

EXTRACTION OF CELLULOSE MICROFIBRILS FROM NON-WOOD LIGNOCELLULOSIC MATERIAL USING BIOREFINERY CONCEPT

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The cellulose microfibrils (CMF) from natural lignocellulosics are newly understood and exciting biomaterial constituent that can provide strong reinforcement in many products, including polymer composites. In this study, the cellulose crystals were extracted from jute and bagasse fibers based on the formic acid/ peroxyformic acid/peroxide process at atmospheric pressure, and their yields were 59.8 and 38.1%, respectively. Considering the biorefinery concept, the dissolved lignin and hemicelluloses in the processes were also isolated from the spent formic acid liquor. The results showed that the spent liquor contained 10.6 and 28.2% (on oven dried raw material) total sugars, and 10.9 and 16.9% lignin for jute and bagasse fibers, respectively. The xylose was the dominant sugar in the spent liquor. The cellulose microfibrils were further prepared from the extracted cellulose based on the acid hydrolysis technique. A very high yield of cellulose microfibrils (48.0 % based on the jute raw material) was obtained from jute fibers, while only 18.2% yield was obtained from the bagasse. The acid hydrolysate of jute cellulose contained 5.52% sugar, while bagasse hydrolysate contained 17.71% of sugars. The CMF samples obtained from the two different raw materials were characterized by means of TGA, FTIR, XRD, and TEM techniques. The average diameter of the CMF was 15-40 nm. The XRD results revealed that both CMF had a high crystallinity index. The thermal stability of MCC/NCC from the jute fibers was higher than that from the bagasse.

Keywords: Cellulose Microfibrils; Jute fiber; Bagasse; Biorefinery; Xylose; Lignin

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INTRODUCTION

A variety of commercial products currently manufactured from declining fossil resources can be replaced from renewable raw materials compatible with sustainable development. In this context, the chemical processing of biomass provides an interesting alternative for manufacturing organic chemicals at an industrial scale. To this end, lignocellulosic materials (LCM) show interesting features, including their widespread availability, renewability, and low cost (especially in the case of waste materials). LCM are mainly composed of cellulose (a homopolysaccharide made up of glucose units), hemicelluloses (heteropolysaccharides made up of sugars and nonsaccharide substituent's), and lignin (a polymer made up of phenyl propane units) as main components along with extractives and ashes as minor components. These polymers have

an incredible potential to fulfill the energy and chemical needs of industry while minimizing environmental impacts and increasing sustainability (Gassan and Bledzki 1997; Hornsby *et. al.* 1997; Panthapulakkal *et. al.* 2006; Sain 1994).

In a biorefinery, all kinds of biomass are separated into cellulose, hemicellulose, and lignin, which are further processed into ethanol, adhesive, sorbierite, lactic acid, and other chemicals. Biorefining is the first step in applying an *integrated biomass technologies* approach. Biorefining covers the use of all components of biomass to yield products, such as liquid transportation fuels, chemical feedstocks, and energy (van Heiningen *et. al.* 2006). The approach is for maximizing value, performance, resource sustainability, and profitability in the agriculture and forest product industries. Cellulose microfibrils is obtained from the cellulose, which is a major fraction of a biorefinery process, will be used to manufacture innovative high-strength biocomposites necessary for advanced structures.

Cellulose is composed of assemblies of microfibrils (O'Sullivan 1997), which form slender and nearly endless rods. Through acid and/or enzymatic hydrolysis, these microfibrils break down into short crystalline rods or “cellulose micro/nano-crystals.” With a very high modulus of elasticity, estimated to be 138 GPa (Nishino *et. al.* 1995) for the crystalline phase and a calculated specific-surface-area of several hundreds of m²/g, low-cost, low density, low energy consumption, easy processability, renewable nature, and recyclability, cellulose nanocrystals have attracted considerable attention for exploring new applications.

Bangladesh is a forest deficient country with only 10.2% forest coverage. So it is hard to produce a sustainable supply of wood for biorefinery. On the other hand, a huge amount of agricultural wastes such as corn stalks, rice straw, wheat straw, bagasse *etc.* is remained as left over after harvesting crops. These agricultural wastes are good sources of cellulose, hemicelluloses, and lignin. So these may be used as starting materials in an integrated forest biorefinery.

Different technologies have been used for the isolation of MCC/NCC from lignocelloses such as high-pressure homogenizer (Zimmermann *et. al.* 2010), cryocrushing (Alemdar and Sain 2008), ultrasonics (Zhao *et. al.* 2007), high shear ultrafine friction grinders (Iwamoto *et. al.* 2008).

In this project, we followed the biorefinery concept to process bagasse and jute fibers. The scope of the study reported here includes: i) Bagasse and jute fibers were fractionated into cellulose, hemicelluloses, and lignin based on the formic acid and peroxyformic acid treatment processes; ii) the cellulose fraction was subsequently transformed into micro- and nano-crystalline cellulose (MCC, NCC) based on acid hydrolysis; iii) the prepared NCC samples were characterized based on the Thermo Gravimetric Analysis (TGA), Fourier Transform Infrared (FTIR), X-ray Diffraction (XRD), and Transmission Electron Microscope (TEM) techniques.

EXPERIMENTAL

Materials

Retted jute fibers and bagasse were collected from the Narayangong and Dhaka district of Bangladesh, respectively. Pith from bagasse was separated by hand. The chemical composition of jute fibers was 63.1% α -cellulose, 12.7% lignin, and 13.5% pentosan (Jahan *et al.* 2007), while the chemical composition of bagasse was 44.2% α -cellulose, 17.9% lignin, and 23.9% pentosan (Jahan *et al.* 2009).

Formic Acid (FA) Treatment

The jute fibers and bagasse were refluxed with formic acid separately in a hotplate under the following conditions:

- 90% (v/v) formic acid concentration
- 120 min reaction time at boiling temperature.
- Liquor to fiber ratio: 8 (v/w).

At the completion of the reaction time, the fibers were filtered in a Büchner funnel and washed with fresh formic acid, followed by hot distilled water.

Peroxyformic Acid Treatment

The formic acid treated fibers were further delignified with peroxyformic acid (PFA) at 80 °C. PFA was prepared by mixing 90% formic acid with 4% H₂O₂. The reaction was carried out in a thermostatic water bath. Upon the completion of 120 min, the fibers were filtered off and washed using an 80%-formic acid solution.

Bleaching

Bleaching experiments of pulp were carried out at a 10% pulp concentration. The pH was adjusted to 11 by adding the required amount of sodium hydroxide (NaOH). The hydrogen peroxide charge was 4% (on fiber material). The temperature and time of bleaching were 80 °C and 1 h, respectively. The pulp yield was determined gravimetrically. The α -cellulose content in the bleached jute fibers was determined according to TAPPI Test Methods (T 203 om-88).

Preparation of CMF

The micro-fibrils were produced by following a literature procedure (Dong *et al.* 1998) under the conditions of 64% w/w sulphuric acid solution (the high acid concentration method) for 5 h at 55 °C with constant stirring. The hydrolysis was stopped by adding a large volume of water to the reaction mixture. The resulting mixture was washed with cold water and centrifuged repeatedly till pH is neutral.

Isolation of Lignin and Sugar

The lignin dissolved during the delignification with formic acid and peroxyformic acid was precipitated by adding water to the concentrated spent liquor (five times more than the volume of formic acid). The residue was filtered in a Büchner funnel and washed with water and vacuum dried over P₂O₅. The filtrate was subjected to the sugar analysis.

Sugar Analysis

The sugar concentrations were determined by using an Ion Chromatography unit equipped with CarboPac™ PA1 column (Dionex-3000, Dionex Cooperation, Canada) and a pulsed amperometric detector (PAD), (Li *et. al.* 2010). The further acidic hydrolysis of the pre-hydrolysis liquor (PHL) in 4% sulphuric acid was carried out at 121 °C in an oil bath (Neslab Instruments, Inc., Portsmouth, N.H., USA) to convert oligosaccharide to monosaccharide. The PAD settings were E1 = 0.1 V, E2 = 0.6 V, and E3 = -0.8 V. Deionized water was used as eluant with a flow rate of 1 mL/min, 0.2 N NaOH was used as the regeneration agent with 1 mL/min flow rate, and 0.5 N NaOH was used as the supporting electrolyte with 1 mL/min flow rate. The samples were filtered and diluted prior to analysis. The sugar content in the PHL before the acid hydrolysis represented the monomeric form while the oligomeric sugars were calculated from the difference with and without the acid hydrolysis (Li *et. al.* 2010).

X- ray diffractometry

The X-ray powder patterns for micro-fibrils were scanned and recorded using the Bruker D8 Advance spectrometer with a D-5000 rotating anode X-ray generator from 10-40 of 2 Θ (scanning angle), using Cu K α radiation generated at 30 mA and 40 kV. The crystalline indices of samples were calculated from the X-ray diffraction patterns based on the following equation 1 (Hermans and Weidinger 1950),

$$Xc = I_{002} - I_{am} / I_{002} \times 100 \quad (1)$$

where Xc is the crystallinity index, I_{002} is the peak intensity from the 002 lattice plane (2-theta= 22°), and I_{am} is the peak intensity of the amorphous phase.

Transmission Electron Microscope (TEM)

The TEM observations were made with JOEL 2011 STEM. For TEM, a 20 μ L drop of solution was pipetted onto a carbon coated copper grid.

Fourier Transform Infrared (FTIR) spectroscopy

The dried samples were embedded in KBr pellets, and were analyzed by using a Shimadzu FTIR spectrometer (model 8201PC). The spectra were recorded in the absorption band mode in the range of 4000 to 400 cm^{-1} .

Thermo Gravimetric Analysis (TGA),

The thermal gravimetrical analysis was performed with about 5 mg of air-dried sample using a Perkin-Elmer set-up (TAQ 500) and a heating rate of 20 °C/min under a Nitrogen atmosphere.

RESULTS AND DISCUSSION

Fiber Fractionation

The FA/PFA/H₂O₂ fractionation of bagasse and jute fiber is shown in Table 1. The cellulose yield was 59.8 and 38.1% for jute fiber and bagasse, respectively. The

cellulose yield in jute fiber was very high in comparison with the bagasse and other nonwood material. For example, the yield from reed canary grass by the formic acid treatment, followed by peroxyformic acid treatment, was 50.9% (Seisto and Poppius 1997). The FA/PFA treatment of dhaincha (a potential industrial crop) resulted in a yield of about 49.2% (Jahan *et al.* 2007a). The high yield from jute (59.8%) in such a process is due to i) very high α -cellulose content in the initial raw materials (Jahan *et al.* 2007b); and ii) the α -cellulose was highly protected, hardly removed, while the lignin and hemicelluloses were removed in such a process (Pan and Sano 2005). The higher purity of cellulose (α -cellulose content 97.8% and 94.8 for jute and bagasse, respectively), indicated that hemicelluloses and lignin were effectively removed by the FA/PFA/H₂O₂ process.

Table 1. FA/PFA/H₂O₂ Fractionation of Jute and Bagasse

Raw materials	Cellulose fraction		Spent liquor	
	Yield (% on original material)	α -cellulose (% on cellulose)	Total solid (% on original material)	Lignin (% on original material)
Jute	59.8	97.8	16.1	10.9
Bagasse	38.1	94.8	32.9	16.9

Mass Balance

The recovered cellulose, lignin, and solid content in the spent liquor after precipitating lignin in the FA/PFA/H₂O₂ process was 86.8 and 87.9%, for jute and bagasse, respectively (Table 1). This solid content (after separating lignin) mainly consists of sugars (mono and oligo) and acid soluble lignin (Table 2). The total recovered biomass was relatively lower due to: i) some biomass components, such as lignin, hemicelluloses, volatile compounds (*e.g.* methanol) was lost during the alkaline peroxide treatment, which has been well supported by the literature results, for example, in the alkaline peroxide process, He *et al.* (2004, 2004a) reported that methanol was formed; ii) the formation of 4-O-methyl glucuronic acid and other degradation products, which were lost from the process (He *et al.* 2004); iii) inorganic compounds dissolved from jute and bagasse, which were not considered.

Table 2. Chemical Compositions of Spent Liquor (% on original material).

Raw materials	Sugars in spent liquor filtrate (%)							Lignin (%)
	Arabinose	Galactose	Glucose	Xylose	Mannose	Ramnose	Total	
Jute	0.31	0.44	0.95	8.45	0.43	0.11	10.69	1.88
Bagasse	1.21	0.48	7.53	15.49	3.51	0	28.22	2.61

Table 3. Chemical Compositions of Cellulose Hydrolysate (% on cellulose)

Raw materials	Arabinose	Galactose	Glucose	Xylose	Mannose	Ramnose	Total
Jute	0	0	5.2	0.32	0	0	5.52
Bagasse	0.072	0.058	11.36	6.22	0	0	17.71

The recovered lignin from the spent liquor was 10.9% and 16.9%, which represented 85.8% 94.4% of the Klason lignin content in jute fiber and bagasse, respectively. Seisto and Poppius (1997) found 11.3 to 13.0% lignin (based on original materials) from different grasses in the FA/PFA process, which accounted for 56 to 59% of the Klason lignin. Following the biorefinery concept, lignin is likely to become valuable source of renewable energy, syngas reformation (*i.e.* Fischer-Tropsch catalysis) and can be the starting material for high value-added applications in renewable polymeric materials development such as plastics, adhesives, *etc.* to the biorefinery due to its phenolic-rich compositions

The sugar compositions (monomeric and oligomeric) in the formic acid spent liquor are shown in Table 2. In the FA/PFA treatment, 10.7 and 28.2% of the sugars of the jute fiber and bagasse were extracted, respectively. Xylose/xylan accounted for nearly 80 and 54.9% of the total sugars dissolved during the treatment from jute fiber and bagasse, respectively, while the glucose/glucan content were only 8.9 and 27.7% of the total sugars in the spent liquor. The high proportion of glucose in bagasse was due to the presence of residual sucrose. Pan and Sano (2005) reported that 63.5% of xylose/xylan was dissolved in the spent liquor during the acetic acid treatment of wheat straw, while cellulose was highly protected. Lam *et. al.* (2001) observed that over 80% of pentose sugars were dissolved from rice straw in the formic acid treatment at atmospheric pressure. Xylose/xylan can be converted into xylitol, furfural, and others by chemical or enzymatic processes.

Cellulose Microfibrils (CMF) Preparation

CMF can be prepared from the acid hydrolysis (Dong *et. al.* 1998). This is because acid hydrolysis is effective in dissolving the amorphous cellulose. The residue is pure cellulose, which is in the form of micro- crystalline cellulose. After acid treatment, fibrillated bagasse and jute cellulose are shown in Fig. 1. The chemical treatment of cellulose resulted in defibrillations to nanofibers from the cell walls. Determination of the width of bagasse fibrils was not possible, as it was mashed.

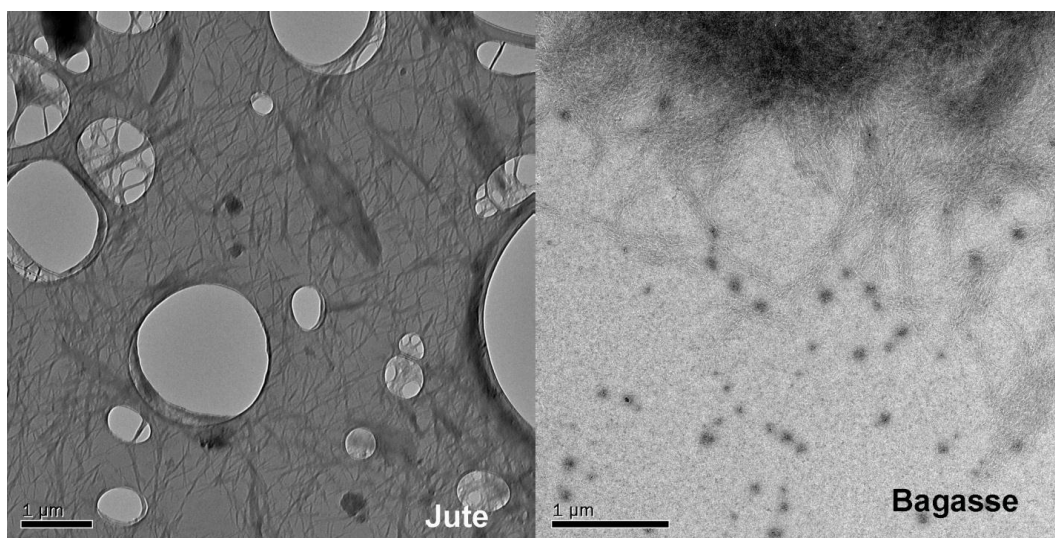


Fig. 1. TEM image of jute and bagasse cellulose micro-fibrils

Fourier Transform Infrared (FTIR) Spectroscopy

FT-IR spectroscopy is a non-destructive method for studying the physico-chemical properties of lignocellulosic materials. The FT-IR spectra of jute and bagasse CMF are shown in Fig. 2. The band for acetyl and uronic ester groups of the hemicelluloses at 1714 cm^{-1} (Sain and Panthapulakkal 2006, Sun *et al.* 2008) was absent in both CMF, which indicates that the prepared NCC was completely pure. The absorbency at 901 cm^{-1} , 1033 cm^{-1} , 1114 cm^{-1} , and 1158 cm^{-1} increased weakly, whereas the absorbencies at 1201 cm^{-1} , 1237 cm^{-1} , 1281 cm^{-1} , 1316 cm^{-1} , 1336 cm^{-1} , 1373 cm^{-1} , 1431 cm^{-1} , and 2900 cm^{-1} did not change. This indicates that the effect of acid first was on the surface and amorphous zone broken, and more C-OH, C-O-C and C-C types of bonds were exposed, thereby the stretching absorbency increased (Sun *et al.* 2008). In the spectra of jute CMF, there was an obvious absorption at 710 cm^{-1} and weak shoulder at 750 cm^{-1} while in bagasse CMF, both bands were observed. The bands at 750 and 710 cm^{-1} were assigned to I_{α} (triclinic) and I_{β} (monoclinic) (Sygiyama et al 1991). These results indicate that both CMF were rich in I_{β} , and the I_{β} proportion in the jute CMF was higher than the bagasse CMF.

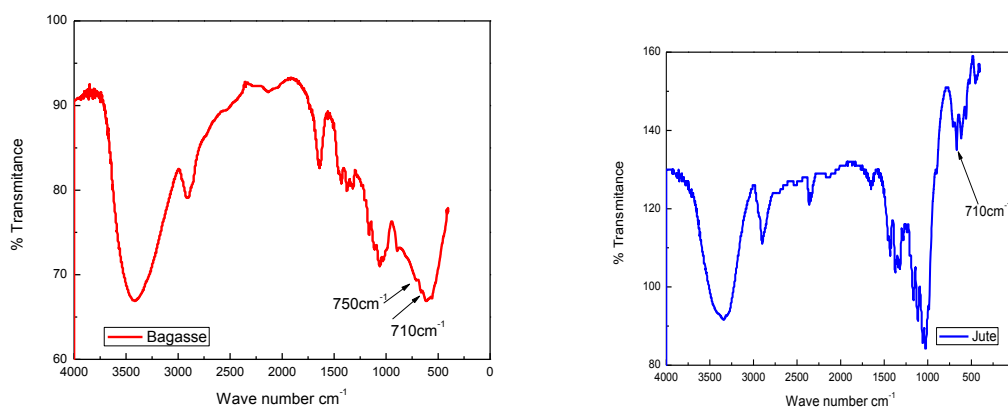


Fig. 2. FT-IR spectra of bagasse and jute cellulose micro-fibrils

Thermo Gravimetric Analysis

Investigation of the thermal properties of the natural fibers is important in order to estimate their applicability for biocomposite processing. Figure 3 shows the TGA results obtained from jute fiber and bagasse micro-fibrils. In general, there were three stages of degradation in the TGA curves of both samples. The initial weight loss of microfibrils ($100\text{--}150\text{ }^{\circ}\text{C}$) is due to the evaporation of the adsorbed moisture. This loss depends on the initial moisture content of the samples. The decomposition peak of the maximum mass loss for jute micro-fibrils was at $315\text{ }^{\circ}\text{C}$, while for bagasse micro fibrils it was at $200\text{ }^{\circ}\text{C}$ and $410\text{ }^{\circ}\text{C}$. It is interesting to note that maximum thermal decomposition of bagasse micro-fibrils starts at 150 and $367\text{ }^{\circ}\text{C}$. Li *et al.* studied the degradation behavior of NCC. They observed that the degradation of NCC occurred within a wider temperature range similar to bagasse CMF (Li *et al.* 2010).

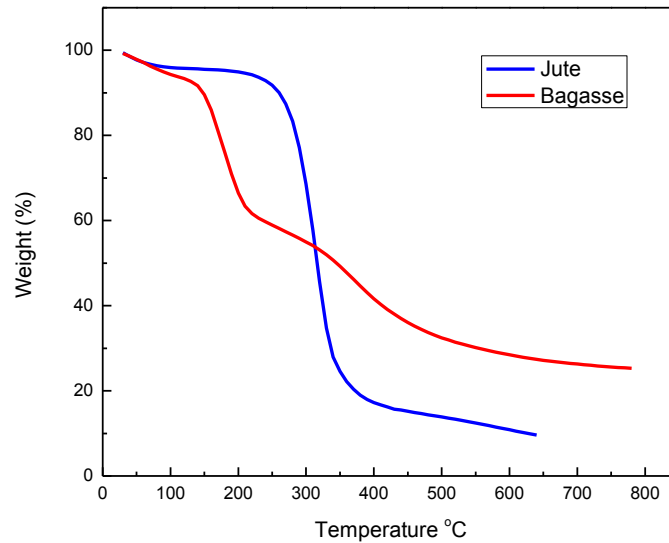


Fig. 3. Thermo Gravimetric Analysis (TGA) of bagasse and jute cellulose micro-fibrils

X-Ray Diffraction

The X-ray diffraction pattern of the jute and bagasse micro-fibrils samples is shown in Fig. 4. The peak at $2\theta = 22^\circ$ is sharper for both samples, indicative of higher crystallinity degree.

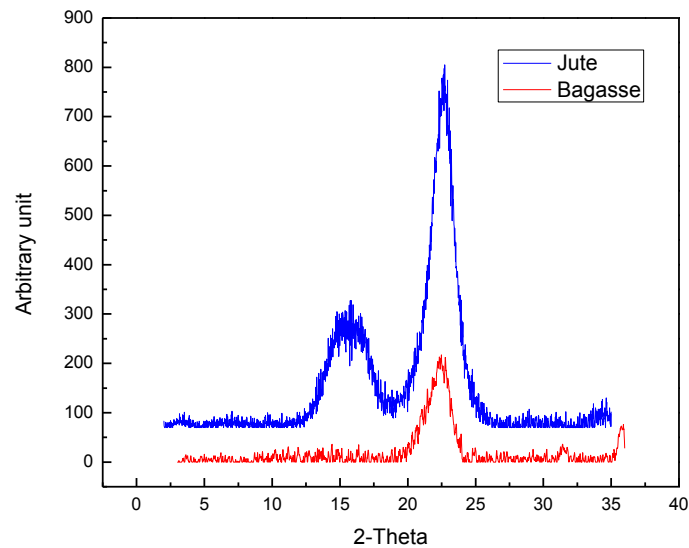


Fig. 4. X-ray defraction of bagasse and jute cellulose micro-fibrils.

The crystallinity index of cellulose was found as 74.9% for the jute microfibrils and 85% for bagasse microfibrils. Acid hydrolysis increased the crystallinity degree might

be due to the removal of amorphous portion of cellulose fibers and residual hemicelluloses (Nuruddin *et al.* 2011). Rosa *et al.* (2010) reported that the preparation conditions affected the degree of crystallinity of cellulose nanowhiskers. They showed that samples hydrolyzed for 120 min had the highest crystallinity. It was reported that the crystallinity degree increased with the transformation of micro-to nano- fibrils (Lee *et al.* 2009). Leonard and Martin (2002) observed that the crystallinity degree of jute fiber was 71%. The crystallinity index of flax and rutabaga nanofibrils was estimated to be 59% and 64%, respectively (Bhatnagar and Sain 2005). Yu *et al.* obtained NCC with crystallinity index of 72% (Yu *et al.* 2012). The higher crystallinity is associated with its higher tensile strength of the micro-fibrils.

CONCLUSION

The formic acid/ peroxyformic acid/ hydrogen peroxide process effectively removed lignin and hemicelluloses from bagasse and jute fibres, as indicated by the very high α -cellulose content in pulp. The measured amount of dissolved lignin and hemicelluloses in the spent liquor were 16.9% and 28.2% for bagasse, and 10.9% and 10.7% for jute fibre, respectively. The acid hydrolysis of bagasse and jute cellulose produced nano-sized microfibrils. Acid hydrolysis removed the amorphous part of cellulose consequently increased crystallinity. Jute CMF had higher monoclinic structure than that of bagasse CMF. The degradation temperature of jute CMF was 315 °C, while bagasse CMF was degraded at 200 and 410 °C, which may be due to wider range of molecular mass.

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