain alcohols in the presence of a catalyst. The use of WCO is a very efficient effort to deal with waste problems by processing them into renewable energy sources.

An important factor associated with biodiesel production is the use of catalysts in synthesis. This fuel large-scale production occurs using mostly homogeneous catalysts, such as NaOH, KOH, etc. However, homogeneous catalysts are difficult to separate, corrosive, and environmentally harmful. Heterogeneous catalysts are an alternative to these problems because of their favorable characteristics such as high selectivity, regeneration ease of separation from the reaction mixture, and the potential to be reused. Among the heterogeneous catalysts in biodiesel synthesis, calcium oxide (CaO) exhibits high activity in transesterification. Besides, it is environmentally friendly and can be synthesized from less valuable residues, namely eggshells, animal bones, snail shells, oyster shells, etc.

However, the disadvantages of CaO are mainly from natural sources that have low stability causing the degradation of the structure of CaO and can dissolve in the biodiesel phase. To improve the catalytic activity and stability of calcium oxide, it is necessary to modify CaO with other metal oxides, including combining magnetic catalysts, so that can be separated by an external magnetic field. Metal-ferrite nanoparticles or MFe₂O₄...
(M=Co, Ni, Mg, Cu, etc) have many benefits including high surface area, great reusability, tunable size, high stability, and magnetic features16,17. Besides that, to increase the surface area the catalyst can be combined with a catalyst support, including zeolite, silica, and alumina (Al2O3)18. Alumina is one of the support catalysts suitable for efficient biodiesel production due to its high specific surface area, porous structure, and high stability19.

Several studies with heterogeneous bases CaO for transesterification in biodiesel production have been investigated, like Hybrid CaO/Al2O3 aerogelsF; Novel SrO/MgFe2O3 magnetic nanocatalysts at low temperatures20; A novel robust CaO/ZnFe2O4 hollow magnetic microspheres with yeast templates21; Metal loading on CaO/Al2O3 pellet catalyst22; Aluminum industrial waste as a precursor of efficient CaO/Al2O3 nano-catalyst23; Mg decorated CoFe2O4 nanocatalyst24; Hybrid CuO/Al2O3 nanoparticles25.

Based on previous research, this paper combines ideas from previous research with new modifications in the preparation of the heterogeneous catalyst-based calcium oxide of chicken eggshell combined by hollow structure ZnFe2O4 using yeast cells as a biotemplate and alumina as a supported catalyst. Therefore, the purpose of this study is to synthesize a catalyst using Al2O3 as a support combined with a CaO and ZnFe2O4 composite which will be used as a catalyst in the transesterification process of waste cooking oil (WCO) into biodiesel or fatty acid methyl ester (FAME). Furthermore, the novel catalyst was characterized by X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FT-IR), Brunauer-Emmett-Teller (BET), scanning electron microscopy (SEM), energy diffraction X-ray (EDX), Elemental distribution mappings by SEM, and transmission electron microscopy (TEM).

2. RESEARCH METHODS
Materials and Instruments

The materials used in this research were chicken eggshell waste as nano-CaO source, Fe(NO3)3·9H2O, Zn(NO3)2·6H2O as ZnFe2O4 precursors, (Al(NO3)3·9H2O) as Al2O3 precursor, CH3OH were procured from Merck, and WCO as the feedstock for biodiesel, yeast was obtained from the local market.

The instruments used were Fourier transform infrared spectrophotometer (FTIR) Alpha II-Bruker, X-ray diffraction (XRD) Panalytical Empyrean X-ray diffraction, scanning electron microscopy (SEM) FEI Quanta 650 scanning electron microscope, Brunauer-Emmett-Teller (BET) quantachrome quadrasorb-evo surface area and pore size analyzer, and transmission electron microscopy (TEM) FEI Tecnai G2 SuperTwin TEM/STEM.

2.1 Synthesis of nano-CaO

Nano-CaO was prepared from chicken eggshell waste using the previously reported method25, the collected chicken eggshells were extensively washed with distilled water and dried for 2 h in an oven at 110 °C, then ground through a ball milling process. The samples were calcined for 3 h at 900 °C with a heating rate of 10 °C/min.

2.2 Synthesis of ZnFe2O4 Hollow Structure

The synthesis of ZnFe2O4 was prepared as a previously reported method21. In the first stage, 2 g of yeast cells used as bio-template was dissolved in 50 ml of distilled water and stirred for 20 min to ensure complete dispersion of yeast cells. In the next stage, Fe(NO3)3·9H2O and Zn(NO3)2·6H2O were added with constant stirring at 60 °C for 1 h. Then, 25% liquid ammonia solution was added drop by drop until the pH of the solution reached between 9 and 10. The precipitate was separated, washed with distilled water, and dried in an oven at 60 ℃ for 12 h.

2.3 Synthesis of nano-Al2O3

Nano-Al2O3 was prepared as a previously reported method26. A 0.5 M Al(NO3)3·9H2O was dissolved in 40 mL of distilled water and 120 mL of 1.5 M NH4OH was added drop by drop by stirring using a magnetic stirrer for 20 min at 60 ℃. The white precipitate was filtered and washed using distilled water and ethanol, dried at 100 ℃ for 2 h, and calcined at 550 ℃ for 5 h.

2.4 Synthesis of CaO-ZnFe2O4 Composite

Synthesis of CaO-ZnFe2O4 using the coprecipitation method as previously reported21. The ZnFe2O4 hollow nanostructures were dispersed in distilled water by ultrasonic waves. The resulting dispersion supplemented with nano-CaO was slowly stirred and adjusted with 2 M NaOH to reach a pH of 12. The mixture was stirred continuously at 600 rpm, 60 ℃ for 3 h. The product was separated, washed with distilled water, and dried at 60 ℃.

2.5 Synthesis of CaO-ZnFe2O4/Al2O3 Nanocomposite

Nanocomposite of CaO-ZnFe2O4/Al2O3 was prepared using a slight modification of a previously reported method27. In the first stage, CaO-ZnFe2O4 composite was added to a solution of 10 mL of 0.25 M NaOH and slowly stirred for 1 h (mixture A). In the second stage, nano-Al2O3 in 50 mL of distilled water and slowly stirred for 1 h (mixture B). Then mixture A was added slowly to mixture B and stirred at 27 ℃ for 6 h. The resulting mixture was filtered and rinsed using water and ethanol, dried at 100 ℃ for 2 h, and calcined at 550 ℃ for 5 h.
2.6 Preparation of Waste Cooking Oil (WCO)

WCO preparation refers to the previous method. The WCO was filtered to remove impurities with gauze, then the washing process was done with warm water with a weight ratio water to WCO of 10:1 stirred for 30 min, and left overnight so that the water and oil phases could be separated. The resulting WCO added silica gel and stirred for 3 h followed by vacuum filtration using Whatman filter paper to remove the silica gel. The WCO is stored in a tightly closed bottle.

2.7 Catalytic activity

The catalytic activity was tested as described in previous studies. The experiments were done in a 100 ml glass reactor equipped with a condenser and a mechanical stirrer, this system is submerged in a water bath under controlled temperature. In a typical test, 2 wt% catalyst was added to WCO and methanol (methanol to WCO molar ratio 9:1). The mixture was refluxed by stirring at different temperatures and times. After the reaction, the catalyst was separated by an external magnet. The products are transferred to a funnel to separate the two phases of biodiesel and glycerol. Biodiesel yield was calculated in Eq (1).

\[
\text{Biodiesel yield (\%) = } \frac{\text{Weight of biodiesel}}{\text{Weight of WCO}} \times 100
\]  

3. RESULTS AND DISCUSSION

3.1 Synthesis of CaO-ZnFe$_2$O$_4$/Al$_2$O$_3$ Nanocomposite

The use of Al$_2$O$_3$ as a catalyst support is used to increase the number of active groups, surface area, and catalytic efficiency of nanocomposites with CaO and ZnFe$_2$O$_4$. The role of yeast as a template in the synthesis of ZnFe$_2$O$_4$ is to create a hollow structure in the ZnFe$_2$O$_4$ that will be formed. This will cause an increase in surface area compared to ZnFe$_2$O$_4$ which does not have a hollow structure.

3.2 Characterization

3.2.1 FTIR Analysis

The molecular vibration of catalysts was analyzed by Fourier Transform Infrared spectroscopy (FTIR) in the range of 400–4000 cm$^{-1}$. Figure 1 shows the FTIR spectra of nano-CaO, ZnFe$_2$O$_4$, nano-Al$_2$O$_3$, CaO-ZnFe$_2$O$_4$ composite, and CaO-ZnFe$_2$O$_4$/Al$_2$O$_3$ nanocomposite. The FTIR spectra of nano-CaO have an intense peak at 874 cm$^{-1}$ related to the stretching of the Ca-O bond and a wide peak at 512 cm$^{-1}$, which is a typical characteristic of CaO nanoparticles. The sharp peak at 3640 cm$^{-1}$ may be assigned to the OH stretching for Ca(OH)$_2$ due to absorption of water by CaO. The FTIR spectra of ZnFe$_2$O$_4$ with a yeast template have a peak around 420 cm$^{-1}$ related to the stretching of the Ca-O bond and a wide peak at 512 cm$^{-1}$, which is a typical characteristic of CaO nanoparticles. The sharp peak at 3640 cm$^{-1}$ may be assigned to the OH stretching for Ca(OH)$_2$ due to absorption of water by CaO.

Figure 1. FTIR spectra of (a) CaO, (b) ZnFe$_2$O$_4$, (c) Al$_2$O$_3$, (d) CaO-ZnFe$_2$O$_4$, and (e) CaO-ZnFe$_2$O$_4$/Al$_2$O$_3$
functional groups. The peak at 2926 cm\(^{-1}\) shows C–H asymmetric stretching and around 1491 cm\(^{-1}\) appointed to the amide group confirmed the presence of the protein in yeast cells\(^{21}\) (Figure 1b). The FTIR spectra of nano-Al\(_2\)O\(_3\) show a peak around 529 cm\(^{-1}\) related to the stretching of an Al-O bending vibration, which is a typical peak for nano-alumina, and around 1384 cm\(^{-1}\) there is the bending vibration of the hydroxyl group\(^{33}\) (Figure 1c). Figure 1d shows the spectra of the CaO-ZnFe\(_2\)O\(_4\) composite which has combined absorption peaks from CaO and ZnFe\(_2\)O\(_4\), namely vibrations from Ca-O, Zn-O, and Fe-O. Furthermore, Figure 1e shows that the CaO-ZnFe\(_2\)O\(_4\)/Al\(_2\)O\(_3\) nanocomposite spectra and indicate combined peaks from nano-CaO, ZnFe\(_2\)O\(_4\), and nano-Al\(_2\)O\(_3\). However, the nanocomposite does not show a sharp peak, possibly due to the groups being embedded in the pores of the alumina support.

### 3.2.2 XRD Analysis

XRD patterns and crystalline structures of nano-CaO, ZnFe\(_2\)O\(_4\), nano-Al\(_2\)O\(_3\), CaO-ZnFe\(_2\)O\(_4\), and compared with CaO-ZnFe\(_2\)O\(_4\)/Al\(_2\)O\(_3\) nanocomposites as shown in Figure 2. The characteristic peak of nano-CaO at 2θ: 17.98°, 28.56°, 34.13°, 47.17°, 50.82°, 54.22°, 64.14°, respectively. These results are similar to previous research\(^{21}\). Figure 2c shows the typical peak of nano-Al\(_2\)O\(_3\) at 2θ: 37.15°, 45.86°, 66.61°, respectively. These results are similar to previous research\(^{19}\). Figure 1d shows the diffraction pattern of the CaO-ZnFe\(_2\)O\(_4\) composite which has combined peaks from CaO and ZnFe\(_2\)O\(_4\). Furthermore, Figure 1e shows the diffraction pattern of CaO-ZnFe\(_2\)O\(_4\)/Al\(_2\)O\(_3\) nanocomposite and indicates combined peaks from nano-CaO, ZnFe\(_2\)O\(_4\), and nano-Al\(_2\)O\(_3\). However, the nanocomposite does not show a sharp peak, possibly due to the groups being embedded in the pores of the alumina support, this is similar to the FTIR spectra. The average crystal size of CaO-ZnFe\(_2\)O\(_4\)/Al\(_2\)O\(_3\) calculated using the Debye Scherrer equation\(^{34}\) was obtained as 23.52 nm.

### 3.2.3 SEM Analysis

The surface morphology was investigated using SEM shown in Figure 3. The nano-CaO have irregular non-uniform and porous (Figure 3A), in accordance with previous research\(^{32,35}\). ZnFe\(_2\)O\(_4\) hollow structure has granular irregular non-uniform, these results are similar to previous studies\(^{21}\) (Figure 3B). The nano-Al\(_2\)O\(_3\) has irregular non-uniform and shows pores (Figure 3C). Meanwhile, the CaO-ZnFe\(_2\)O\(_4\) composite (Figure 3D)
3.2.4 BET Analysis

The N₂ sorption isotherms of CaO-ZnFe₂O₄ and CaO-ZnFe₂O₄/Al₂O₃ (Figure 6) show typical type IV isotherms indicating the presence of mesopores for pores with diameters in the range of 2–50 nm². Figure 6 displays the results of the BET surface area and pore volume for the CaO-ZnFe₂O₄ composite and CaO-ZnFe₂O₄/Al₂O₃ nanocomposite showing that CaO-ZnFe₂O₄/Al₂O₃ has a higher BET surface area (134.426 m² g⁻¹) and pore volume (0.204 cm³ g⁻¹) compared to CaO-ZnFe₂O₄ (15.314 m² g⁻¹) and a pore volume of 0.022 cm³ g⁻¹). These surface area results indicate that the addition of alumina as a support for the CaO-ZnFe₂O₄ composite succeeded in increasing the surface area after it was formed into a CaO-ZnFe₂O₄/Al₂O₃ nanocomposite.
3.2.5 TEM Analysis

The results of TEM characterization are shown in Figure 7. Figure 7A-B shows the surface morphology of CaO-ZnFe$_2$O$_4$/Al$_2$O$_3$ with scales of 500 nm and 100 nm, respectively. The CaO-ZnFe$_2$O$_4$/Al$_2$O$_3$ nanocomposite shows that its constituent particle components have bonded one each other. The CaO-ZnFe$_2$O$_4$ composite with a non-uniform shape (the dark colors) attached to the Al$_2$O$_3$ surface (the bright colors) was observed clearly in Figure 7B. Figure 7C presents a high-resolution TEM image of CaO-ZnFe$_2$O$_4$/Al$_2$O$_3$ on a scale of 10 nm.

3.3 Catalytic Activity of CaO-ZnFe$_2$O$_4$/Al$_2$O$_3$

The catalytic activity for the conversion of waste cooking oil into biodiesel was investigated for 2 h at a temperature of 65 °C using a quantity of waste cooking oil of 5 mL, with catalyst amount of 2%, and the volume ratio of waste cooking oil: methanol of 1:9.

3.3.1 Effect of Al$_2$O$_3$: CaO-ZnFe$_2$O$_4$ Mass Ratio on Biodiesel Yield

The structure of alumina as catalyst support has a high surface area desired site active CaO-ZnFe$_2$O$_4$ to evenly spread on the pore surface, resulting in enhanced catalytic activity. Therefore, we investigated the influence of the mass ratio of Al$_2$O$_3$ to CaO-ZnFe$_2$O$_4$ in CaO-ZnFe$_2$O$_4$/Al$_2$O$_3$ nanocomposites (Figure 8). The biodiesel yield obtained using a catalyst of Al$_2$O$_3$/CaO-ZnFe$_2$O$_4$ mass ratio 1:1; 1:2; and 1:3 is 80.43%, 93.41%, and 90.14%, respectively. This shows that at the 2:1 mass ratio, the entire surface of the Al$_2$O$_3$ pores is filled by the active site and is evenly distributed, resulting in efficient biodiesel production. Therefore, the Al$_2$O$_3$/ CaO-ZnFe$_2$O$_4$ with a mass ratio of 2:1 provides optimal conditions for this transesterification reaction.
3.3.2 Effect of Catalyst Type on Biodiesel Yield

Subsequently, we investigated the effect of catalyst type on the biodiesel yield as shown in Figure 9. The usage of the nano-Al2O3 support catalyst achieved a biodiesel yield of 36.86%, nano-CaO catalyst of 67.16%, ZnFe2O4 of 74.83%, CaO-ZnFe2O4 of 86.54% and CaO-ZnFe2O4/Al2O3 nanocomposite of 93.41%. The biodiesel yield uses the CaO-ZnFe2O4 catalyst increases compared to the nano-CaO and ZnFe2O4. This is due to CaO-ZnFe2O4 having both acidic and basic properties, which are the base site (CaO) and acid site (ZnFe2O4). The acid-base properties of the CaO-ZnFe2O4 hollow structure could accelerate the transesterification and esterification reaction. Hence, CaO-ZnFe2O4/Al2O3 catalyst has the highest biodiesel yield. These indicate that the supported catalyst of the Al2O3 in nanocomposite can increase biodiesel yield due to the Al2O3 having a high surface area compared to CaO.

Figure 7. TEM image of CaO-ZnFe2O4/Al2O3 (a) 500 nm and (b) 100 nm, HR TEM image of CaO-ZnFe2O4/Al2O3 (c) 10 nm

Figure 8. Effect of Al2O3 to CaO-ZnFe2O4 mass ratio on percent yield

Figure 9. Effect of type catalyst on percent yield
ZnFe₂O₄ (Figure 6) and acid-base properties of the CaO/ZnFe₂O₄ to the synergistic effect between CaO-ZnFe₂O₄ and Al₂O₃.

3.4 Physicochemical Properties of Biodiesel

The results of biodiesel with the best and optimal have been done to test some physicochemical properties to be a suitable substitute for fossil diesel. Some properties of biodiesel tested in this study are acid number, density, kinematic viscosity, flash point, and cetane number. Table 1 displays that these properties are close to the required international standards as specified by the American Society for Testing Materials (ASTM) 6751 reference standard.

<table>
<thead>
<tr>
<th>Physical Properties</th>
<th>Biodiesel product</th>
<th>ASTM 6751</th>
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<tbody>
<tr>
<td>Acid number (mg KOH/g)</td>
<td>0.530</td>
<td>&lt;0.80</td>
</tr>
<tr>
<td>Density (g/mL) at 25 °C</td>
<td>0.873</td>
<td>0.85–0.90</td>
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<tr>
<td>Kinematic viscosity (mm²/s) at 40 °C</td>
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<td>1.00–6.00</td>
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<tr>
<td>Flash point (°C)</td>
<td>125</td>
<td>100–170</td>
</tr>
<tr>
<td>Cetane number</td>
<td>49.00</td>
<td>&gt;47</td>
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4. CONCLUSIONS

In this study, hybrid CaO/ZnFe₂O₄ modified with Al₂O₃ as a green novel catalyst for biodiesel production from WCO with high catalytic activity. The catalyst properties were investigated by FTIR, XRD, SEM, EDX, SEM-mapping, BET, and TEM analyses. The catalytic activity increased with the combination of nanoparticles effect and support catalysts obtained biodiesel yield of nano-Al₂O₃, nano-CaO, ZnFe₂O₄, CaO-ZnFe₂O₄, and CaO-ZnFe₂O₄/Al₂O₃ is 36.86%, 67.16%, 74.83%, 86.54%, and 93.41%, respectively. The best biodiesel yield was 93.41% with a mass ratio of Al₂O₃ to CaO-ZnFe₂O₄ (2:1). The physicochemical properties (acid number, density, kinematic viscosity, flash point, and cetane number) of the produced biodiesel were within the ASTM limits, demonstrating a promising replacement with diesel.

Acknowledgments

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