Synthesis of nanocomposites cellulose-Fe₃O₄/ZnO as novel green catalyst for biodiesel production from coconut oil

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Abstract. Cellulose-Fe₃O₄/ZnO nanocomposites have been successfully synthesized. This process was supported by characterization using Fourier Transform InfraRed (FTIR), X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and Scanning Electron Microscopy-Mapping (SEM-Mapping) instruments. The successfully synthesized nanocomposites then were tested for a catalytic activity in the transesterification reaction to form biodiesel. The results of the biodiesel production were characterized using Gas Chromatography-Mass Spectroscopy (GC-MS). The highest conversion of coconut oil into biodiesel was 90.6%, with a catalyst amount of 0.6% wt and a 120 minutes reaction time. The biodiesel production using GC-MS shows that the most formed methyl esters are dodecanoic acid methyl esters (lauric acid methyl esters). The use of cellulose as a catalyst support by combining Fe₃O₄/ZnO composites is very promising to be a green catalyst in the reaction of biodiesel production.

1. Introduction

Recently, environmental pollution and global warming have been increasing along with the uplift in the use of fossil resources, so it is crucial to develop alternative energy sources that are clean and renewable [1, 2]. The total energy consumption worldwide has increased significantly due to overpopulated population, which cause huge impacts to the environment throughout the world. According to the projection of international energy use in 2016, the total of world energy consumption increased by 48% from 2012 to 2040. This results in the demand for fossil fuels facing two main challenges namely the scarcity of resources and their negative impacts on the environment [3]. Biodiesel is known as one of the most promising alternative fuels that is renewable, non-toxic and biodegradable, and a suitable fuel to replace diesel derived from petroleum. Biodiesel can be obtained from several renewable sources, such as vegetable oils and animal fats [4]. Biodiesel is also known as fatty acid methyl ester (FAME) which can be obtained by a transesterification reaction. It is a chemical reaction between triglycerides and alcohol in the presence of a catalyst to produce methyl esters (biodiesel) and glycerol [5, 6].

Vegetable oil is a potential candidate as a substitute source for fossil fuels. It is a natural oil containing a mixture of triacylglycerol, with several advantages, renewable, non-toxic, and a biodegradable source [7]. Coconut oil is one of the vegetable oils which is a raw material of compounds. It consists of various types of triglyceride fatty acids and around 90% of it is a saturated fatty acid compound, especially lauric acid and myristic acid [8].

In order to accelerate the process of biodiesel production, it is necessary to add both homogeneous and heterogeneous catalysts [9]. Heterogeneous catalysts are mostly used as an alternative of homogeneous catalysts in the chemical reactions. This is because the use of heterogeneous catalysts can
minimize the impact of environmental damages, easy to separate from the reaction mixture, regenerable, and reusable [10, 11]. A lot of studies have been conducted using inorganic substances as catalysts such as Fe$_3$O$_4$, CaO, ZnO, Al$_2$O$_3$, and MgO. However, the use of inorganic catalysts is not modified and it may cause low thermal stability and release in water [12].

ZnO (metal oxide) is an inorganic catalyst that is commonly used and widely applied as a heterogeneous catalyst, because of its low cost, good stability, non-toxic and environmentally friendly properties [13]. By combining ZnO nanoparticles with other metal oxides, it can produce nanoparticles with a high surface area, a good dispersion, and smaller crystal sizes [14]. Besides that, the disadvantage of ZnO is it tends to form an agglomeration that has reduced its surface catalytic activity. In order to overcome this problem, a modification was carried out by magnetizing the ZnO nanoparticle catalyst with magnetite nanoparticles [15]. Combining ZnO with Fe$_3$O$_4$ can increase the overall catalytic activities compared to using only pure ZnO, because the addition of Fe$_3$O$_4$ can improve the stability, the catalyst surface area and is also easily separated using external magnets [16]. Iron (II) nanocatalysts which are doped with ZnO nano particles have been successfully synthesized as a promising catalyst for biodiesel production with 91% conversion [17]. CaO-Fe$_3$O$_4$ nanocatalysts have also been successfully synthesized for the transesterification reaction of palm kernel oil into methyl ester with a 69.7% conversion value [18].

It is interesting to develop metal oxides nano composites supported by biopolymers to be heterogeneous catalysts. This is because biopolymer-based nanocomposites have a synergistic effect with inorganic materials to produce a good catalytic activity. The advantage of biopolymers is that they are abundant in nature, inexpensive, environmentally friendly, and biocompatible [19]. One of biopolymers like cellulose is an attractive compound for a catalyst support. Cellulose-Fe$_3$O$_4$ nanocomposite has been successfully synthesized which was applied as a heterogeneous catalyst for the synthesis of biodiesel using oleic acid with a conversion of 89.21% and a 5 hours reaction time [12] ZnO/SiO$_2$ nanocomposites with cellulose support derived from rice husk have been successfully synthesized and used as a biodiesel catalyst from coconut oil with 95% conversion during 270 minutes [20].

In this research, a new group of catalysts from a combination of ZnO, Fe$_3$O$_4$, and cellulose as the support is used as a catalyst for biodiesel synthesis through a transesterification process of coconut oil. The effect of the catalyst amount and the reaction time during the transesterification process on coconut oil are investigated.

2. Experimental

2.1. Materials
Pure cellulose powder (Merck) is used as a catalyst support, FeCl$_3$-6H$_2$O (Merck), FeCl$_2$-4H$_2$O (Merck) for the synthesis of nano Fe$_3$O$_4$, Zn(CH$_3$COO)$_2$ (Merck) as a precursor of ZnO nano, NaOH (Merck) as a pH regulator, also methanol (Merck) and coconut oil (local brand) for biodiesel production.

2.2. Synthesis of Fe$_3$O$_4$ nanoparticles
Nanomagnetite synthesis (Fe$_3$O$_4$) refers to a research conducted [15] through modifications. Mixed the FeCl$_2$-4H$_2$O solution with FeCl$_3$-6H$_2$O in a stoichiometric ratio of Fe$^{2+}$:Fe$^{3+}$ (1:2), stirred for 45 minutes at 80°C. Then, added it to 1M NaOH solution around pH ≤ 11, maintained the solution at 80°C for 1.5 hours until a black precipitate was obtained. The precipitate obtained then was rinsed with distilled water and ethanol, dried it in an oven at 103°C. The Fe$_3$O$_4$ nanoparticles obtained were characterized using FTIR, and XRD.

2.3. Synthesis of cellulose - Fe$_3$O$_4$/ZnO nanocomposites
Synthesis of cellulose-Fe$_3$O$_4$/ZnO nanocomposites was divided into two steps. The first step was the synthesis of Fe$_3$O$_4$/ZnO composites which refers to [21] through a modification by firstly combining ZnO and Fe$_3$O$_4$ nanoparticles. Fe$_3$O$_4$ nanoparticles were dispersed in 150 mL of distilled water and sonicated for 30 minutes, then added zinc acetate and stirred for 30 minutes, pH of the solution was
adjusted to 9 using 5M NaOH addition, and stired it for 30 minutes, then refluxed at 100°C for 1 hour. The obtained \( \text{Fe}_3\text{O}_4/\text{ZnO} \) composites were washed with distilled water and ethanol, dried it in an oven at 60°C for 24 hours, and characterized using FTIR, and XRD.

The second stage was that synthesis of cellulose-\( \text{Fe}_3\text{O}_4/\text{ZnO} \) nanocomposites, refers to [22]. The \( \text{Fe}_3\text{O}_4/\text{ZnO} \) composite was dispersed in 10 ml of 0.25 M NaOH and stirred for 1 hour at a room temperature. Then, the cellulose dispersion in distilled water was added slowly into \( \text{Fe}_3\text{O}_4/\text{ZnO} \) dispersion and stirred for 6 hours at a room temperature. Then the precipitate was filtered, rinsed, and dried in an oven at 60°C for one night. Cellulose-\( \text{Fe}_3\text{O}_4/\text{ZnO} \) nanocomposites were characterized using FTIR, XRD, and SEM.

2.4. Application of cellulose-\( \text{Fe}_3\text{O}_4/\text{ZnO} \) nanocomposites as a catalyst in biodiesel production

The catalytic activity of cellulose-\( \text{Fe}_3\text{O}_4/\text{ZnO} \) nanocomposites was evaluated for the transesterification reaction of coconut oil with methanol based on the research of [8, 12]. The reaction was conducted with various amount of catalyst (0.45%; 0.60%; 0.75% wt) and reaction times (60 minutes, 120 minutes, 180 minutes). The reaction experiment was conducted in a 500ml round neck flask containing coconut oil, methanol and cellulose-\( \text{Fe}_3\text{O}_4/\text{ZnO} \) nanocomposites as a catalyst. After that, the calculation of conversion percentage was done using equation (1) [23].

\[
\text{Conversion (\%)} = \frac{\text{weight of biodiesel that obtained}}{\text{weight of oil that used in reaction}} \times 100\%
\]

3. Result and discussion

3.1. Cellulose-\( \text{Fe}_3\text{O}_4/\text{ZnO} \) nanocomposites

Synthesis of cellulose-\( \text{Fe}_3\text{O}_4/\text{ZnO} \) in which cellulose acts as a catalyst support of \( \text{Fe}_3\text{O}_4/\text{ZnO} \) composites by combining \( \text{Fe}_3\text{O}_4/\text{ZnO} \) with cellulose biopolymer, it is hoped that \( \text{Fe}_3\text{O}_4/\text{ZnO} \) composites will be dispersed evenly on the surface of cellulose biopolymer. The illustration of cellulose-\( \text{Fe}_3\text{O}_4/\text{ZnO} \) structure is shown in figure 1.

![Figure 1. Illustration of cellulose-\( \text{Fe}_3\text{O}_4/\text{ZnO} \) nanocomposites structure.](image)

3.2. Characterization of cellulose-\( \text{Fe}_3\text{O}_4/\text{ZnO} \) nanocomposites

The characterization using FTIR was carried out in an absorption area of 4000-400 cm\(^{-1}\) to determine the functional group of synthesized-\( \text{Fe}_3\text{O}_4/\text{ZnO} \). FTIR spectra from the result of cellulose-\( \text{Fe}_3\text{O}_4/\text{ZnO} \) synthesis can be seen in figure 2. Figure 2a shows \( \text{Fe}_3\text{O}_4 \) with a typical peak absorption at 577.83 cm\(^{-1}\) which indicates the presence of Fe-O functional group. Figure 2b shows that ZnO with a typical peak absorption at 432.24 cm\(^{-1}\) indicating the presence of Zn-O functional group. Figure 2c shows the FT-IR spectra of cellulose. A typical absorption at 800 cm\(^{-1}\) can be seen which is a typical absorption of the 1.4 β glycosidic bond. Figure 2d shows the cellulose-\( \text{Fe}_3\text{O}_4/\text{ZnO} \) nanocomposite spectra. It can be seen that the absorption peaks appear from the constituent compounds and there is a shift from each of the absorption peaks. It can be seen also, a typical peak arises from cellulose which is indicated by a 1.4 β glycosidic bond, a typical peak of \( \text{Fe}_3\text{O}_4 \) that indicates the presence of a Fe-O functional group, and a typical peak of ZnO that indicates the presence of a Zn-O functional group.
Figure 2. FTIR spectra synthesis result of: (a) Fe$_3$O$_4$, (b) ZnO, (c) cellulose, and (d) cellulose-Fe$_3$O$_4$/ZnO.

The characterization of Fe$_3$O$_4$/ZnO using XRD can be seen on the XRD diffractogram shown in figure 3. Figure 3a is a diffraction pattern of Fe$_3$O$_4$. The peaks can be observed at 2θ: 21.29°; 35.65°; 43.33°; 53.53°; and 63.04 which shows the typical peak of Fe$_3$O$_4$, this peak is in accordance with JCPDS No. 75-0033 [24]. Figure 3b is a diffraction pattern of ZnO nanoparticles, where peaks can be seen at 2θ: 31.92°; 34.56°; 36.39°; 47.68°; 56.75°; 62.97°; 66.53°; 68.09°; 69.24°, this peak is in accordance with JCPDS No. 36-1451 [25] which shows the typical peak of ZnO. Figure 3c is a diffraction pattern of composite Fe$_3$O$_4$/ZnO. The peaks can be seen at 2θ: 31.72°; 34.46°; 36.21°; 47.65°; 55.83°; 62.91°; 66.49°; 67.85°; and 69.19° which show the presence of ZnO compared to Figure 3b where there is a shift at peak 2θ. The presence of Fe$_3$O$_4$ peaks in Fe$_3$O$_4$/ZnO composites can be seen from 2θ: 36.21; 55.83°; and 62.91°, compared to Figure 3a where there is a shift at peak 20. This showed the successful synthesis of Fe$_3$O$_4$/ZnO.

The characterization of Cellulose-Fe$_3$O$_4$/ZnO using XRD can be seen on the XRD diffractogram shown in figure 4. Figure 4a, is a Fe$_3$O$_4$/ZnO composite diffractogram. Figure 4b shows the diffraction pattern of peak 2θ pure cellulose: 15.09°; 22.64°; and 34.71°, which is a typical characteristic of cellulose. Figure 4c shows the diffraction pattern of cellulose-Fe$_3$O$_4$/ZnO nanocomposites, from Figure 4c if it is compared with Figure 4a and Figure 4b it can be seen that the peaks of each cellulose and Fe$_3$O$_4$/ZnO remain exist and a shift in diffraction patterns occurs in the cellulose-Fe$_3$O$_4$/ZnO nanocomposite. This supports that cellulose-Fe$_3$O$_4$/ZnO nanocomposite had been successfully synthesized.
Figure 3. Diffractogram of: (a) Fe₃O₄, (b) ZnO, and (c) Fe₃O₄/ZnO.

Figure 4. Diffractogram of: (a) Fe₃O₄/ZnO, (b) Cellulose, and (c) Cellulose-Fe₃O₄/ZnO.

The characterization using SEM was used to analyze the morphology surface of synthesized-cellulose-Fe₃O₄/ZnO nanocomposites. The results of cellulose-Fe₃O₄/ZnO nanocomposite characterization using SEM can be seen in figure 5. Figure 5a shows the SEM result of cellulose-Fe₃O₄/ZnO nanocomposite with 3000 times magnification. There were white fine and even granules which were Fe₃O₄/ZnO composites on the surface of cellulose in the form of fiber. Figure 5b is the SEM result of cellulose-Fe₃O₄/ZnO nanocomposite with 6000 times magnification. It was clearly visible that there was an even distribution of Fe₃O₄/ZnO composites on the surface of cellulose which was a catalyst support. The morphology of cellulose-Fe₃O₄/ZnO nanocomposites supported by SEM-Mapping can be seen in figure 6. SEM-Mapping was carried out aiming to determine the distribution of the elements in cellulose-Fe₃O₄/ZnO nanocomposites.

Figure 5. SEM results of cellulose-Fe₃O₄/ZnO with magnification: (a) 3000x and (b) 6000x.
Figure 6. Morphology of cellulose-Fe$_3$O$_4$/ZnO nanocomposites with: (a) 1000x magnification, (b) distribution of whole elements, (c) element Zn, (d) element Fe, (e) element O, and (f) element C on nanocomposites.

In figure 6a can be seen that on the surface of the cellulose, in the form of smooth fibers and on its surface, there are small white granules that were evenly distributed as Fe$_3$O$_4$/ZnO composites. Figure 6b shows the overall distribution of nanocomposite elements. It was clearly seen the distribution of each element and on the surface there exists elements of Fe and Zn. Figure 6c shows the color distribution of Zn elements in blue and it can be explained that the presence of Zn elements comes from dispersed ZnO on the surface of cellulose evenly. In addition, the distribution of Fe elements derived from Fe$_3$O$_4$ is also seen scattered on the surface of cellulose which can be seen in figure 6d in a color of purple. Figure 6e shows the distribution of O elements in red which is distributed quite a lot and evenly, because the amount of O elements comes from cellulose and Fe$_3$O$_4$/ZnO composites. Figure 6f is the distribution of
element C in a uniformly distributed green color derived from cellulose. The results of SEM-Mapping analysis supported the success of cellulose-\(\text{Fe}_3\text{O}_4/\text{ZnO}\) nanocomposite synthesis and it can be observed that cellulose had successfully become a support for \(\text{Fe}_3\text{O}_4/\text{ZnO}\), this result was strengthened by the results of FTIR and XRD characterizations.

3.3. \textit{Cellulose-Fe}_3\textit{O}_4/\textit{ZnO} nanocomposite activity as a catalyst in biodiesel production

Cellulose-\(\text{Fe}_3\text{O}_4/\text{ZnO}\) nanocomposites that have been successfully synthesized are used as heterogeneous catalysts for the conversion of coconut oil into biodiesel through transesterification reaction using methanol. The use of catalysts in the transesterification reaction aiming to accelerate the conversion of triglycerides into biodiesel with a by-product in the form of glycerol.

3.3.1. Effects of catalysts concentration on biodiesel production

In this study, the effects of catalyst concentration in biodiesel production (0.45%; 0.6%; and 0.75% wt) can be seen in figure 7. The increased amount of catalyst also result in the escalation of biodiesel conversion results due to an increase in the active side derived from \(\text{Fe}_3\text{O}_4/\text{ZnO}\) composites. Furthermore, cellulose as a support can increase the adsorption of reactants on the catalyst so the reaction becomes more effective and the transesterification reaction for biodiesel production can be accelerated. The optimum amount of catalyst was obtained at 0.60% wt with 90.6% conversion and the addition of the catalyst amount do not show any significant differences in conversion. This result was better than our previous study where the obtained conversion was 89.21% with a weight of 1.5% wt catalyst using a cellulose-magnetite nanocomposite catalyst [12].

![Figure 7. Biodiesel conversion with effect of catalysts concentration.](image)

3.3.2. Effect of reaction time on biodiesel production

In this study the effect of reaction time on biodiesel production (60 minutes, 120 minutes, and 180 minutes) can be seen in figure 8. Based on figure 8, it can be seen that with an increase in the reaction time from 60 minutes to 120 minutes, a rise in conversion percentage from 83.55 % to 90.60% was obtained. This is because the reaction time increases the collisions between particles, the interaction of reactants, and catalysts. Thus the biodiesel production also increases. When, the reaction time is increased to 180 minutes, there is a decrease in biodiesel conversion results, this is because the conditions have reached equilibrium, it is known that the reaction occurs was a reversible reaction that was likely to react back towards the reactants [26].
3.4. Characterization of biodiesel products with GC-MS

The biodiesel products obtained then were characterized using GC-MS instrument which can be seen in figure 9. The GC-MS characterization is carried out to determine biodiesel produced from the conversion of coconut oil with methanol using a cellulose-Fe$_3$O$_4$/ZnO nanocomposite based-catalyst. Figure 9 shows the chromatogram of the product resulting from the transesterification reaction of coconut oil using a cellulose-Fe$_3$O$_4$/ZnO nanocomposite catalyst. The result was that the highest area percentage of biodiesel appeared at the retention time of 12,653 minutes and dodecanoic acid methyl esters biodiesel was obtained with the highest area percentage of 23.89%. In addition, there were also other types of biodiesel that have been successfully produced from coconut oil using a cellulose-Fe$_3$O$_4$/ZnO nanocomposite catalyst, which is shown in table 1. Based on table 1, an abundant biodiesel type gained is myristic acid methyl ester with an area percentage of 17.12%. This is because coconut oil is a triglyceride that contains mainly lauric acid and myristic acid [8].
Table 1. Biodiesel from coconut oil transesterification results.

| Biodiesel (Methyl Esters type)       | Retention time | Area (%) |
|-------------------------------------|----------------|----------|
| Hexanoic acid, methyl ester         | 4.089          | 1.29     |
| Octanoic acid, methyl ester         | 8.374          | 11.40    |
| Decanoic acid, methyl ester         | 10.811         | 9.81     |
| Undecanoic acid, methyl ester       | 11.693         | 0.08     |
| Dodecanoic acid, methyl ester       | 12.653         | 23.89    |
| Myristic acid, methyl ester         | 14.249         | 17.12    |
| Hexadecanoic acid, methyl ester     | 15.671         | 13.28    |
| 11-Octadecanoic acid, methyl ester  | 16.819         | 13.76    |
| Octadecanoic acid, methyl ester     | 16.994         | 6.22     |
| Tetracosanoic acid, methyl ester    | 20.194         | 0.20     |

4. Conclusion
Cellulose-Fe$_3$O$_4$/ZnO nanocomposites were successfully synthesized from the combination of Fe$_3$O$_4$/ZnO composites with Cellulose biopolymers, where Fe$_3$O$_4$/ZnO was dispersed on the surface of cellulose. This result was supported by the characterization of FTIR, XRD, SEM, and SEM-Mapping. The best conversion biodiesel product was obtained using a catalyst amount of 0.6% wt and the reaction time was 120 minutes with a conversion of 90.6%. Test results using GC-MS instruments show that the most formed methyl esters are dodecanoic acid methyl esters (lauric acid methyl esters) with a retention time of 12,653 minutes and with an area percentage of 23.89%.

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