Cellulose-Fe.O. nanocomposite based on rice husk as catalyst for synthesis of methyl ester from waste cooking oil

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Abstract. Cellulose-Fe.O. nanocomposite has been successfully synthesized by modifying Fe.O. onto nanocellulose acetate surface derived cellulose from rice husk. It was supported by Fourier Tranform-Infrared (FT-IR) characterization, where there was absorption at 900 cm\(^{-1}\), which was a characteristic for cellulose absorption, and at 572 cm\(^{-1}\), which was the absorption of Fe-O. The morphology of cellulose-Fe.O. nanocomposite by Scanning Electron Microscopy (SEM) having fibers shape were the characteristic of cellulose and Fe.O. nanoparticle attached on the surface of nanocellulose and supported by SEM mapping. The characterization of Tunneling Electron Microscopy (TEM) obtained nano Fe.O. on the nanocellulose surface with average size around 55 nm. The cellulose-Fe.O. nanocomposites have the capability, as catalyst for the synthesis of methyl esters from waste cooking oil with the optimal conditions at 60 °C for 120 minutes with the obtained conversion is 77.56 %. The nanocomposite of based biopolymer with nanomagnetite active side is potential for catalysts from the used cooking oil to biodiesel as renewable energy and can replace limited fossil energy.

Keywords: cellulose, catalyst, nanocomposite, rice husk, waste cooking oil

1. Introduction

Rice husk is one of the agricultural wastes, which is by-product in the process of rice mill into rice [1,2]. Rice husk contains organic material about 40 % cellulose, 30 % hemicellulose, 10 % lignin and other mineral components, therefore rice husk is considered as a potential source of cellulose from agricultural plant waste [3]. Cellulose is one of the most abundant biopolymers in nature, which is biodegradable, non-toxic, and environmentally friendly materials [4,5].

In the recent years, nanocomposite materials have been evolved as heterogeneous catalysts for various applications. Cellulose can be utilized as supporting materials for catalyst, cellulose-based nanocomposite biopolymers as a catalyst for the synthesis of methyl oleate [6].

Nanocomposite polymer is a combination of polymer matrix and nanoparticle inorganic. When an inorganic nanoparticle is added to the nanocellulose polymer matrix it will be affected to the strength of the resulting nanocomposite [7,8]. The resulting nanocomposite will provide superior properties derived from the properties of nanocellulose and inorganic nanoparticles, which will form better properties [9,10]. Waste cooking oil (WCO) can be utilized as the main ingredient for the production of methyl ester by oil transesterification and short-chained alcohol reaction in the presence of a catalyst [11]. Methyl ester biodiesel can be utilized as alternative fuels that are environmentally friendly, non-toxic and produce low emission [12]. Waste cooking oil contains triglycerides and free fatty acids. It can be an effective and economical solution related to the disposal of WCO into the environment [13].

In this study, the synthesis of Fe.O. nanocomposite based on cellulose biopolymer isolated from rice husk has been done and nanocomposite have been synthesized to be used as a catalyst for the synthesis
of methyl ester from WCO derived from household waste. The several stages carried out in this study were cellulose isolation from rice husk, nanocellulose synthesis, FeO. synthesis, cellulose- FeO. nanocomposite synthesis, and nanocomposite application as a catalyst for synthesis of methyl ester from WCO. Characterizations of synthesis products were done using Fourier Transform-Infrared (FT-IR), X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM) and Tunneling Electron Microscopy (TEM).

2. Experimental

2.1. Materials
Rice husk from Bukittinggi as the source material for cellulose; toluene and ethanol (Merck), KOH (Merck), sodium chlorite (Merck) for cellulose extraction of rice husk; anhydrous acetate (Merck) for the synthesis of nanocellulose; iron (III) chloride (FeCl₃·6H₂O) (Sigma Aldrich) and iron (II) chloride (FeCl₂·4H₂O) (Sigma Aldrich) for the synthesis of iron oxide; methanol (Sigma Aldrich) and waste cooking oil (WCO) as material for methyl ester production.

2.2. Synthesis of nanocellulose from rice husk
In the first step, cellulose was isolated from rice husks refer to our previous studies [14]. Then, nanocellulose acetate synthesis from cellulose refers to the previous reported [6]. Second step, cellulose soaked in HCl with stirring at 60 °C for 2 hours, after washing and filtering the nanocellulose will be obtained. The last step, the nanocellulose was functionalized with anhydrous acetic acid and nanocellulose acetate was obtained and characterized by FTIR, XRD and SEM.

2.3. Synthesis of cellulose-FeO. nanocomposite
The first stage was conducted the synthesis of magnetite (Fe₃O₄) by co-precipitation method refers to previous reported [8]. The second stage was synthesis of cellulose-Fe₃O₄ nanocomposite refers to the reported method [16]. The nanocomposite formed were filtered and rinsed with distilled water, ethanol, and acetone. Then, they were dried at 60 °C for 24 hours, and the cellulose-Fe₃O₄ nanocomposite was obtained and characterized by FTIR, XRD, SEM and TEM.

2.4. Catalytic activity of cellulose-FeO. nanocomposite
Catalytic activity of cellulose-Fe₃O₄ nanocomposites as catalysts was applied to waste cooking oil to produce biodiesel-using methanol with a transesterification reaction. The effect of temperature and reaction time was carried out to observe the conversions.

3. Results and discussion

3.1. Characterization
Characterization using FTIR for determination of the functional groups, FTIR analysis used IR-Prestige-21 Shidmazu IR-type instrumentation with a wavelength of 4000-400 cm⁻¹. The results of the spectrum can be seen in figure 1. Figure 1a is the spectrum of rice husks, which the characteristic absorption band around 3200-3450 cm⁻¹ is O-H stretching and the absorption band at 2920 cm⁻¹ shows C-H stretching. The peaks at 1516 cm⁻¹ is lignin, and at 500 cm⁻¹ is Si-O-Si group. These two peaks only appear for rice husks and did not appear at the spectrum of nanocellulose rice husk. Figure 1b shows the spectrum of pure nanocellulose, there is an appearance of characteristic band absorption of cellulose at 900 cm⁻¹, 1060 cm⁻¹ and 1680 cm⁻¹ is β-glycosidic bond. The peak around 3200-3450 cm⁻¹ is the vibration of the O-H group and at 2913 cm⁻¹ shows the C-H stretch. Figure 1c is nanocellulose rice husk, it shows that lignin, hemicellulose, and silica have disappeared. The characteristic band absorption of cellulose appears at 900 cm⁻¹, 1050 cm⁻¹ and 1690 cm⁻¹ is β-glycosidic bond, which is similar to the pure nanocellulose spectrum in figure 1b. Figure 1d is the spectrum of the nanocellulose acetate, in which this spectrum is similar to the nanocellulose rice husk in figure 1c. There is no significant change between nanocellulose rice husk with nanocellulose acetate, which proves that anhydrous acetic acid did not change the structure or functional groups of nanocellulose. It only changed the size of the nanocellulose to be smaller. Figure 1e shows the spectrum of magnetite (Fe₃O₄), there is appearance of a typical peak of Fe-O at 572 cm⁻¹. Figure 1f shows the spectrum of the cellulose- FeO₃ nanocomposite. It can be observed that the identical absorption band of cellulose appear at 850 cm⁻¹, 1020 cm⁻¹ and 1690 cm⁻¹ is the β-glycosidic bond and there is absorption peak of
Figure 1. FTIR spectra of (a) rice husk, (b) pure nanocellulose, (c) nanocellulose rice husk, (d) nanocellulose acetate, (e) magnetite (Fe₃O₄), and (f) cellulose-Fe₃O₄ nanocomposite.

Fe-O at 572 cm⁻¹. The results of the spectrum indicated that cellulose-Fe₂O₃ nanocomposites have been successfully synthesized.

The characterization of XRD was used to analyze the crystal structure of the synthesized sample. XRD pattern is shown in figure 2. Figure 2a is the diffraction pattern of nanocellulose acetate, there are three peaks appear at 2θ = 18.10°, 22.4°, and 34.5° with the sharpest peak appeared at 2θ = 22.8°. These peaks are characteristics for cellulose [2,15]. Figure 2b is the nano Fe₃O₄ diffraction pattern, it can be observed that the peaks at 2θ = 30.1°, 35.2°, 43.4°, 53.2°, 57.2°, 60.5° and 64.5° with the highest and sharpest peak appeared at 2θ = 35°. This result is similar to the previous report [8]. In figure 2c, cellulose-Fe₃O₄ nanocomposite have typical peaks derived from nanocellulose at 2θ = 18.0°, 22.9° and the peaks of nano Fe₃O₄ are at 2θ = 30.5°, 35.6°, 43.8°, 53.9°, 61.1° and 65.5°. The peaks are dominated by Fe₃O₄, due to the nano Fe₃O₄ attached on the surface of the nanocellulose. The crystallinity index of cellulose-Fe₃O₄ nanocomposite obtained is 64.06 % and the crystal size calculated using the Debye Scherrer equation is 26.89 nm. The results of XRD-pattern supported that the cellulose-Fe₂O₃ nanocomposite has been synthesized successfully.

The SEM micrograph is shown in figure 3. Figure 3a shows that the surface morphology of cellulose rice husk with magnification of 1500 times have the form of fibers with its surface quite smooth. Figure 3b is the surface morphology of nanocellulose acetate with magnification of 1500 times has smoother fibers and evenly distributed. This shows that the addition of anhydrous acetate did not alter the structure of the cellulose, but it has capability to modify the nanocellulose into a smaller size. Figure 3c shows that the morphological results of Fe₂O₃ nanoparticles with a magnification of 2000 times have granular shape. Figure 3d shows that the morphology of cellulose-Fe₂O₃ nanocomposite with magnification of 2000 times have fibers that were the characteristic of cellulose and Fe₂O₃ nanoparticle attached on the surface of nanocellulose. This supports the results of the diffraction pattern by XRD. This result shows that nanocomposite of cellulose-Fe₂O₃ have been successfully synthesized.

The SEM-mapping is shown in the figure 4, for observing the distribution of the elements on the nanocomposite. Figure 4a shows the overall distribution of elements of the nanocomposite, the largest parts are the cellulose support material colored in green. Figure 4b is the distribution of C elements...
Figure 2. The XRD-patterns of (a) nanocellulose acetate, (b) nanoparticles Fe₃O₄, and (c) cellulose-Fe₃O₄ nanocomposites.

Figure 3. SEM micrograph of (a) nanocellulose rice husk, (b) nanocellulose acetate, (c) nanoparticles Fe₃O₄, and (d) cellulose-Fe₃O₄ nanocomposite.
Figure 4. SEM-Mapping of (a) the overall of elements (b) C elements, (c) O elements, and (d) Fe elements in nanocomposite.

colored in light blue evenly because C element is the main component of nanocellulose. Figure 4c is the distribution of element O colored in red evenly, due to O element is the main component of nanocellulose and nano Fe₃O₄. Figure 4d is the distribution of Fe elements colored in bright purple derived from nano Fe₃O₄, but its element was not so much within the nanocomposites as compared to the distribution of C and O elements. It is due to nanocellulose as support meanwhile the nano Fe₃O₄ as the active side of the catalyst [6]. From the result of SEM-Mapping, it shows that nanocomposite of cellulose-Fe₃O₄ have been successfully synthesized.

Characterization using TEM was performed to determine the morphology and size of the nanocomposite. The result of TEM characterization can be seen in figure 5. Figure 5 shows the surface morphology of cellulose-Fe₃O₄ nanocomposite with a scalebar of 100 nm. It can be observed gray colored is nanocellulose in the form of fiber and the distributed nano Fe₃O₄ on the surface nanocellulose with granular shape small dark-colored have an average size of 55 nm. This indicates that nano Fe₃O₄ was successfully composited on the surface of nanocellulose. This result supported the previous characterization. The nanocomposite used as a catalyst of waste cooking oil with methanol to biodiesel methyl ester.

3.2. Catalytic activity of cellulose-Fe₃O₄ nanocomposite

The catalytic activity of synthesized cellulose-Fe₃O₄ nanocomposite used for conversion of waste cooking oil with methanol to methyl ester and evaluated by the effect of temperature, and time reaction. The reaction temperature has an effect to the trans esterification reaction, it is caused by the temperature effect on the reaction rate [17]. The effect of temperature was conducted at 50 °C, 55 °C, 60 °C, and 65 °C as shown in figure 6. The temperatures rise will increase conversion of methyl esters. The conversion of optimum methyl ester is obtained about 77.56 % with reaction temperature at 60 °C. However, the conversion of methyl esters decreased at 65 °C, because at high temperature before reacting with WCO, methanol may evaporate because the boiling point of methanol about 64.5 °C so that the conversion of methyl ester decreased. The effect of time reaction to conversion of waste cooking oil to methyl esters was conducted at 30, 60, 90, 120 and 150 minutes as shown in figure 7. As the reaction time increased, the conversion of methyl ester was also increased, it can be
4. Conclusions
Cellulose-Fe₃O₄ nanocomposite has been successfully synthesized, which was supported by FT-IR characterization, where there was absorption at 900 cm⁻¹, which was a characteristic for cellulose absorption, and at 570 cm⁻¹ which was the absorption of Fe-O. The morphology of cellulose-Fe₃O₄ nanocomposite by SEM having fibers shape that were the characteristic of cellulose and Fe₃O₄ nanoparticle attached on the surface of nanocellulose and supported by SEM mapping. The characterization of TEM obtained nano Fe₃O₄ on the surface nanocellulose of the average size around 55 nm. The cellulose-Fe₃O₄ nanocomposites have the capability, as catalyst for the synthesis of methyl esters from waste cooking oil with the optimal conditions at 60 °C for 120 minutes obtained conversion is 78.56 %.

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