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Preparation and characterization of nanocellulose from sugarcane bagasse

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ABSTRACT
Nanocellulose (NC) was extracted from sugarcane bagasse (SCB) by acid hydrolysis. Alkalization and bleaching were used to treat SCB before the acid hydrolysis. The hydrolysis was carried out at 45 and 60°C for 90 and 180 min. Chemical structure, crystallinity and thermal stability of the materials were studied using Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD) analysis and thermogravimetric analysis (TGA), respectively. Morphology and particle size of nanocellulose were also studied using field emission scanning electron microscope (FE-SEM). FTIR results confirmed that lignin and hemicellulose were eliminated after alkali and bleaching treatments. These chemical treatments resulted in an improvement in the crystallinity and thermal stability of SCB. Sphere shape nanocellulose particles were observed by FE-SEM. With increasing hydrolysis time and temperature, the crystallinity of nanocellulose was increased but particle size and thermal stability were decreased.
Keywords: *sugarcane bagasse; nanocellulose; acid hydrolysis; crystallinity; morphology; thermal stability.*

1. INTRODUCTION
Nowadays, nanocelluloses fillers are of great interest in regenerative medicine, printing applications, optical application, food packaging, cosmetics packaging, and composites materials [1,2]. Nanocellulose has superior properties such as high specific surface area, high modulus, low axial thermal expansion coefficient [3]. The extraction of nanocellulose from cellulosic materials such as rice straw, coconut coir, corn cob, hemp, sisal, cassava bagasse, sugarcane bagasse and wood has received great attention because of their environmentally friendly materials, renewable nature, low density, low toxicity [4-9]. Nanocellulose can be extracted by acid hydrolysis, steam explosion or mechanical process [8,10,11]. Acid hydrolysis is one of the main processes to extract nanocellulose from materials. Sulfuric acid is mostly used for acid hydrolysis because it strongly isolates nanocellulose and makes nanocellulose dispersed as a stable system [3, 12].

Sugarcane bagasse (SCB) is a waste from the sugar industry. Sugarcane bagasse fiber consists of cellulose 47.4 %, hemicellulose 29.1 % and lignin 23.5 % [4]. In Thailand, there are more than 130 million tons of sugarcane production in recent years and tend to increase the amount of bagasse as much as 29% [13]. Using SCB to prepare nanocellulose is not only adding value to SCB but also benefiting material waste.

The objective of this study was to investigate the effects of hydrolysis time and temperature on particle size, chemical structure, crystallinity and thermal stability of nanocelluloses.

2. MATERIALS AND METHODS
2.1. Materials.
Sugarcane bagasse (SCB) was collected from Nakhon Ratchasima, Thailand. Sugarcane bagasse was cleaned and dried in sunlight for 4 days, and then cut into 1-3 cm. The cut bagasse was ground and sieved under 60 mesh sieves. The ground bagasse was dried in an oven at 40°C for 24 h.

Other reagents used were sulfuric acid (ACL Labscan), sodium hydroxide (ACL Labscan), sodium chlorite (Ajax Finechem), and glacial acetic acid (ACL Labscan). All chemicals were used as received.

2.2. Methods.
2.2.1. Isolation of cellulose.
The ground bagasse was treated with sodium hydroxide aqueous solution of 15% (w/v) (fiber to liquor ratio of 1:50) for 4 h at 100°C under mechanical stirring and then washed with distilled water until neutral, and finally dried at 40°C for 24 h in a hot air oven. After that, the fibers were bleached with an equal parts (v/v) solution of acetate buffer and sodium chlorite aqueous solution of 1.7% (w/v) for 6 h at 80°C. The bleached cellulose (BC) was washed in distilled water until the pH of the fibers became neutral and dried at 40°C for 24 h in a hot air oven [14].

2.2.2. Preparation of nanocellulose.
The bleached cellulose (BC) was hydrolyzed with a sulfuric acid solution of 60% (v/v) (fiber to solution ratio of 1:20) The hydrolysis was performed at 45 and 60°C for 90 and 180 min. The suspension was sonicated for 10 min in an ice bath to avoid overheating. The prepared nanocelluloses (NC) were referred as NC45/90, NC45/180, NC60/90 and NC60/180 for 45 and 60°C hydrolysis temperature and at 90 and 180 min hydrolysis time.

2.3. Characterization.
2.3.1. Fourier transform infrared spectroscopy (FTIR) analysis.
FTIR spectra of SCB, BC, NC45/90, NC45/180, NC60/90 and NC60/180 were performed in the attenuated total reflection mode(ATR) at a resolution of 4 cm^{-1} and number of scan of 64 in the range of 4000-400 cm^{-1} using Fourier transform infrared spectrometer (FTIR, Bruker, T27/Hyp2000).

2.3.2. X-ray diffraction (XRD) analysis.

The crystallinity of SCB, BC, NC45/90, NC45/180, NC60/90 and NC60/180 was measured by X-ray Diffractometer (XRD, Bruker D2 PHASER), operating at 40 kV/40 mA with Cu Kα radiation in the range of 2θ = 5-50° The crystallinity index (I_C) is calculated using equation (1) [15].

$$I_C = \left[\frac{I_{200}-I_{am}}{I_{200}}\right] \times 100 \quad (1)$$

where I_{200} is the overall intensity of the peak at 2θ about 22° and Iam is the intensity of the baseline at 2θ about 18° .

2.3.3. Thermogravimetric analysis (TGA).

Thermogravimetric analysis of the samples was performed using a thermogravimetric analyzer (TGA, Mettler Toledo). The scanning range was 35 to 600 ℃ at a heating rate of 10 ℃/min in nitrogen atmosphere.

2.3.4. Morphological analysis.

Nanocellulose morphologies were determined by field emission scanning electron microscope (FE-SEM, Zeiss AURIGA). The nanocellulose was diluted with distilled water and dropped into an aluminium stub and then air-dried. The samples were coated with gold before analysis.

3. RESULTS

3.1. Fourier transform infrared spectroscopy (FTIR) analysis.

Figure 1 shows the FTIR spectra of SCB, BC, NC45/90 NC45/180, NC60/90 and NC60/180. A peak at 1735 cm^{-1} represented C=O of either acetyl groups in a hemicellulose or the ester linkages of lignin. A peak at 1591 cm^{-1} was C=C of an aromatic ring in lignin [15,16]. The peaks located at 1037 cm^{-1} and 3360 cm^{-1} were attributed to C-O-C of pyranose ring skeletal and OH of acid, methanol in cellulose. A peak at 1270 cm^{-1} was C-O-C of aryl-alkyl ether in lignin [16]. The peaks at 1735 cm^{-1}, 1591cm^{-1} and 1270 cm^{-1} were disappeared after alkali and bleaching treatments due to the removal of lignin and hemicellulose [17]. However, there was no change of FTIR spectra of NC when compared to BC. This confirmed the lignin and hemicellulose were removed during cellulose isolation process [14].

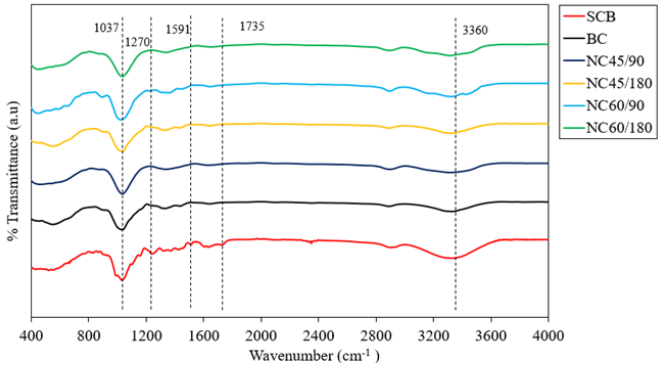

Figure 1. FTIR spectra of SCB, BC and NC.

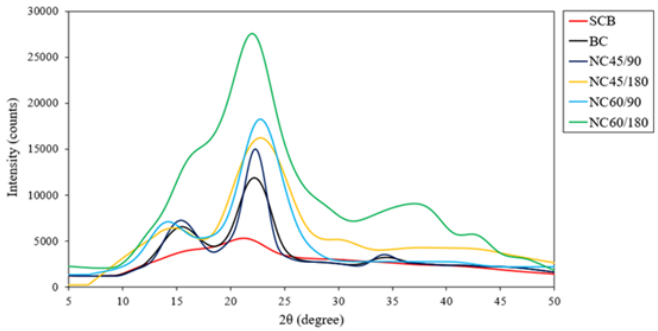

Figure 2. X-ray diffraction patterns of SCB, BC and NC.

3.2. X-ray diffraction (XRD) analysis.

X-ray diffraction patterns of SCB, BC and NC are displayed in Figure 2. The high peak intensity around 2θ = 22° was represented the crystalline structure of cellulose. The peak at 2θ = 14-16° was indicated in the amorphous region of cellulose [18,19]. The crystallinity index of SCB, BC and NC are listed in Table 1. The crystallinity index of BC was higher than that of SCB because lignin and hemicellulose were removed during alkali and bleaching processes [20,21]. The crystallinity index of nanocellulose was increased with increasing hydrolysis time and temperature. This was because paracrystalline domains were eliminated during the acid hydrolysis [14].

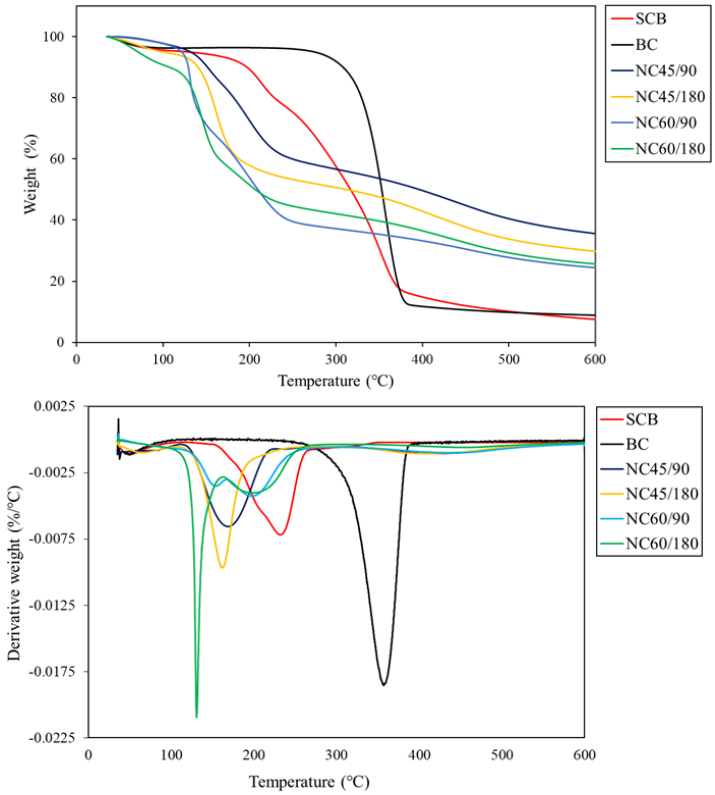

Figure 3. TGA and DTG curves of SCB, BC and NC.

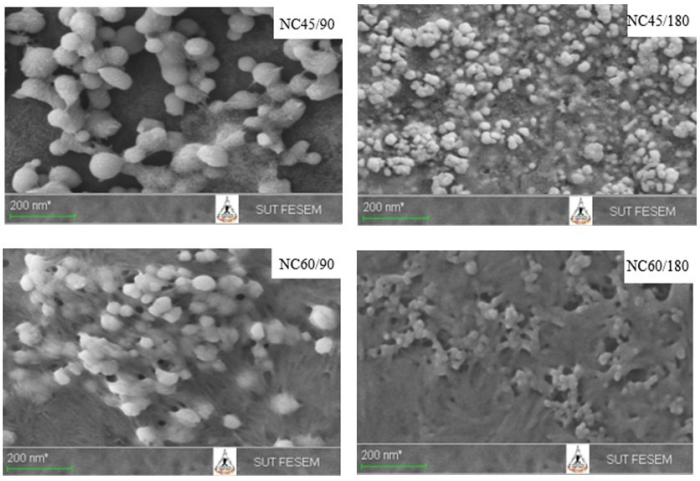

Figure 4. FE-SEM micrographs of NC (magnification: 50000x).

Table 1. Crystallinity index of SCB, BC and NC.

	Crystallinity index (%)
SCB	48
BC	52
NC45/90	59
NC45/180	60
NC60/90	65
NC60/180	89

3.3. Thermogravimetric analysis (TGA).

TGA and DTG curves of SCB, BC, NC45/90, NC45/180, NC60/90 and NC60/180 are shown in Figure 3. The initial weight loss below 100°C was evaporation of the water of the materials. The first stage thermal decomposition of SCB was at 185°C which was a decomposition of hemicellulose. The second stage decomposition temperature at 233°C was a decomposition of cellulose [21,22]. For BC, the weight loss occurred in the range of 260-390°C, maximum at 357°C due to cellulose degradation [15, 20,23]. Thermal stability of BC was higher than SCB because lignin and hemicellulose which had lower thermal stability were removed. It was found that NC had lower thermal stability than BC due to their nano-size, a greater number of free ends in the chain of NC and a drastic reduction in molecular weight and highly sulfated amorphous regions during acid hydrolysis [9,21,22]. With increasing hydrolysis time and temperature, thermal stability of NC was decreased. This may result from a dramatic reduction in molecular weight [15].

3.4. Morphological analysis.

FE-SEM micrographs of NC are shown in Figure 4. The sphere shape nanocellulose particles were observed. The average particle size of NC45/90, NC45/180, NC60/90 and NC60/180 were 104.87±1.35, 43.09±1.27, 80.39±2.06 and 39.15±1.52 nm, respectively. Particle size of nanocellulose decreased with increasing hydrolysis time and temperature. This may be because during acid hydrolysis, not only amorphous parts were eliminated but also some parts of cellulose crystalline were destructed [14].

4. CONCLUSIONS

The sphere shape nanocellulose was successfully prepared from sugarcane bagasse by acid hydrolysis. Hemicellulose and lignin were removed during alkali and bleaching processes. Particle size of nanocellulose decreased when hydrolysis time and temperature were increased. Increasing hydrolysis time and temperature resulted in an enhancement of crystallinity index of nanocellulose but a decrease in thermal stability.

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