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PREPARATION AND CHARACTERIZATION OF SUGARCANE BAGASSE NANOCELLULOSE CRYSTALLINE USING ACID HYDROLYSIS WITH AND WITHOUT ULTRASONICATION

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ABSTRACT

The utilization of sugarcane bagasse to be nanocellulose as filler in polymer composites has been isolated. Nanocrystalline cellulose from bagasse was investigated using homogeneous hydrolysis of hydrochloric acid (HCl) with and without ultrasonication. The homogeneous process by using ultrasonication for 30 minutes. Four nanocellulose samples were prepared with and without homogeneous with HCl concentrations of 10 and 20%. Nanocellulose characterization was analyzed by Fourier transform infrared spectroscopy which indicated the presence of carboxyl groups from cellulose. The X-ray diffraction spectrum proved the presence of cellulose, with high crystallinity 68 and 65% by ultrasonication and 53 and 48% without ultrasonication with increased HCl concentration. The sizes of crystalline nanocellulose were decreased with increased HCl concentration, even though with and without ultrasonication. Furthermore, the nanocrystalline size was reduced from 4.37, 4.15, and 3.94 nm. Finally, with scanning electron microscopy, nanocrystalline cellulose analysis showed that the nanocellulose structure was like individual crystallites and was uniformly dispersed showing a needle-shaped structure. Nanocrystalline cellulose was found for this method can be used for reinforcement for polymer composites.

Keywords: Sugarcane Bagasse, Nanocellulose, Acid Hydrolysis, Ultrasonication

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INTRODUCTION

One method for isolating nanocellulose from lignocellulosic fibers is acid hydrolysis. The successful acid hydrolysis form cellulose particles in micron size that is called microcrystalline cellulose (MCC) to be nano-sized known as nanocrystalline cellulose (NCC) is very important. As green resources and environmentally friendly, agriculture waste such as sugarcane bagasse, oil palm solid waste, corncob, rice straw, and wheat straw are lignocellulosic fibers that can be used as sources to produce MCC and NCC. MCC and NCC can be used for many applications in the medical, packaging industries, cosmetics, and food.[1]

Cellulose $(C_6H_{10}O_6)n$ are contained about 40 to 50% in the plant cell walls.[2] The size of cellulose is very dependent on the sources as well as the manufacturing process and condition state during the isolation process.[3] By acid hydrolysis, conjunctival acid will be formed, if a complex heterogeneous reaction occurs so that cellulose is degraded. During acid hydrolysis, the dimensions of cellulose depend largely on the material from which it is originated and the method of preparation and process conditions chosen[4]. Homopolysaccharide consists of β-1-4 glucopyranose units and polymerization degree about 10.000 to 15.000 that has three hydroxyls (-OH) groups in each repeating unit of cellulose.[5,6] The hydroxyl groups and their capability are a crystalline form in the package and also arrange the physical properties of cellulose. In-plant fibers, cellulose is in the amorphous part and related to the crystalline part through intra-molecular and inter-molecular hydrogen bonds.[2] The user of an acid such as hydrochloric acid (HCl),

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Sulphuric acid (H_2SO_4), nitric acid (HNO_3), phosphoric acid (H_3PO_4), and formic acid in the isolation of MCC to be NCC effects in removing the amorphous part in the biomass. The use of acid hydrolysis in isolating cellulose is depending on the acid concentration and the hydrolysis time. Natural cellulose from biomass can be a transformer in the scale of micro to nanoscale materials, the kinds of product in form of cellulose microcrystalline, cellulose microfibrillar, and cellulose nanocrystals. In this form is very good properties as reinforcement in polymer composites. Isolated cellulose fibers given to different treatments produce different crystals. This is a good choice as a reinforcing agent because of its abundant hydroxyl groups, which allows it to be obtained from derivative materials that have adequate differences incompatibility, high crystallinity, strong mechanical, has a large specific surface area, and high aspect ratio, as well as good thermal stability.[7]

Many researchers have isolated MCC and NCC with various concentrated acids and from different lignocelluloses sources. However, the use of acid in process isolation is still lacking such as modifying the surface of cellulose to a surface that is has a negative charge and resulting from esterification of the hydroxyl groups in the presence of sulfate ions.[1] Until now, the mechanical method to isolate cellulose nanoparticles has still been produced. The different methods including mechanical treatment have been investigated such as ultrasonication, electrospinning, high pressure homogenizing, and steam explosion. The Ultrasonication process is needed to create strong ultrasonic waves of mechanical property due to cavitation, and to cause the disaggregation of MCC to NCC. In the high-pressure homogenizer instrument, the cellulose suspension is passed through a small high-pressure nozzle. To solve this problem, the researchers have used pre-treatment like refining, cryo crushing, and milling to reduce the size of the MCC. This process also needs high energy consumption when processing. Parameters that greatly influence the properties of nano cellulose obtained are pressure, time traversed on the machine, suspension concentration, and temperature. The main parts of the electrospinning process need to supply the high voltage, carry polymer solutions through syringes for and to collect nano cellulose.[8] One of the important parts of micron size to become nano size of cellulose that must increase the hydrophilic properties of cellulose at the environment in polar and nonpolar, and thus will increase compatibility with a wider variety of polymer matrices, therefore it is necessary to modify the process. The other reason, combination process has been done by researchers for a low yield of NCC production. As result, a huge amount of liquid slurry occurs and potential degradation of cellulose. Used acid hydrolysis and continue with ultrasonication help the decrease of size the nanostructure of NCC production.

In this study, the NCC prepared from sugarcane bagasse based on a combination process between acid hydrolysis and continues with the ultrasonication process. The result was also compared with and without ultrasonication. The morphology features, yield, and crystalline of NCC were analyzed by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The characteristic of the NCC structure of the functional group was determined by Fourier to transform infrared (FTIR).

EXPERIMENTAL

Preparation Samples

Sugarcane bagasse was collected from the seller of sugarcane juice in Darussalam, Banda Aceh, Indonesia. Sodium hydroxide (NaOH 1M) was used for pulping process. Sodium hypochlorite (NaOCl 5%) was used for bleaching sugarcane bagasse pulp. Various concentration of hydrochloride acid (HCl) was used for isolation nanocrystalline.

Preparation sample has done by drying sugarcane bagasse under the sun. The sample was cut into size ± 2 cm, then the sample was washed 3 times with distilled water. After that, the samples were dried at 60ºC in an oven for 24 hours and then stored at room temperature before use.

Preparation of Bleaching Pulp

The previously prepared sample was put into a three-neck flask containing approximately 25 grams of dry bagasse then hydrolysed using 500 ml of NaOH for one hour 30 minutes at 80ºC. Then the bleaching pulp was washed with distilled water 3 times in a centrifuge. Furthermore, added 150 ml NaOCl 5% and the reaction was continued for 20 minutes and a process temperature of 80ºC. The bleached pulp is washed with distilled water with a centrifuge several times to a pH of 7. Then the pulp is dried in an oven at 70ºC for 3 hours. This process follows the previous literature.[4]

Extraction of NCC

NCC prepared from drying bleaching pulp sugarcane bagasse by adding HCl 10 and 20% with a ratio of 1:30. The hydrolysis process is extinguished by stirrer at 450 rpm at temperature 80ºC and then continues with ultrasonication for 30 minutes as the homogeneous process. But for the other sample, it was without ultrasonication. The suspension of bleaching pulp was centrifuge at 4500 rpm for 30 minutes. NCC obtained was washed with distillate water and repeated several times by centrifuge. The last, NCC was dried for 2 hours at 80ºC. NCC from sugarcane bagasse has shown in Fig.-1. The NCC results are calculated accordingly Eq.-1[2].

$$yield\ (\%) = \frac{M_1 - M_3}{M_2 - M_0} x\ 100 \tag{1}$$

Where M_o is the initial mass of the NCC sample used, M_1 is the weight of the NCC that is ultimately the product obtained. M_2 is the mass of the NCC suspension used to prepare dry powders. M3 is the NCC mass suspension at the end of the process.

Fig.-1: Nanocellulose from Sugarcane Bagasse with and without Homogeneous

XRD Analysis

NCC crystallinity index and NCC crystal size were analysed by XRD. The XRD diffractometer uses measurement conditions at 40 kV and a current of 30 mA. The range of scattering angles was taken at (2θ) with an intensity of 10º to 80º and a speed of 10º / minute. The crystallinity index (CI) and crystal size (D) were calculated using the equation Eq.-2 and 3. Crystal sizes depend on the Scherer equation.

$$C_I\ (\%) = \left(1 - \frac{I_{am}}{I_{200}}\right) x\ 100 \tag{2}$$

$$D = \frac{0.9\lambda}{\beta_{hkl}\ cos\theta_{hkl}} \tag{3}$$

The crystallinity index (CrI) can be calculated from the intensity at the maximum peak of the diffraction grating (I_{200}) and I_{am} is calculated from the minimum intensity between 200 and 110 peaks. The amorphous has shown at I_{200} and the fraction of crystalline and I_{am} has shown as an amorphous region. To calculate the crystal size, K is used as the Scherrer constant (K = 0.9), λ is the wavelength of X-ray radiation (λ = 1.5406 Å) and β1/2 is the full width and half of the maximum Reflection, and θ is the Bragg angle.[1]

SEM Analysis

The surface morphology of NCC was analysed by SEM a Hitachi TM300 model. 0.01 g of NCC was dispersed in acetone and stirred evenly, then a drop of the solution was placed on cylindrical steel, then air-dried, then coated with a thin layer of platinum under vacuum. Surface morphologies were examined with an acceleration voltage of 10 and 15 keV.

FTIR Analysis

The functional group analysis of NCC was performed using FTIR. This analysis was used to find out the chemical bond of the sample. The analysis was recorded by Shimadzu Prestige FT-IR 6400 in the range of wavelength 4000 cm^{-1} to 400 cm^{-1} with room temperature. Before analysing the samples were milled together with KBr, with a ratio of 1:9 (NCC: KBr).

RESULTS AND DISCUSSION

Degree of Crystalline, Size of the Crystal and Yield

XRD studies for NCC HCl hydrolysis with and without ultrasonication were conducted to investigate the crystalline NCC behavior and results are shown in Fig.-1. Figure-2 shows the XRD analysis for crystallinity of NCC from sugarcane bagasse that has isolated from HCl 10% and 20%, with and without ultrasonication. All graphs showed the same pattern. The crystalline part of NCC showed three distinctive peaks around 2θ degrees at 15.64, 22.48, and 34.76. The primary peaks of cellulose attend at the peak of 22.48 degrees, which is the present crystalline part of NCC. At 2θ around 15.76 and 34.56 degrees are assigned to the amorphous region of NCC. The high peaks are crystalline region and the low peaks show the amorphous region[9,10]. This phenomenon applies to all four graphs, it can be concluded that not different for native cellulose between NCC with and without homogeneous with ultrasonication. The intensity of the peak decrease when continuous with homogeneous so that with homogeneous with ultrasonication cause increase the intensity. This pattern was consistent with the diffraction pattern report by the previous research.[11]

Table-1 shows the yield, percentage of crystallinity, and size of NCC from sugarcane bagasse. The yield of NCC increase with the increase of HCl concentration, and the yield of NCC increase with the ultrasonication process. The percentage of crystalline NCC decreases with the increase of HCl concentration and the percentage of crystalline NCC increase with the ultrasonication process. The degrees of crystalline NCC increased from the base on cellulose but slightly increase without ultrasonication. When homogeneous with ultrasonication, the degree of crystalline high increase at 76.30% and 68.09% for NCC HCl 10% and 20% respectively, but NCC HCl 10% still has a high value. With the high concentration of acid hydrolysis, the percentage of crystalline NCC decreases slightly. This result suitable for Aprilia and Abral [1,11] that implied raise in reaction time for acid hydrolysis caused the crystallinity value is decreased, this occurs because of the NCC crystalline damage during the longer reaction time. This was relevant that high concentration of acid, the partial destruction of crystalline part of NCC. In this study, the time of reaction hydrolysis will be longer because of continuing with ultrasonication. Cellulose crystallites are categorized as amorphous because they are imperfect and thus most of the cellulose structures are less regular. The relative amount of crystal portion in cellulose is called the crystal index parameter.

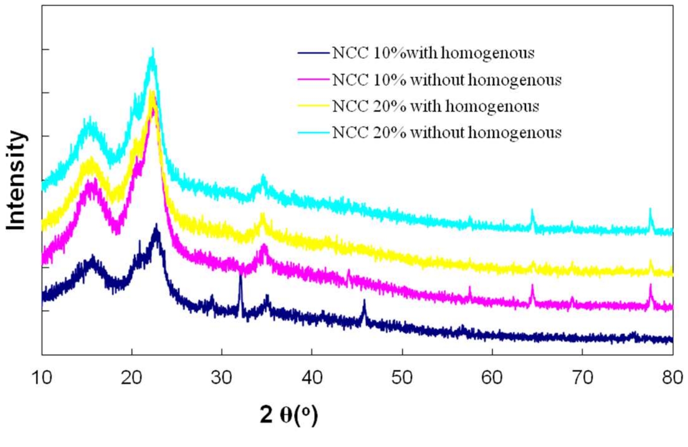

Fig.-2: XRD Analysis of NCC with and without Ultrasonication

Table-1 shows the size of NCC from XRD analysis calculates from Scherrer's formula (Eq.-2). This formula can imply crystallite sizes of 200 nm or less. XRD analysis was used to determine the crystallinity index and crystal size of nanocrystalline cellulose. Crystallinity index and crystal size are calculated by Eq.-1 and Eq.-2.

Table-1: Yield, Percentage of Crystalline, and Size of NCC From Sugarcane Bagasse

Sample	Yield (%)	Crystallinity (%)	Size of Crystalline (nm)
Cellulose	-	44.03	4.55
NCC 10%-with ultrasonication	68.56	76.30	4.17

NCC 10% without ultrasonication	67.33	53.15	4.35
NCC 20%-with ultrasonication	68.72	68.09	4.12
NCC 20% without ultrasonication	66.76	50.17	4.24

The crystal size of NCC from sugarcane bagasse decrease when continuing with ultrasonication increase for both concentration of acid. The high concentration of acid hydrolysis could be reducing of size NCC. The crystal size of NCC also became decrease when continuing with ultrasonication for both acid concentrations. The density fluctuation increases because of the removal of lignin and hemicelluloses and leaving behind the solid cellulose at the sources by continuing with ultrasonication. In this study, cellulose crystal was not disrupted after homogeneous with ultrasonication. The reduction of the crystalline size of the NCC suggests that the layer of the surface becomes more disordered and with the characteristic of the amorphous part. The crystallite size is also reduced because the cellulose chain present in the crystallite may become more irregular after modification. The difference that can be observed is to see a slight change in the peak intensity, which is to have a change in the crystalline of the fiber. In fibers with high cellulose content, generally, observed two peaks at 16° but, in this result, only one peak observed at about 15° confirms an amorphous part. This can be said that acid hydrolysis of cellulose is dissolved amorphous and less regular areas in cellulose fiber, leaving the whole crystal area[17].

Surface Morphology

The surface morphology of NCC is shown in Fig.-3 and 4. Figure-3(a) shows the surface morphology for NCC without ultrasonication and Figure-3(b) with homogeneous. The structure of NCC visually shows that the SEM structure of NCC with ultrasonication will decrease of the size than NCC without ultrasonication. Here, Fig.-3 and Fig.-4 are the SEM image for magnification 500x and 1000x in order. It was observed that the morphology of the NCC before and after homogeneous differs with the acid hydrolysis and ultrasonication process.

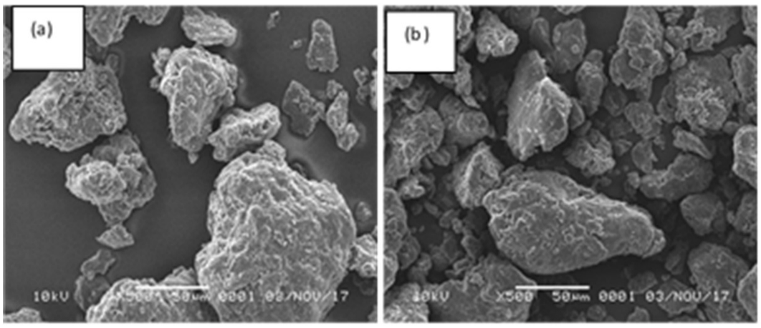

Fig.-3: Surface Morphology NCC Magnification 500x (a) without and (b) with Ultrasonication

Agglomerations form of NCC shows that the cellulose chain has strong intermolecular hydrogen bonds and hydrophilic interactions[12]. Nascimento[13] stated that the bundles of cellulose become individuals after acid hydrolysis. This occurred after the lignocellulosic complex removes from the fibers. They stated that in plant cells, lignin and hemicellulose are present between the cellulose microfibrils to form a discontinuous lamellar structure. The non-cellulosic compounds can be removed with bleaching agents. Fatah[14] concluded that the surface morphology of the treated NCC was not affected by acid hydrolysis, but was seen in the smaller particle dimensions on the formation of microfibrils. Kumar[12] mentions that after the ultrasonic process, the oligodynamic shear force is produced, which causes it to occur the nucleation, growth, and collapse of microbubbles inside the solution, and nanocrystalline was produced. Park[16] employed that structure of cellulose still not fully understood because of the complexity of its structure.

In the first step of acid hydrolysis, acid can diffuse favorably in the amorphous part of cellulose fibers and hydrolyzed the glycosidic bonds which easily accessible. The addition of the reaction time at the reduction end and on the surface of the remaining crystal portion occurs much more slowly.[1] Combination processes between acid hydrolysis continue with ultrasonication was able to break long cellulose from microfiber into cellulose nanocrystal, and finally resulting to reduce the size from micron to nano scale.[14]

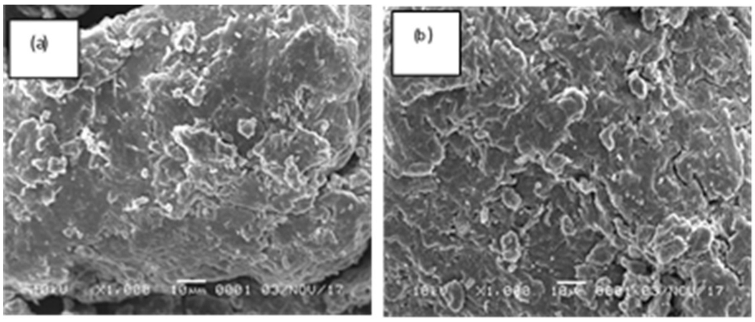

Fig.-4: Surface Morphology NCC Magnification 1000x (a) without and (b) with Ultrasonication

Functional Group

Figure-5 shows the functional group NCC from sugarcane bagasse that have functional groups at peak 3400 to 3500 cm^{-1}. All graphs show the same peak but different intensities. These show that no effect acid concentration with homogenous and without homogenous. The spectra at peak 3344 cm^{-1} the presence of a stretching vibration of –OH groups. This peak indicates H-bonding interactions in NCCs. The existence of -OH due to the moisture content, where the hydroxyl groups were obtained in cellulose, hemicelluloses and lignin[13]. The peaks observed at 2880 cm-1 corresponds to $-CH_2$ stretching. In these spectra, the vibration of CH_2 was observed of all the types of NCC.

The spectra at peak 1662 cm^{-1} indicated that carbonyl C=O stretching vibrations of the acetyl and uranic ester groups of hemicelluloses in the raw materials. The peak at 1510 cm^{-1} is a sign of the aromatic vibration of C=C in the lignin. The presence of the spectra at 1288 cm^{-1} indicates the C-O bond in the raw materials that out of plane stretching vibrations of aryl group in the presence of lignin[14]. The band at peak 1033 and 989 cm^{-1} estimated C-O-C stretching vibration which is considered as a typical bond of cellulose[2]. The peak corresponds to the glycosidic deformation of C-H, with the contribution of the vibration ring and the O-H bending[15]. Overall, all of the graphs were change slightly for intensity without and with ultrasonication in acid hydrolysis. The observation of FTIR spectra on the NCC with and without ultrasonication did not disrupt the chemical structure of the cellulose molecule.

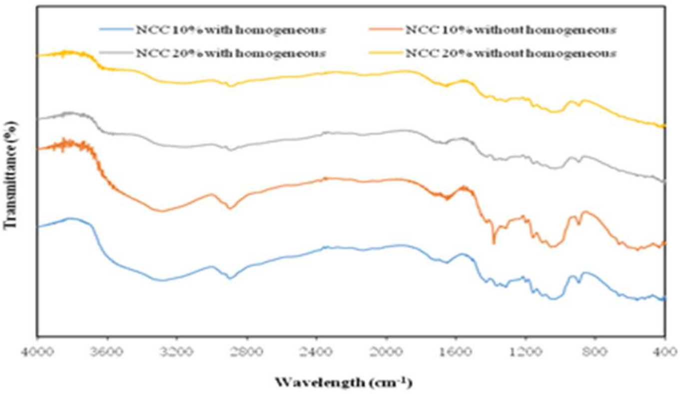

Fig.-5: Functional Group of NCC with and without Ultrasonication

CONCLUSION

1. The acid concentration and the ratio between acid and cellulose play an effective role in the form of NCC crystals. Analysis of XRD showed that the percentages of crystallinity increased from the based line of cellulose by 44.03%.
2. Percentage of crystalline of NCC HCl 10% and 20% decrease 2.98% without homogeneous and decrease 8% with homogeneous. For each NCC, the percentage of crystallinity increase 23.15% for NCC HCl 10% and 17.92% for NCC HCl 20%.
3. SEM analysis showed that acid hydrolysis did not affect the morphological structure of the NCC with and without homogeneity, but was shown in smaller particle dimensions.
4. FT-IR analysis showed that acid hydrolysis had no effect on the chemical structure of NCC with and without being homogeneous and was effective in removing lignin and hemicellulose from crude

cellulose fibers. The high concentration of acid (HCl 20%) and continuous homogeneities with ultrasonication give good NCC production.

5. The combination process of hydrochloric acid hydrolysis and homogeneous with ultrasonication process could be utilized as an effective chemical and mechanical process for nanocellulose production from various cellulosic sources.

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