Nanocomposite of cellulose and magnetite-magnesia as catalyst for biodiesel from coconut oil

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Abstract. In this work, a heterogeneous catalyst was developed using MgO-Fe\textsubscript{3}O\textsubscript{4} composite and cellulose biopolymer as support catalyst in the synthesis of biodiesel for transesterification reaction from coconut oil. The nanocomposite catalyst was analyzed using Fourier transform infrared (FTIR), X-ray diffraction (XRD), Scanning electron microscopy-mapping (SEM- Mapping), and transmission electron microscope (TEM) to observe the structure, elemental composition and surface morphology. The parameters of reaction time and catalyst loading were studied to optimize the biodiesel yield. The maximum yields were obtained at 120 minutes and 2 wt.% having the yield of 89.93 %. This result shows high biodiesel yield in short reaction time. The biodiesels products have physical properties close to ASTM standards, with a density of 0.885 g/cm\textsuperscript{3} and acid number of 0.442 mg KOH/g. The biodiesel was tested using the gas chromatography (GC) pertaining the greatest abundance at the retention time of 8.817 minutes which indicating that methyl dodecanoic (lauric methyl ester) have area 39.68 %. The cellulose biopolymer combined with MgO-Fe\textsubscript{3}O\textsubscript{4} composite as green catalyst for heterogeneous catalysts which is promising in biodiesel production.

Keywords: Biodiesel, biopolymer, coconut oil, heterogeneous catalyst, nanocomposite

1. Introduction
The fuels of non-renewable sources are continuously decreasing. On the other hand, the need of energy is increasing. Application of renewable energies such as biofuel and biodiesel has received more attention accompanied by the rapid development of industry [1, 2]. The world energy usage will be increased by 28 % between 2015 and 2040 [3]. The conventional fuels are hazardous to atmosphere as it emits various harmful gases. The toxic gases are known to cause global warming and environmental pollution [4].

Renewable energies represent one of the main challenges facing by the nowadays world. Introducing alternative forms of fuels which can be obtained from energy that are sustainable, ecofriendly and it draws attention of the researchers around the world [5, 6]. The one type of green energy sources that has high potential is biodiesel, because it has several advantages such as sulfur-free, non-toxic, and environmental-friendly [7-9].

Catalysts used in the synthesis of biodiesel to accelerate reactions can be either homogeneous or heterogeneous catalysts. Heterogeneous catalysts were used because the properties can minimize the impact of environmental damage, separable, and reusable [10]. Fe\textsubscript{3}O\textsubscript{4} nanoparticles are magnetic, widely used in catalysts, because of their unique properties including a large surface, low toxicity and
biocompatibility [11]. Magnesium oxide (MgO) is heterogeneous base catalyst have been widely used for transesterification because it can retain its catalytic properties under ambient conditions, even in the presence of excessive moisture [12]. To improve the catalytic performance of single oxides, it would be interesting to develop mixed oxides that could provide the better catalytic activities [13]. Nanocomposite of MgFe$_2$O$_4$-MgO as catalyst from oleic acid to biodiesel [14]. Diatomite@CaO/MgO catalyst of the waste cooking oil into biodiesel [15].

In recent year, the combination of biopolymers used as a catalyst support with inorganic nanoparticles will form nanocomposites that have superior properties because it has a synergistic effect [16]. Biopolymer cellulose can be used as a catalyst support because it has unique properties such as non-toxic, biocompatible, biodegradable, and providing multiple pores [17]. Catalyst of Zr-SO$_3$H@CMC for oleic acid esterification with high biodiesel yields [18]. The rice straw based heterogeneous solid acid catalyst (RS-SO$_3$H) indicated that the catalyst was highly operative in biodiesel production up to 7 cycles [19]. Cellulose-ZnO/SiO$_2$ was applied as heterogeneous catalyst for transesterification of coconut oil into biodiesel [20].

However, the study of cellulose biopolymer impregnated with bimetal oxide Fe$_3$O$_4$-MgO are limited. This work aims to synthesize heterogeneous catalyst by using cellulose and Fe$_3$O$_4$-CaO composites cellulose for esterification reaction with high biodiesel yield in short reaction time.

2. Materials and method

2.1. Materials

Pure nanocellulose powder (Merck) was applied as a support catalyst, FeCl$_3$·6H$_2$O (Merck) and FeCl$_2$·4H$_2$O (Merck) to synthesize the nano Fe$_3$O$_4$. Mg(NO$_3$)$_2$·6H$_2$O (Merck) as a precursor MgO, NaOH (Merck) as pH adjustment, methanol (Merck), coconut oil (local brand) for biodiesel production.

2.2. Synthesis of Fe$_3$O$_4$ and MgO nanoparticles

Synthesis of Fe$_3$O$_4$ nanoparticle referred to the previous study [21] with modifications. Furthermore, synthesis of MgO nanoparticle referred to the previous study [22] with modifications. The nanoparticles Fe$_3$O$_4$ and MgO obtained were characterized by FTIR and XRD.

2.3. Synthesis of cellulose/Fe$_3$O$_4$-MgO nanocomposites

The first stage was the synthesis of Fe$_3$O$_4$-MgO composites which referred to study [23]. The second stage was the synthesis of cellulose/Fe$_3$O$_4$-MgO nanocomposites which referred to study [24] with modifications. Fe$_3$O$_4$-MgO composites and cellulose/Fe$_3$O$_4$-MgO nanocomposites were characterized by FTIR, XRD, SEM-Mapping, and TEM.

2.4. Catalytic activity

Catalytic activity of cellulose/Fe$_3$O$_4$-MgO nanocomposites was performed for transesterification of coconut oil, methanol referred to the previous study [10]. The reaction was carried out with variations of catalyst loading (1, 2, 3 wt. %) and reaction time (60, 90, 120, 180 minutes). The biodiesel formed was characterized by GC by using Shimadzu GC-2010 Plus of detectors and injectors: single FID with EPC injectors. Operating at a temperature of 105 °C with nitrogen carrier gas. Biodiesel yield was calculated by following the equation [25]:

\[
\text{Yield (\%)} = \left( \frac{\text{weight of biodiesel}}{\text{weight of oil}} \right) \times 100
\]
3. Results and discussion

3.1. Characterization by FTIR
Characterization using FTIR to analyze the functional groups (figure 1). Figure 1a shows the spectrum of Fe$_3$O$_4$, the presence of a typical absorption peak of Fe-O stretch around 600 cm$^{-1}$ [16]. Figure 2b shows the peaks around 500 and 880 cm$^{-1}$ represents the formation of MgO nanoparticles [26]. Figure 2c shows cellulose spectrum the presence of O–H stretch at 3250–3500 cm$^{-1}$, C–H stretch at 2950 cm$^{-1}$, O-H bend at 1600 cm$^{-1}$ and around 1440, 1050 and 937 cm$^{-1}$ indicating the C–O–C stretch from the glycosidic bond. Figure 2d shows that the cellulose/Fe$_3$O$_4$-MgO nanocomposite featuring the peak that corresponds to cellulose and the typical peak of the Fe$_3$O$_4$-MgO composite and there are shifting of each absorption peak.

3.2. Characterization by XRD
The XRD pattern of Fe$_3$O$_4$/MgO shows at 2$\theta$ = 30.09°, 35.62°, 42.98°, 54.79°, 57.49°, and 62.38° which are typical peaks for Fe$_3$O$_4$ based on JCPDS No. 00-003-0863, whereas the peak at 2$\theta$ = 35.62°, 42.98°, 62.38°, 74.43°, 78.71° are the typical peaks of MgO in accordance with JCPDS No. 01-089-7746 (figure 2a). Figure 2b shows the diffraction pattern of pure cellulose which has peaks of 2$\theta$: 15.05°, 22.51°, and 34.97° [20]. In figure 2c shows the diffraction pattern of Cellulose-Fe$_3$O$_4$/MgO, featured that corresponds to cellulose and the typical peak of the Fe$_3$O$_4$-MgO and there are shifting of each absorption peak. This indicates that the cellulose-Fe$_3$O$_4$/MgO nanocomposites have been successfully synthesized.

3.3. Characterization by SEM
Surface morphological analysis of cellulose/Fe$_3$O$_4$-MgO is shown in figure 3. Figure 3a with magnification of 1000 times shows that the white grains are smooth and evenly distributed of the particles Fe$_3$O$_4$-MgO on the cellulose surface. Figure 3b and figure 3c, with a magnification of 2500 and 5000 times were clearly shown the presence of Fe$_3$O$_4$-MgO in the form of grains irregular spread evenly on the surface of cellulose. The distribution of Fe$_3$O$_4$-MgO on the cellulose surface was observed by elemental mapping and to determine the mass percent of each element by SEM-EDS as shown in figure 4.

Figure 1. FTIR Spectra of (a) MgO, (b) MgO, (c) Cellulose and (d) Cellulose/Fe$_3$O$_4$-MgO.
Figure 2. XRD patterns of (a) Fe$_3$O$_4$-MgO, (b) Cellulose, (c) Cellulose/Fe$_3$O$_4$-MgO.
The results of SEM-Mapping are used to observe the distribution of elements in cellulose/Fe$_3$O$_4$-MgO. Figure 4a is the overall distribution of the elements where it can be observed that the presence of Fe and Mg element spread evenly on the surface of cellulose in nanocomposite. Figure 4b shows the SEM-EDS analysis to determine the mass percent of each element in the cellulose/Fe$_3$O$_4$-MgO nanocomposite with composition of O, C, Mg and Fe are 39.8, 32.6, 17.7 and 9.9 wt.%, respectively. Figure 4c to figure 4f show the constituent elements of Mg, Fe, O and C, respectively. When associated with figure 4a, it can be observed that Fe and Mg element were evenly distributed on the nanocomposite surface. These results support the successful synthesis of the nanocellulose-supported catalyst.

![SEM micrograph with magnifications](image1)

**Figure 3.** SEM micrograph with magnifications of (a) 1000, (b) 2500, and (c) 5000 times of Cellulose/Fe$_3$O$_4$-MgO.

![Distribution mappings](image2)

**Figure 4.** Distribution mappings (a) overall element, (b) EDS, (c) Mg, (d) Fe, (e) O, and (f) C of Cellulose/Fe$_3$O$_4$-MgO.
3.4. Characterization by TEM
TEM characterization of the synthesized cellulose/Fe\textsubscript{3}O\textsubscript{4}-MgO is used to observe the structure of the nanocomposites. Figure 5a and figure 5b with 100 dan 50 nm scale bar revealed that the catalyst particles had an irregular shape, with dark granules corresponding to the Fe\textsubscript{3}O\textsubscript{4}-MgO composite. Figure 5c presents the high-resolution TEM images (10 nm scale), it can be observed the presence of Fe\textsubscript{3}O\textsubscript{4}-MgO crystals and the porous cellulose of nanocomposite.

3.5. Catalytic activity

3.5.1. Effect of reaction time. The effect of reaction time on the biodiesel yield is shown in figure 6. The increase of reaction time will increase the percentage of yield. By increasing the reaction time, the reaction between the catalyst and the reactants will be more complete to form an activated complex which is adsorbed on the surface of the catalyst and a reaction occurs, then the desorption process forms the biodiesel product \cite{2}. The optimal reaction time of the transesterification reaction is 120 minutes with biodiesel yield of 89.93 %, this result shows high biodiesel yield in short reaction time compared to our previous study \cite{16, 20}. However, when the reaction time was increased to 180 minutes, the yield obtained was 87.17 %. The decrease in the yield is due to the condition that has reached the equilibrium and the reaction is likely to undergo a reversible reaction with the longer reaction time \cite{16}.

3.5.2. Effect of catalyst loading. The effect of the catalyst loading on the biodiesel yield is shown in figure 7. The increase of the catalyst loading increases the percentage yield, and it is similar to the previous studies \cite{7}. The optimum catalyst loading is 2 % with 87.78 % yield.

![Figure 5. TEM image (a) 100 nm, (b) 50 nm and (c) 10 nm scale of Cellulose/Fe\textsubscript{3}O\textsubscript{4}-MgO.](image)

![Figure 6. Effect of the reaction time to yield.](image)

![Figure 7. Effect of catalyst loading to yield.](image)
3.6. Properties of biodiesel

Biodiesel has physical properties as a measure of the quality for application in engines as the specifications of ASTM standard [27]. Based on the analysis results obtained that the density is 0.885 g/cm$^3$, it was obtained that the values were close to the ASTM D6751 standard (0.875–0.90 g/cm$^3$). The acid value of biodiesel is important because it could affect the stability of biodiesel [27]. In this work, the acid value of biodiesel produced was 0.442 mg KOH/g, which is in the range of ASTM standard (< 0.5 mg KOH/g) [2, 28].

3.7. GC-MS analysis

The biodiesel products were characterized using a gas chromatography (GC) as shown in figure 8. The chromatogram of the biodiesel product obtained from the transesterification reaction of coconut oil using a cellulose/Fe$_3$O$_4$-MgO nanocomposite catalyst shows that the highest percent of biodiesel appeared at the retention time of 8.817 minutes with the percent area of 39.68 %. The other types of biodiesel component from coconut oil using a cellulose/Fe$_3$O$_4$-MgO nanocomposite catalyst is shown in table 1. Methyl myristic have the second percentage area of 22.36 % at the retention time of 10.29 minutes. This is due to the fact that coconut oil is a triglyceride that mostly contains with lauric and myristic acids.

![Figure 8. Chromatogram GC methyl ester in biodiesel from coconut oil.](image)

| Biodiesel (methyl ester type) | Retention time (minutes) | Area (%) |
|-------------------------------|--------------------------|----------|
| Methyl hexanoate              | 3.135                    | 3.131    |
| Methyl octanoate              | 5.096                    | 5.090    |
| Methyl decanoate              | 6.988                    | 6.960    |
| Methyl dodecanoate            | 8.817                    | 39.68    |
| Methyl myristate              | 10.298                   | 22.36    |
| Methyl hexadecanoate          | 11.659                   | 11.96    |
| Methyl 10-octadecenoate       | 12.787                   | 9.87     |
| Methyl stearate               | 12.911                   | 4.48     |
4. Conclusion
The cellulose/Fe$_3$O$_4$-MgO nanocomposites have been successfully synthesized by combining Fe$_3$O$_4$-MgO composites with cellulose biopolymer. The cellulose/Fe$_3$O$_4$-MgO nanocomposite has been applied as a catalyst in the synthesis of methyl ester from coconut oil with a catalyst loading of 1%, reaction time of 120 minutes with a yield of 89.93%. This result shows high biodiesel yield in short reaction time. The characteristics of biodiesel are close to the ASTM standards, with a density of 0.885 g/cm$^3$ and acid number of 0.442 mg KOH/g. The biodiesel characterization using GC shows that the most formed methyl ester was methyl dodecanoic. This study indicates that cellulose biopolymer as support catalyst with Fe$_3$O$_4$-MgO composite can be used as an effective catalyst for biodiesel synthesis from coconut oil.

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