Research article

Highly efficient synthesis of biodiesel catalyzed by a cellulose@hematite-zirconia nanocomposite

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ABSTRACT

The depletion of fossil fuels calls for the development of renewable alternatives such as biodiesel and has inspired much research on catalysts for the production of biodiesel through the esterification of biomass-derived materials. Herein, a green heterogeneous catalyst for highly efficient biodiesel synthesis was fabricated from rice straw-derived cellulose, hematite, and zirconia and was shown to contain porous irregularly shaped α-Fe₂O₃–ZrO₂ composites (average particle size ¼ 42.5 nm) evenly distributed on the nanocellulose surface. The optimal catalyst (nanocellulose:α-Fe₂O₃–ZrO₂ = 2:1, w/w) afforded biodiesel in a yield of 92.50% and with specifications close to those prescribed by international standards. This catalyst could be reused for up to five cycles without a marked activity loss, with the biodiesel yield in the fifth cycle equaling 80.0%. The developed nanocomposite holds great promise for cutting the costs of biodiesel production, as it is derived from biodegradable raw materials and is renewable, non-corrosive, easy to handle, and green. In addition, the large-scale discharge of this catalyst after use does not pose a hazard to the environment.

1. Introduction

Inexpensive modified lignocellulosic materials hold great promise for the development of biopolymer-based catalysts [1]. Biomass-derived biopolymers play an important role in the mitigation of fossil fuel depletion and global warming caused by the use of synthetic polymers [2, 3]. As a representative sustainable biopolymer, cellulose features high natural abundance, belonging to the green support group [3, 4], and can be isolated from rice straw (among other sources), which is an abundant, cheap, and green material that is generated in large quantities as a byproduct of rice production [5, 6] and has a high cellulose content [7, 8].

Rice straw is often disposed of by burning, however, causes serious environmental pollution when performed in the open air [9]. Therefore, the usage of rice straw as a source of cellulose allows one to reduce the environmental impact of rice straw, improve the overall economy [10], conserve natural resources, and mitigate the health problems associated with air pollution due to rice straw burning [11].

The β-1,4-glycosidic bonds of cellulose make it a durable support for the formation of catalytically active nanocomposites with inorganic substances [12]. Nanocomposites produced from nanopolymers and inorganic nanoparticles offer the advantages of natural abundance and biodegradability, often benefitting from the synergy between their components [13], as exemplified by the numerous synthetic applications of cellulose-based catalysts (e.g., Pd/cellulose nanocomposites [14], γ-Fe₂O₃/Cu@cellulose [15], magnetic nanocellulose [13], cellulose/ZrO₂ [16] and cellulose@Fe₂O₃ [17].

The depletion of crude oil resources has encouraged research on the production of renewable fuels such as biodiesel [18, 19] which can be obtained from renewable sources such as edible vegetable oils, inedible oils, and animal fats [20] through catalytic triglyceride transesterification and free fatty acid esterification and offers the advantages of renewability, reduction of greenhouse gas emissions, biodegradability, and non-toxicity [21, 22, 23, 24].

Indonesia has a great opportunity to convert agricultural biomass such as coconuts, corn, peanuts, cassava, and palm oil into renewable energy sources. In particular, coconut oil is well suited for biodiesel production, as it is rich in fatty acids, cheap, and readily available in Indonesia [25].

Several catalysts with nanocellulose as a support and inorganic compounds as active ingredients have been synthesized for biodiesel production [26, 27]. Nonetheless, very few studies have evaluated the effect of nanocellulose supports on the catalytic activities of nanohematite and...
nano-zirconia. To bridge this gap, the present study probes the effect of nanocellulose loading on the performance of cellulose@α-Fe2O3–ZrO2 nanocomposites for biodiesel production from lauric acid.

2. Materials and methods

2.1. Materials

Rice straw was sourced from Central Java, Indonesia. FeCl2·4H2O and FeCl3·6H2O as nanο-α-Fe2O3 precursors, ZrOCl2·8H2O as a nano-ZrO2 precursor, and H2SO4 used for nanocellulose synthesis were procured from Merck, and lauric acid was isolated from locally produced coconut oil.

2.2. Synthesis of nanocellulose from rice straw

Cellulose was isolated from rice straw as described in our previous study [28] and converted into nanocellulose by 2 h ultrasonication-assisted hydrolysis in 65 wt.% H2SO4 at 45 °C [29]. The obtained nanocellulose precipitate was washed with water to neutral pH, centrifuged for 15 min, dried, and characterized by Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET), and scanning electron microscopy (SEM).

2.3. Synthesis of nano-α-Fe2O3

Nano-α-Fe2O3 was prepared using a slight modification of a previously reported method [30]. FeCl2·4H2O and FeCl3·6H2O were separately dissolved in distilled water to concentrations of 2 M and 1 M, respectively, and the respective solutions were mixed in a 2:3 (v/v) ratio. The mixture was slowly supplemented with 2 M NaOH to reach a pH of 10 and vigorously stirred for 2 h. The brown precipitate was separated, rinsed with distilled water and ethanol, dried at 60 °C overnight, and calcined at 600 °C for 1 h.

2.4. Synthesis of nano-ZrO2

Nano-ZrO2 was prepared using a slight modification of a previously reported method [31]. A 1 M solution of ZrOCl2·8H2O was slowly treated with 2 M NaOH to reach a pH of 10, and the mixture was stirred for 15 min. The white precipitate was separated, sequentially rinsed with water and acetone, dried at 60 °C, and calcined at 700 °C for 1 h.

2.5. Synthesis of cellulose@α-Fe2O3–ZrO2 nanocomposites

The first stage, α-Fe2O3–ZrO2 composites were prepared as described elsewhere [32]. Briefly, α-Fe2O3 was added to a solution containing H2O, ethanol, and ammonia, and the mixture was ultrasonicated to form a homogeneous suspension. The resulting dispersion was slowly supplemented with ZrOCl2·8H2O and stirred for 6 h. The precipitate was separated, sequentially rinsed with ethanol and water, and oven-dried at 60 °C for 12 h to afford α-Fe2O3–ZrO2. In the second stage, cellulose@α-Fe2O3–ZrO2 nanocomposites were prepared using a slight modification of a previously reported method [33]. Briefly, nanocellulose was homogenously dispersed in an aqueous solution of NaOH and urea at −4 °C, the solution was supplemented with a dispersion of α-Fe2O3–ZrO2 in aqueous NaOH, and the resulting mixture was stirred for 6 h. The product was separated, sequentially rinsed with ethanol and water, and dried. The resulting cellulose@α-Fe2O3–ZrO2 nanocomposites were characterized by FTIR, XRD, BET, SEM, and transmission electron microscopy (TEM).

2.6. Catalytic activity assessment

Catalytic activity was evaluated in terms of the ability to promote the esterification of lauric acid, the major fatty acid (52.68%) of coconut oil [34], with methanol, as described in previous studies [35, 36, 37]. Herein, we varied the nanocellulose:α-Fe2O3–ZrO2 mass ratio (0.5:1, 1:1, 2:1, 3:1) and catalyst type (nano-α-Fe2O3, nano-ZrO2, α-Fe2O3–ZrO2, and cellulose@α-Fe2O3–ZrO2). Biodiesel yield was calculated as Eq. (1) [36]:

\[
\text{Biodiesel yield (\%) = } \frac{\text{Weight of biodiesel}}{\text{Weight of lauric acid}} \times 100\% \tag{1}
\]

2.7. Determination of biodiesel properties

Biodiesel parameters, such as acid number (AN), cetane number (CN), American petroleum institute (API), higher heating value (HHV) were calculated as Eqs. (2), (3), (4), and (5) [38, 39]:

\[
\text{AN} = \frac{V_{\text{KOH}} \times N_{\text{KOH}} \times 56.1}{W} \tag{2}
\]

\[
\text{CN} = 46.3 + \frac{5458}{\text{SN}} - 0.225 \times \text{IN} \tag{3}
\]

\[
\text{API} = \frac{141.5}{\text{Specific gravity}} - 131.5 \tag{4}
\]

\[
\text{HHV (MJ/kg)} = 49.43 - 0.041(\text{SN}) - 0.015(\text{IN}) \tag{5}
\]

The saponification number (SN) and the iodine number (IN) were calculated as Eqs. (6) and (7) [40]:

\[
\text{SN} = \frac{V_{\text{KCl}} \times N_{\text{KCl}} \times 56.1}{W} \tag{6}
\]

\[
\text{IN} = \left( \frac{V_{\text{NaI} \cdot \text{KCl}} \text{blank} - V_{\text{NaI} \cdot \text{KCl}} \text{sample}}{N_{\text{NaI} \cdot \text{KCl}}} \right) \times 12.69 \frac{W}{\text{sample}} \tag{7}
\]

2.8. Reusability of catalysts

The reusability of cellulose@α-Fe2O3–ZrO2 nanocomposites were observed using a slight modification of a previously reported method [41]. The catalyst was separated and washed several times with hot ethanol and then hexane to remove the residual of lauric acid and product which adsorbed on the catalyst surface, and then dried in an oven at 100 °C for 12 h. To observe the leaching of the catalyst species into the reaction medium causes contamination of the final product and so lead to a decrease in catalyst activity [42]. We tested the nano-composite weight of reused catalysts after each cycle were measured by gravimetry to confirm the quantity of catalyst leached and to confirm the catalytic system behave a heterogeneous.

3. Results and discussion

3.1. Formation of cellulose@α-Fe2O3–ZrO2 nanocomposites

Rice straw cellulose was activated by hydrolysis under strongly acidic conditions to increase the active group content, surface area, and catalytic efficiency. This hydrolysis resulted in the cleavage of glycoside bonds to form nanocellulose sulfonates, which, in turn, were hybridized with α-Fe2O3–ZrO2 to form cellulose@α-Fe2O3–ZrO2 nanocomposites (Figure 1).

3.2. Characterization

3.2.1. FTIR analysis

Figure 2 shows the results of FTIR analysis. The spectrum of nanocellulose (Figure 2a) featured an O–H stretch at 3250–3500 cm⁻¹, a C–H stretch at 2940 cm⁻¹, and absorption bands of β-glycoside bonds at 1678, 1055, and 930 cm⁻¹ characteristic of cellulose [13]. The bands at 1140
and 1310 cm\(^{-1}\) were assigned to the symmetric vibration of SO\(_3\), the symmetric vibration of the O–S=O unit in the SO\(_3\)H group, and the asymmetric vibration of SO\(_2\), respectively, and indicated the successful formation of nanocellulose sulfonates. The spectra of \(\alpha\)-Fe\(_2\)O\(_3\) (Figure 2b) and ZrO\(_2\) (Figure 2c) featured peaks at 543 cm\(^{-1}\) (Fe–O) [43, 44] and 540 cm\(^{-1}\) (Zr–O) [45], respectively. The spectrum of cellulose@\(\alpha\)-Fe\(_2\)O\(_3\)–ZrO\(_2\) (Figure 2d) featured a band at 530 cm\(^{-1}\) that corresponded to the overlap of Fe–O and Zr–O peaks. The observation of this band, together with the sloping nature and position shift of the typical peaks of \(\beta\)-glycosidic bonds, SO\(_3\) bonds, and O–H bonds indicated the successful hybridization of nanocellulose with \(\alpha\)-Fe\(_2\)O\(_3\)–ZrO\(_2\).

3.2.2. XRD analysis

The XRD pattern of nanocellulose (Figure 3a) featured peaks at 2\(\theta\) = 16°, 22° (most intense), and 35°, corresponding to reflections from the (101), (002), and (040) planes [46], respectively. These data were in line with the results of our previous studies [13, 27, 43]. The diffraction pattern of \(\alpha\)-Fe\(_2\)O\(_3\) (Figure 3b) featured peaks at 2\(\theta\) = 25.3°, 33.5°, 40.3°, 50.2°, 55.2°, 57.8°, 63.5°, 65.2°, and corresponding to the (012), (104), (110), (113), (024), (116), (122), (214), and (300) planes of Fe\(_2\)O\(_3\), respectively. The strongest peaks were assigned to the (104) and (110) planes, in line with the results of our previous study [44, 47]. The diffraction pattern of nano-ZrO\(_2\) (Figure 3c) featured peaks of the monoclinic (2\(\theta\) = 24.5°, 28.0°, 31.0°, and 34.0°) and tetragonal (2\(\theta\) = 35.0°, 50.0°, and 60.0°) forms [45]. The pattern of cellulose@\(\alpha\)-Fe\(_2\)O\(_3\)–ZrO\(_2\) (Figure 3d) showed the peaks of the above three constituents, and the shift of \(\alpha\)-Fe\(_2\)O\(_3\) and ZrO\(_2\) peaks indicated that these oxides were bonded to nanocellulose, in line with the results of FTIR analysis. The average crystallite size was calculated using Debye-Scherrer equation [24] was obtained as 40.5 nm.

3.2.3. BET

The N\(_2\) sorption isotherms of nanocellulose and after loading hematite and zirconia as cellulose@\(\alpha\)-Fe\(_2\)O\(_3\)–ZrO\(_2\) (Figure 4) displayed a typical type IV isotherm denoting the existence of mesopores for pores with diameters in the range 2–50 nm [48]. Figure 4 featured the resulted
from the BET surface area and pore volume for nanocellulose and nanocomposite reveal cellulose@α-Fe₂O₃–ZrO₂ a higher BET surface area (852 m²g⁻¹) and pore volume (0.85 cm³g⁻¹) than nanocellulose (720 m²g⁻¹, 0.52 cm³g⁻¹). The pore size of nanocellulose and cellulose@α-Fe₂O₃–ZrO₂ were 24 and 13 nm, respectively, and indicated that composite of α-Fe₂O₃–ZrO₂ had embedded on the pore surface of nanocellulose.

3.2.4. SEM
Surface morphology was probed by SEM. Nanocellulose comprised fibers with a smooth, uniform, and homogeneous surface (Figure 5a), which agreed with the results of previous study [35]. α-Fe₂O₃ comprised hexagonal particles (Figure 5b), whereas ZrO₂ (Figure 5c) featured particles of diverse shapes (e.g., spherical, elliptical, and angular), which suggested the monoclinic structure of the latter oxide, in line with XRD data. Cellulose@α-Fe₂O₃–ZrO₂ particles had an uneven surface (Figure 5d), and the distribution of α-Fe₂O₃–ZrO₂ on the nanocellulose surface was observed by elemental mapping (Figure 6).

Figure 6a–d show that the constituent elements were evenly distributed on the cellulose@α-Fe₂O₃–ZrO₂ surface, and α-Fe₂O₃–ZrO₂ was also evenly distributed on the nanocellulose surface, which confirmed the successful synthesis of the nanocellulose-supported catalyst.

3.2.5. TEM
Nanocomposite structure was probed by TEM. Low-resolution TEM imaging (Figure 7a) revealed that the catalyst particles had an irregular shape, with dark hexagonal and spherical particles corresponding to the α-Fe₂O₃–ZrO₂ composite (red circle). The average size of α-Fe₂O₃–ZrO₂ particles was determined as 42.5 nm and cylindrical particles corresponding to nanocellulose fiber (blue circle). Figure 7b–d present high-resolution TEM images of the porous cellulose@α-Fe₂O₃–ZrO₂ nanocomposite.

3.3. Catalytic activity of cellulose@α-Fe₂O₃–ZrO₂
Catalytic activity for the conversion of lauric acid into biodiesel was probed for 3 h at 60 °C using a lauric acid amount of 10 g, a methanol:lauric acid molar ratio of 12:1, and a catalyst loading of 2 wt.%.

3.3.1. Effect of nanocellulose: α-Fe₂O₃–ZrO₂ mass ratio on biodiesel yield
The fibrous and porous structure of nanocellulose allowed α-Fe₂O₃–ZrO₂ to be embedded and evenly spread on the pore surface,
which resulted in enhanced catalytic activity. Herein, we investigated the effect of the nanocellulose: $\alpha$-Fe$_2$O$_3$–ZrO$_2$ mass ratio ($r$) on (i) biodiesel yield after 3 h, (ii) the highest attainable biodiesel yield, and (iii) the time needed to obtain this maximal yield (Figure 8). At a fixed reaction time of 3 h with the bar chart in grey color, the yield increased with increasing $r$, equaling 35.00, 70.50, 92.50, and 92.50% at $r = 0.5:1$, 1:1, 2:1, and 3:1, respectively. This shows that at $r = 2:1$, all nanocellulose pores were filled with $\alpha$-Fe$_2$O$_3$ and ZrO$_2$ nanoparticles as active sites, which resulted in efficient biodiesel production. To observe the mass ratio effect to the reaction rate by extending the time indicated by a black bar chart and red line is the reaction time so that the perfect reaction is achieved. When the reaction time was extended, the maximal yields for $r = 0.5:1$, 1:1, 2:1, and 3:1, equaling 90.00, 90.50, 92.50 and 92.50%, respectively. Therefore, the catalyst with $r = 2:1$ was concluded to be optimal condition for this esterification reaction.

### 3.3.2. Effect of catalyst type on biodiesel yield

Next, we probed the effect of catalyst type on (i) biodiesel yield after 3 h, (ii) the highest attainable biodiesel yield, and (iii) the time needed to obtain this maximal yield (Figure 9). At a fixed time of 3 h with the bar chart in dark blue color, $\alpha$-Fe$_2$O$_3$, ZrO$_2$, $\alpha$-Fe$_2$O$_3$–ZrO$_2$, and cellulose@$\alpha$-Fe$_2$O$_3$–ZrO$_2$ ($r = 2:1$) achieved yields of 30.00, 51.50, 86.80, and 92.50%, respectively. The fact that pure ZrO$_2$ achieved a greater yield than $\alpha$-Fe$_2$O$_3$ means that the former oxide provided more important active sites than $\alpha$-Fe$_2$O$_3$. The fact that the highest yield was observed for cellulose@$\alpha$-Fe$_2$O$_3$–ZrO$_2$ was ascribed to the synergetic effects arising upon the hybridization of the biopolymer with inorganic nanoparticles [13]. Furthermore, we also observed the effect of catalyst type to the reaction rate by extending the time indicated by light green the bar chart and red line is the reaction time so that the perfect reaction is achieved.

When the reaction time was extended, $\alpha$-Fe$_2$O$_3$, ZrO$_2$, $\alpha$-Fe$_2$O$_3$–ZrO$_2$, and
Figure 7. TEM image [(a) 50 nm, (b) 10 nm, (c) 10 nm and (d) 5 nm scale] of cellulose@α-Fe₂O₃–ZrO₂.

Figure 8. Effect of nanocellulose to α-Fe₂O₃–ZrO₂ mass ratio on percent yield and reaction time.
cellulose@α-Fe2O3–ZrO2 achieved maximal yields of 92.50% after 7, 5, 4, and 3 h, respectively. Therefore, the cellulose@α-Fe2O3–ZrO2 nanocomposite is the best suited for the studied esterification reaction, owing to the existence of both acidic and basic sites, besides the presence of pores and large BET surface area (Figure 4) to accommodate the reactants and activate the reaction. Briefly, our explanation for the catalytic activity of the cellulose@α-Fe2O3–ZrO2 catalyst in the reaction by eliminating protons from methanols which attacked the carboxylic group of acids to form an activated complex which is adsorbed on the surface of the catalyst and a reaction occurs then the desorption process forms methyl esters product (Figure 10).

3.4. Physicochemical properties of biodiesel

To be a suitable substitute of fossil diesel, biodiesel should comply with the international standards set by the American Society for Testing Materials (ASTM). Table 1 lists the selected properties of biodiesel obtained using cellulose@α-Fe2O3–ZrO2 as a catalyst. The biodiesel was a slightly yellowish liquid with properties either compliant (water content, flash point, density, kinematic viscosity, acid number, cetane number, and American petroleum institute) very close to the required values ASTM standards. The higher heating value of the produced biodiesel was comparable to that reported in previous studies [49].

| Parameters                        | Biodiesel product | ASTM 6751 |
|-----------------------------------|-------------------|-----------|
| Water content (mg kg⁻¹)           | 0.031             | <0.05     |
| Flash point (°C)                  | 135               | >93       |
| Density (g cm⁻³) at 25 °C         | 0.853             | 0.85–0.90 |
| Kinematic viscosity (mm² s⁻¹) at 40 °C | 4.20           | 1.00–6.00 |
| Acid number (mgKOH g⁻¹)           | 0.15              | <0.50     |
| Cetane number                      | 65.00             | >47       |
| American petroleum institute      | 34.48             | 36.95     |
| Higher heating value (MJ kg⁻¹)     | 40.10             | Not specified |

Figure 9. Effect of type catalyst on percent yield and reaction time.

Figure 10. Proposed reaction mechanism for the esterification of lauric acid over the cellulose@α-Fe2O3–ZrO2 catalyst.

3.5. Reusability of the cellulose@α-Fe2O3–ZrO2 nanocomposite

When cellulose@α-Fe2O3–ZrO2 was sequentially used five times for biodiesel production, the yield did not significantly change, decreasing from 92.50 of first cycle to 80.0% of fifth cycle (Figure 11). Decreasing of the product may be caused by deactivation of catalysts by product species adsorption and the unreacted lauric acid onto the surface of catalysts that could block the active sites [50].

The leaching of species into the reaction medium causes contamination of the product and also leads to a decrease in catalyst activity. Thus, we tested the catalytic heterogeneity of the reaction by gravimetry. The results of these studies showed that the weight of catalyst reused after five cycles is obtained constant (initial weight of 0.2 g for the first cycle until after the fifth cycle remains 0.2 g). These results demonstrated that the catalytic system behave a heterogeneous.

The results of this study suggest that the strategy of using nanocellulose in combination with α-Fe2O3ZrO2 composites for highly efficient biodiesel production can be recoverable and reusable in biodiesel synthesis from free fatty acids sourced from coconut oil which is easily available and renewable.
4. Conclusions

Herein, we report a nanocomposite derived from rice straw cellulose embedded hematite, and zirconia as a heterogeneous green catalyst for the highly efficient synthesis of biodiesel through the esterification of lauric acid with methanol. This catalyst was shown to comprise porous and irregularly shaped α-Fe₂O₃–ZrO₂ particles evenly distributed in the nanocellulose support. The presence of nanocellulose was important role for improving high catalytic activity for biodiesel production. The optimal cellulose@α-Fe₂O₃–ZrO₂ nanocomposite (nanocellulose:α-Fe₂O₃–ZrO₂ mass ratio = 2:1) achieved a biodiesel yield of 92.50%, and the properties of the obtained biodiesel were close to those stipulated by international standards. Moreover, the developed catalyst could be reused for five times without any significant activity loss.

Declarations

Author contribution statement

Helmiyati Helmiyati: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Yuni Budiman: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Gusma Harfiana Abbas: Contributed reagents, materials, analysis tools or data.

Fitriyah Wulan Dini: Performed the experiments; Analyzed and interpreted the data.

Munawar Khalil: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.

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Data availability statement

Data included in article/supplementary material/referenced in article.

Declaration of interests statement

The authors declare no conflict of interest.
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