

Isolation and Characterization of Cellulose Nanofiber (CNF) from Sugarcane Bagasse by Acid Hydrolysis with Addition of Ferric Chloride Catalyst (FeCl_3)

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Abstract

Sugarcane bagasse was used as effect of hydrolysis time for isolation of cellulose nanofiber (CNF) was done. The other components such as lignin and hemicellulose were removed from the biomass by adding NaOH and NaOCl and continue to synthesist of CNF has done using formic acid hydrolysis wiht addition of ferric chloride catalyst. FTIR analysis showed that were no significant variations in peak positions, This result did not affect the chemical compounds of CNF. XRD analysis showed increase the hydrolisis time also increase the crystallinity percentage and crystalline size. Increasing hydrolysis time would decreased the percentage yield of CNF.



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Introduction

Sugarcane (*Sacarrharum officiarum*) is the main raw material in a sugar factory. A bagasse is a by-product of sugar cane extraction. A factory can produce bagasse ranging from 35-40% of the weight of the ground cane. The average composition of bagasse is composed of 46-52% water, 43-52% coir, and 2-6% of the dissolved solids. The bagasse contains a residue of fiber, at least 50% of the fiber is required as a boiler fuel, while the remaining 50% is only dumped as a low economic value (1).

National sugarcane production in 2016 is estimated at 2,715,883 tons (2), assuming the percentage of bagasse reaches 35-40% of their initial weight, it can be estimated that there are approximately 1,086,353.2 tons of bagasse per year. The composition of bagasse is made up of 40-50% cellulose, 25-35% hemicellulose, and 18-24% lignin (3). Cellulose contained in bagasse can be used as nanocellulose to increase the economic value of bagass. CNF obtained can be applied in various fields, such as biotechnology, composites, adsorbents, emulsions and dispersions, and biomedicine (4).

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Synthesis of CNF can be done by several methods, ie mechanical, chemical, and biological methods. Chemical methods can be performed using the acid hydrolysis method, the organosolv method, the alkaline solvent method, the oxidation method, and the ionic liquid method. Acid hydrolysis can be carried out by the amorphous portion of a cellulose so that the isolation in the cellulose crystalline part can be carried out (4). Acid hydrolysis can be performed using formic acid, hydrochloric acid (HCl), nitric acid (HNO₃), phosphoric acid (H₃PO₄) and sulfuric acid (H₂SO₄) (5).

Synthesis of CNF with hydrolysis acids method has been done by many scientists using a variety of materials such as residual oil palm biomass (6), rice husks (7), corn cobs and husks of grain (8), Eucalyptus Kraft Pulp (9), bagasse (3), bamboo (10), and kenaf bast (5).

Hydrolysis conditions, such as temperature, reaction time, and acid concentration, affect the characteristic of the hydrolyzed bagasse. Many research using high acid concentration and temperature, moreover with long reaction time. As stated by Aprilia *et al* (5), acid concentration and reaction time are two important parameters in the acid hydrolysis process. It was observed that an increase in hydrolysis time decreased particle size, including both the diameter and length of microcrystalline cellulose (MCC). As the result of Aprilia *et al* (5), using kenaf bast and HCl-hydrolysis, the diameter was found to be 10.05 μm , 8.89 μm , and 7.9 μm at 1 h, 2 h, and 3 h hydrolysis time, respectively.

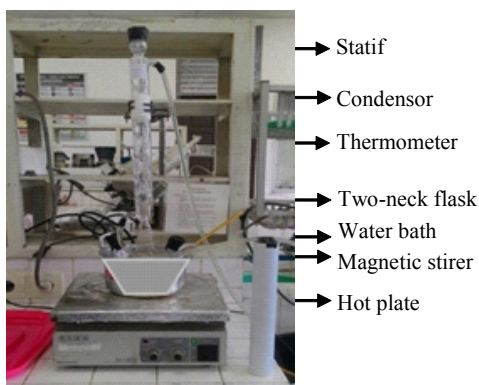


Fig. 1: Cellulose isolation tools and acid hydrolysis

Today, many chemical reactions using a catalyst. One of catalyst that often used is ferric chloride (FeCl₃). FeCl₃ is used as a catalyst for a variety of purposes, such as oxidation, esterification, and condensation, with the advantage that raises efficiency, lowers costs and can recycle (9)(12)..

Although the acid hydrolysis for the production of CNF from sugarcane has been reported, the study of catalyst, which is the important parameters affecting the characteristic of hydrolyzed bagasse. In this study, CNF has extracted from sugarcane bagasse with acid hydrolysis (formic acid) and FeCl₃ catalyst effect of hydrolysis time.

Material and Tools

The materials used include bagasse obtained from sugarcane seller at around Syiah Kuala University, Banda Aceh, Indonesia. Formic acid (FA, 56%), anhydrous ferric chloride (FeCl₃, 1.28 M), sodium hypochlorite (NaOCl, 15%), sodium hydroxide (NaOH), and aquades. All chemicals can be obtained in Sigma-Aldrich and used as received without purification process.

The tool used consists of a two-neck flask equipped with a thermometer and condenser. Heating device used is a hot plate with water bath above, while the stirrer used is a magnetic stirrer (Fig 1).

The cellulose isolation from bagasse

In this study, there are two steps process. First, cellulose isolation from bagasse, and then acid hydrolysis to get CNF. The cellulose isolation procedure refers to Ahmad *at al*, (7). At this step, the delignification and bleaching process was done to remove the lignin and hemicellulose in bagasse, so it is expected that the result obtained from this step is the cellulose powder. Then the cellulose powder was analyzed by Fourier Transform Infrared Spectroscopy (FTIR) and than compare with the standard cellulose based on the literature.

Sample preparation was started by drying the bagasse in the sun for 2-3 days. Then the dried bagasse was cuted 3-5 cm size and washed with distilled water for 3 times. Then it dried in the oven at 60oC temperature for 24 hours. Delignification process was started by taking 10 grams of bagasse, then added 300 ml of NaOH 1M for 1 hour 36 minutes

at a temperature of 80°C. Then the bagasse was washed by distilled water in a centrifuge for 3 times. After that, continue with added 150 ml of NaOCl 5% for 20 minutes at a temperature of 80°C. And then, the bagasse washed by distilled water in a centrifuge for several times. The cellulose was dried in an oven at 70°C for 3 hours and mill by mortar and pestle until powder.

Formic Acid Hydrolysis

This method refers to Du et al., 2016. It began by mixing 3 grams of cellulose powder, 90 ml of formic acid and 1 grams of FeCl₃ in the two-neck flask. The temperature of this process is 90°C and stirring at 400 rpm. The concentration of formic acid was 50%. The time of hydrolysis was too varied to 3 and 6 hours. After that, CNF was washed with distilled water in the centrifuge as many times. The temperature of the centrifuge is room temperature with 1400 rpm during 30 minutes. The CNF was dried in an oven at 70°C for 3 hours and mill by mortar and pestle until powder.

Percentage Yield Analyses

Percentage yield was determined using the following equation (7):

$$yield(\%) = \frac{M_1 \times M_3}{M_2 \times M_0} \times 100 \quad \dots(1)$$

Fourier Transform Infrared (Ftir) Analyses

FTIR analyses were purposed to determine the spectrum of the samples, they were cellulose and CNF. FTIR analyses were on a Shimadzu Prestige FT-IR 6400 in the wavenumber range of 400 - 4000

cm⁻¹. Before analysis, the sample was mixed with KBr with a ratio of 1: 9 (sample: KBr).

X-Ray Diffraction (Xrd) Analyses

X-Ray diffraction analyses were purposed to determine the crystallinity index and crystal size of samples. XRD analyses were on an X-Ray diffractometer with measurement condition are 40 kV and current 30 mA. The range of scattering angle (2θ) was from 10° to 80° with the scan rate of 10o/min. The crystallinity index (Crl) was calculated using the empirical equation (2) and crystal size was calculated using Scherrer equation (3) (10).

$$C_r(\%) = \left(1 - \frac{I_{am}}{I_{200}}\right) \times 100 \quad \dots(2)$$

$$D = \frac{0.9\lambda}{\beta_{hkl} \cos \theta_{hkl}} \quad \dots(3)$$

Crystallinity index (Crl) was calculated from the maximum peak intensity at lattice diffraction (200) and I_{am} is the intensity minimum between the 200 and 110 peaks. While for calculating crystal size, K is the Scherrer constant (K = 0.9), λ is the wavelength of X-ray radiation (λ = 1,5406 Å) and β_{1/2} is the full width at half-maximum of the Reflection, and θ is the Bragg angle.

Result and Discussion

Yield

Cellulose nanofiber (CNF) was produced from bagasse using two different formic acid hydrolysis times, there are 3 h and 6 h, while formic concentration, volume formic acid, weight cellulose, ferric chloride

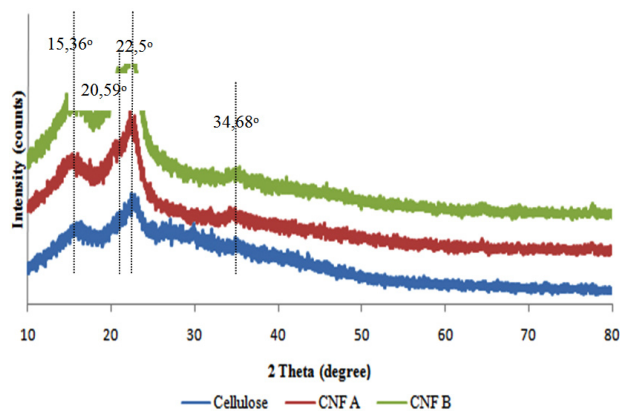


Fig. 2: FTIR of CNF from sugarcane bagasse with differential hydrolysis time.

concentration, and temperature are constant. The yield of CNF was calculated and tabulated in Table 1. The yield of the three-hour is 74,66% and decreased until 70,52% in six-hour hydrolyzed.

Similar results were achieved by Haishun Du *et al* (9) that using FA 88% and ferric chloride catalyst 0,005 M, and 6 h reaction time, while used eucalyptus kraft as raw material, obtained the percentage yield 79,97% then decreased when the concentration of ferric chloride was increased. Sri Aprilia *et al* (5) also reported when increasing the hydrolysis time, the percentage yield of MCC decreased.

Increasing the hydrolysis time affected the yield of CNF. The reduction of yield occurred because probably due to the break-down of the more β -1,4, glycosidic bond at long reaction time and easier removal of short chains during hydrolysis (5).

The percentage yield of CNF different from sample to sample. The variation was depending on the type of the sample, the sample preparation and variables in acid hydrolysis (7).

Fourier Transform Infrared Spectroscopy (Ftir)

The FTIR spectra of cellulose and CNF are depicted in Fig. 2. All the spectra seem like same, it because the chemical compositions of all samples. Similar results were achieved by Haishun Du *et al* (7). Moreover, Wulandari *et al* (3), reported the similar results using bagasse and sulfuric acid-hydrolyzed.

Fig. 2 shows the FTIR spectra of cellulose, CNF A is for reaction time 6 h, and CNF B is for 3 h. Except for a new strong band at 1714 cm^{-1} and 2538 cm^{-1} in the spectrum of CNF, other bands (e.g. the bands at 3300, 2900, 1620, 1428, 1369, 1315, 1156, 1056, and 898 cm^{-1}) in the spectrum of CNF and cellulose were parallel. The absorption peaks found

at 3300 cm^{-1} and at 2900 cm^{-1} were attributed to O-H stretching vibration and C-H stretching vibration in CH_2 groups. The band 1620 cm^{-1} was assigned to hydroxyl bending vibration of the adsorbed. And the peaks at 1428, 1369, 1156, and 898 cm^{-1} were assumed the typical bonds of cellulose I β (9).

It is evident from Fig.2 that by increasing the reaction time, the intensity of the hydrogen bonds increased. This assumed because of the degradation of amorphous portion while enriching the crystallinity of the CNF. Moreover, the O-H band changed into lower wavenumbers when increasing reaction time. Sri Aprilia *et al* (5) also reported a same conclusion: by increasing reaction time, the hydrogen bond of kenaf bast would shift a lower wave number.

The new band at 1714 cm^{-1} might be the C=O stretching in the adsorbed FA or cellulose formate. It was reported that FA could be adsorbed onto the surface of cellulose molecules (9). The new band at 2538 cm^{-1} is H-C=O : C-H stretch might be from formic acid (HCOOH).

In a short, hydrolysis time not influence the chemical components of the fibers, it only affected the intensity of transmittance and might be appear a new band because several factor.

X-Ray Dffraction (Xrd)

The XRD diffractograms of cellulose and CNF are depicted in Fig. 3 . All spectra also seem like similar, but the difference of them is the intensity. The crystallinity percentage calculated by Eq. 2, while the crystal size measured by Eq. 3. The results are tabulated in Table 1. XRD patterns of F-CNC (Fig. 3) show diffraction peaks at $2\theta = 15,36^\circ; 20,59^\circ; 22,5^\circ;$ and $34,68^\circ$ as resultan of cellulose and CNF. Similar result were achived too by Du *et al* (9).

The crystallinity percentage and cystalline size showed the value of CrI increase while the cellulose to CNF. HaishunDu *et al* (9) also reported a similar result, the crystallinity of eucalyptus kraft pulp was 65,25% and crystalline size is 4,10 nm while after FA-hydrolysis using catalyst, the crystallinity increase until 75,45% and 4,66 nm. From the Table 1. It is evident by increasing the hydrolysis time also increasing the crystallinity percentage and crystalline size. The similar result also described by Sri Aprilia

Table 1: Characteristic of samples

No	Samples	Yield (%)	Cristallinity (%)	Crystallinity size (Å)
1	Cellulose	-	44,03	2,22
2	CNF A 6 h	79,33	76,296	3,54
3	CNF B 3 h	72,66	64,228	3,04

et al (5), at 1 h HCl-hydrolysis the crystallinity percentage is 82,3% with 6,23 nm crystalline size, and at 3 h HCl-hydrolysis the crystallinity percentage increase to 82,7% with 6,56 nm size.

The crystallinity percentage of cellulose is 44,03%, while Wulandari et al (3) reported, it was 70,62% although using a same raw material. It might be caused the different isolation of cellulose method. High crystallinity characterizes a regular arrangement of cellulose chains or a perfect crystal lattice. The crystalline structure is formed by the interaction of the hydrogen bonds through the intramolecular and extra molecular hydroxyl groups in adjacent cellulose. This increase in crystallinity is due to the decrease in amorphous fiber composition due to chemical treatment. Chemical treatment is directed to remove the amorphous fiber component. The amorphous part is more easily hydrolyzed than the crystalline portion, so treating the hydrolysis causes the fibers to become more crystalline (11) and (13).

Conclusions

1. Increasing the hydrolysis time is decreasing the yield of CNF. The yield of the F-CNF from bagasse was found increased from 74,66% for 3 h and 70,52% for 6 h.
2. Increasing the hydrolysis time does not affect the chemical compounds of CNF, but affected the transmittance intensity and new band might be appear.
3. Increasing the hydrolysis time also increasing the crystallinity percentage and crystal size. The CrI of the F-CNF for 3 h is 64,23% and 76,30% for 6 h. The crystal size is 3,04 Å for 3 h and 3,54 Å for 6 h

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