

Utilization of cajuput (*Melaleuca leucadendron*) twigs and sugarcane (*Saccharum officinarum*) bagasse agricultural waste for cellulose acetate production by environmentally friendly approach

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Abstract

This study was carried out to investigate the extraction of cellulose acetate (CA) from cajuput (*Melaleuca leucadendron*) twigs and sugarcane (*Saccharum officinarum*) bagasse using an environmentally friendly method. At first, cellulose was extracted from cajuput twigs (CT) and sugarcane bagasse (SB) through prehydrolysis followed by soda (NaOH) pulping and elementary chlorine-free (ECF) bleaching. Later, the extracted cellulose was acetylated using iodine (I) as a catalyst. The obtained CA was characterized by Fourier-transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR), thermal gravimetric analysis (TGA), scanning electron microscope (SEM) and X-ray diffraction. FTIR and NMR analysis proved the replacement of free OH (hydroxyl) groups by acetyl groups. The degree of substitution (DS) showed the acetylation capability of cellulose extracted from CT and SB as well. The cellulose diameter and its crystallinity index were measured by SEM and X-ray diffraction, respectively. Furthermore, the thermal gravimetric analysis showed that CA extracted from CT and SB was thermal resistance. Therefore, CT and SB could be potential alternative resources for CA production using the mentioned method.

1. Introduction

In recent years, research on the utilization of biomass for producing biomaterials and biofuel are increasing [1,2]. Cellulose, the most abundant component of biomass has been known as the essential material for the production of textile fibers, cellulose derivatives, pharmaceuticals substances, food additives, etc. Cellulose derivative, namely, cellulose acetate (CA), is the most commercially used and widely applied in the industrial sectors. Several CA applications are in the field of food packaging; textile industries; and membranes for gas separation, reverse osmosis, ultrafiltration membrane, coating and bioplastics [3–11]. CA has also been applied in the military and defense area, such as for less-prone low-vulnerability ammunition (LOVA) systems. LOVA has been developed recently and cellulose derivatives such as CA, ethyl cellulose, and CA propionate were reported as promising binders for LOVA gun propellant [12–13]. Meanwhile, from environmental point of view, cellulose fiber has been studied and showed that viscose has a higher impact than the other man-made cellulose fibres and is comparable to PET.

Generally, wood pulps are used as raw materials for CA production [14]. However, because of the decline of wood supply and deforestation issues, other sources such as agricultural waste have been considered to be potential substitutions for raw materials. Indonesia has abundant biomass sources that are specially generated from agro-industrial sectors. Cajuput twigs (CT) and sugarcane bagasse (SB) are among the potential biomass sources besides biomass from oil palm industries. Regarding the cajuput plant, currently, Indonesia is known as one of the largest cajuput oil producers worldwide. East Nusa Tenggara, Sulawesi, Java, and Moluccas islands are known for cajuput plantation in Indonesia. Cajuput oil produced via the steam distillation of leaves and twigs is usually used as herbal remedies. Reportedly, Indonesia produces 600 to 650 tons of cajuput oil, yearly [15–16]. The yield of cajuput oil is approximately 1–2% of all materials. After distillation, twigs and leaves are the leftovers. The calculated biomass potency from cajuput oil distillation mills is approximately 32,500–65,000 tons/year.

In the case of SB, the Indonesian Ministry of Agriculture reported that sugar production is approximately 3.82 million tons in 2019 from 0.5 million hectares of planted area [17]. In the mill, sugarcane is crushed to extract the juice, and the bagasse is the leftover and usually combusted in the boiler. However, the residue can be used as potential a resource for biorefinery. SB potency was approximately 9.9–11.2 million tons in 2014 and was continuously increasing in 2019 [18]. In this article, we reported the utilization of both CT and SB as raw materials for CT production.

In the CA production, the preparation of high-purity cellulose is an important step. Pretreatment is one of the key factors to separate cellulose from other components especially lignin and hemicellulose before the acetylation process. The biological pretreatment of biomass has been reported previously [19, 20]. Meanwhile, other methods such as mechanical, thermal, and chemical pretreatments have been studied to purify cellulose [21–27]. Sodium hydroxide, the most commonly used chemical in the pulp and paper industries, was chosen for chemical pulping of CT and SB in this study because of its effectiveness to remove lignin and availability worldwide. Subsequently, elementary chlorine-free (ECF) bleaching was applied to remove residual lignin from CT and SB pulps. ECF bleaching is a chlorine-free process in which no elemental chlorine is used. Hence, ECF is considered more environmentally friendly and can improve sustainable ecosystem recovery.

CA, an ester of cellulose, was produced by introducing the acetyl group to the cellulose. Generally, acetic anhydride is used as an acetylating agent by using H_2SO_4 as a catalyst [28]. However, this strong acid is considered less environmentally friendly among

other catalysts because of its toxicity properties. It was studied that NaHSO_4 was used as a catalyst to reduce H_2SO_4 and acetylation reaction temperature [29]. Meanwhile, Wu et al reported synthesis CA in the absence of any catalysts by using ionic liquids at room temperature [30]. Moreover, the use of iodine was proposed for the esterification of corn starch and rice husk (RH) [31–33].

In this article, the hypothesis that cellulose di-acetate can be produced from CT, which is the first reported raw material for CA resulted from waste of cajuput oil mill, will be evaluated. Additionally, SB, a non-wood material, was studied as a comparison. The novelty of this study is the application of sodium hydroxide in the pretreatment process that is followed by a two-step ECF bleaching by using NaClO_2 and H_2O_2 for preparing cellulose from CT and SB. In this work, we reported the preparation of CA from CT and SB by using an iodine catalyst that is more environmentally friendly than sulfuric acid, in a heterogeneous medium.

2. Materials And Methods

2.1 Material

CT and SB were collected from the cajuput oil mill and sugarcane mill in Yogyakarta province, Indonesia. After collection, the CT and SB were washed and sun-dried to a moisture content of $\sim 10\%$. The CT and SB fiber fragments of 5–10 cm were then cut to lengths of 0.5–1 cm. The CT and SB samples were air-dried for 3 days at $20^\circ\text{C} \pm 2^\circ\text{C}$ to obtain a moisture content of approximately 8–10%. Next, the size of the samples was reduced to 40–80 mesh for analytical purposes. Meanwhile, as standard, CA with average $M_n \sim 30,000$ by GPC was obtained from Aldrich chemistry, and commercial pure cellulose C6228 was obtained from Merck. The reagents used for the acetylation were acetic acid (glacial) 100% from Merck, acetic anhydride from ajax chemicals, iodine from Merck, sulfuric acid 95–97% from Merck, sodium hydroxide from Merck, sodium thiosulfate pentahydrate from Merck, and sodium hydrogen sulfate monohydrate from Merck.

2.2 Method

2.2.1 Delignification

Each 25 g of CT and paddy SB was prepared in a stainless-steel reactor, 255 mm in height and 76 mm in diameter. Prehydrolysis was conducted by using distilled water with a solid-to-liquid ratio of 1:12. The reactors were then heated at $150 \pm 2^\circ\text{C}$ for 2 h. After the process, the solid residue was filtered and subjected to the delignification process. Delignification was conducted in the same reactor by adding sodium hydroxide 10% with a solid-to-liquid ratio of 1:7. The reaction condition was 150°C for 2 h. After the process, the solid residue rich in cellulose was filtrated from its black liquor.

2.2.2 Bleaching

As much as 10 g each pulp of CT and SB was subjected into Erlenmeyer flask and NaClO_2 0.5% was added with a solid-to-liquid ratio of 1:12. Subsequently, 0.5 ml CH_3COOH p.a. was added; the solution was heated at 80°C for 1.5 h. After the first bleaching step, the solid and liquid phase was filtrated, and the solid residue was washed until the pH was approximately 7. The second bleaching was conducted by adding H_2O_2 10% with a solid-to-liquid ratio of 1:12. The conditions were 70°C for 5 h. After heating and then cooling, the solid residue was filtrated and washed until neutral pH.

2.2.3 Acetylation

Each 1 g of CT and SB cellulose was prepared in a 250 ml Erlenmeyer flask. As much as 50 ml acetic anhydride and 1.5 g iodine were added to the cellulose and mixed at 100°C for 5 h. Then, to the mixture, sodium thiosulfate pentahydrate was added to the Erlenmeyer flask until the solution color changed. Furthermore, 150 ml ethanol was added and stirred for 60 min at room temperature. Finally, the solid residue was then filtrated and washed by ethanol 75% and distilled water. The residue was dissolved in the dichloromethane and filtrated, and the filtrate was evaporated. The final residue was CA. The experiment was repeated two times.

2.2.4 Degree of substitution

The average value of $-\text{COCH}_3$ that replace hydroxyls group in the glucose is defined as degree of substitution (DS). The saponification reaction based on Zhou et al., 2016 [34] was used to determine the DS of the acetylated samples. Sample was dried

for 2 h at 105°C and then 0.1 g of sample was added to 40 mL ethanol 75 % in a flask. After that, it was heated at 60°C for 30 min. Subsequently, 40 mL NaOH 0.1 mol/L was added to the flask and heated to 60°C for 15 min. Finally, The flask was allowed at room temperature for 48 h. The HCl 0.5 mol/L was used to titrate the excess alkali with using indicator phenolphthalein.

2.2.5 Materials characterization

Cellulose, hemicellulose, and lignin content were analyzed based on a method from the National Renewable Energy Laboratory [35]. The experiment was repeated three times. For CT and SB, as much as 300 mg were subjected to hydrolysis by using H₂SO₄ 72% and 4%, respectively. After hydrolysis, glucose and xylose were then analyzed by using high-performance liquid chromatography waters e2695, and insoluble lignin after hydrolysis was analyzed using the gravimetric method. Spectrophotometer Optizen 2120 UV at 205 nm was used to measure soluble lignin. Functional groups of cellulose and CA were studied by using Fourier transmission infrared (FTIR) spectroscopy IR Prestige 21 Shimadzu. The samples were blended with KBr and followed by compressing this mixture in the sample disk and analyzed with the transmission wavenumber range of 4000–400 cm⁻¹. The ¹H nuclear magnetic resonance (NMR) spectra were recorded on a Jeol 500 MHz instrument, and chemical shifts are reported in parts per million from tetra methyl silane. Meanwhile, the surfaces of the samples were analyzed by using the scanning electron microscope SU-3500 from Hitachi, Tokyo, Japan, with SE 5 kV 500× to 2500× magnification. A panalytical X-ray diffractometer with Cu K α 1.5405 nm radiation at 400 kV and 300 mA was used to investigate the X-ray diffraction spectra. Linseis Thermal Gravimetric Analysis (TGA) was used to analyze its thermal property.

3. Results And Discussion

3.1 Pulping and bleaching

The acetylation of CT and SB cellulose to produce CA was conducted with an excess of acetic anhydride and iodine catalyst. Pretreatment and bleaching were conducted to prepare high-purity cellulose from CT and SB. This study showed an interesting phenomenon regarding the pulping of CT. It was observed that the color of the CT pulp was darker than that of the SB pulp and was similar to the color of black liquor. It is assumed that lignin condensation reaction occurred during CT delignification. Santos et al. studied that the depolymerization of lignin in the alkaline condition that involved the cleavage of nonphenolic β -aryl (C–O) linkages [36]. The hardwood biomass was known to have a higher S/G ratio than those of softwood and non-wood materials. In the case of CT, a hardwood, depolymerization could occur at a high rate during the pulping, and some of the lignin monomers could perform re-polymerization reaction and then was absorbed by the pulp. Moreover, the black color of CT pulp could be due to extractive substances. Pujiarti et al. [37] reported that *Melaleuca leucadendron* leaf oils comprise monoterpene hydrocarbons, oxygenated monoterpenes, sesquiterpene hydrocarbons, oxygenated sesquiterpenes, eugenol, and 2-pentanone. Vice versa, it was observed that, after the bleaching process, CT pulp turned into bright white and brighter than those of SB pulps. The chemical composition of CT and SB has been analyzed and is presented in Table 1.

Table 1 Chemical composition of cajuput twigs (CT) and sugarcane bagasse (SB)

Raw material	after delignification	Sugarcane bagasse		Cajuput twigs		Sugarcane bagasse						
Cajuput twigs	SD		SD		SD		SD					
Cellulose	34.71	±	1.44	43.88	±	2.91	64.34	±	2.76	83.16	±	3.85
Hemicellulose	13.63	±	0.78	19.65	±	1.41	11.56	±	1.06	2.73	±	0.93
Acid insoluble lignin	31.90	±	1.27	22.85	±	2.74	16.48	±	1.02	5.49	±	0.92
Acid soluble lignin	3.30	±	0.11	2.12	±	0.18	1.80	±	0.28	0.30	±	0.07
Water extractive	19.36	±	0.84	12.30	±	1.56	-	-				

The cellulose and hemicellulose contents of SB material were higher than those of CT material. Conversely, the total lignin and water extractive contents of CT were higher than those of SB. Furthermore, after the delignification, the cellulose content of CT increased by 85.4%, a little lower than that of SB, that is, 89.5%. This result showed that the higher the lignin content will be, the harder the delignification reaction occurred. It was shown that the delignification of SB was easier than that of CT.

Meanwhile, regarding acid-insoluble lignin, the decreasing percentage of SB (75.9%) was higher than that of CT (48.3%).

After the pulping, the remaining lignin in the pulps was removed via the ECF method by using NaClO_2 and H_2O_2 . Hypochlorite preferentially destroys certain groups of lignin. Meanwhile, peroxides have been known to be effective bleaching agents and can improve brightness without significant yield loss [38]. After the bleaching, it was shown that both chemicals effectively oxidized the remaining lignin in the pulps and the cellulose content was increased to $93.5 \pm 1.88\%$ and $92.7 \pm 1.25\%$ for CT and SB, respectively. The higher cellulose content of CT could be due to the lignin structure in the hardwood, which is a higher syringyl type than those of non-wood materials.

3.2 CA characterization

By using acetic anhydride, the acetylation of CT and SB bleached pulps was conducted. The method in this study was different from the conventional CA production method, in which the acetylation of cellulose comprises activation, acetylation, and hydration steps. In this work, acetate anhydride and iodine were directly mixed with cellulose. Reportedly, iodine can form a complex with glucose polymers such as cellulose, and this reaction may help the solubility of cellulose in the acetic anhydride. Biswas et al. showed that the CA increases as a function of iodine concentration [39]. Moreover, Das et al. reported that the degree of substitution (DS) and acetylation reaction increased when the iodine concentrations increased. The ratio of the iodine concentration to the pulp weight in this study was 1.5:1. The CA produced was then characterized via FTIR, as shown in Figure 1.

In Figure 1, the IR spectra of CT CA and SB CA to IR spectra of cellulose and CA commercial is compared. It was presented that there was neither stretching nor vibration of carbonyl ester at approximately 1730 cm^{-1} for cellulose. Meanwhile, for commercial CA, as well as CT CA and SB CA, carbonyl ester the peaks were clearly detected at this bandwidth. Das et al. (2014) reported that the peak height of approximately $1728\text{--}1743\text{ cm}^{-1}$ is an indication of C=O stretching of carbonyl ester band that is specific for CA. Therefore, the CA from CT and SB was successfully produced.

In cellulose esterification, the heterogenous acetylation of both CT and SB cellulose, acetate anhydride was used as an acetylating agent in the presence of iodine. During the acetylation, polar hydroxyl groups ($-\text{OH}$) in the cellulose were substituted by acetyl groups ($-\text{CH}_3\text{COO}$). Table 2 presents the DS and yield of the product.

Table 2 Degree of substitution and yield of acetylated cellulose

	cellulose to I_2 ratio	Degree of substitution (DS)	SD	Yield (%)	SD
Cajuput twigs CA	01:01.5	1.88	± 0.11	89.30	± 3.58
Sugarcane bagasse CA	01:01.5	1.78	± 0.18	99.30	± 2.94
Rice husk*	01:01.5	2.91		66.00	

*Das et al. 2014

Theoretically, the DS for CA will be from 1 to 3, for mono-acetate, di-acetate, and tri-acetate, respectively, which correspond to the hydroxyl group that could be acetylated. In this study, acetylated celluloses were 1.90 and 1.78 for cajuput CA and bagasse CA, respectively. Both cajuput CA and bagasse CA are close to DS 2 that is usually categorized as diacetate and could be the mix of mono-acetate and di-acetate that will be confirm further by ^1H NMR. Das et al. (2014) reported that the DS will be influenced by reaction conditions such as reactants concentration, time, and temperature. In the reaction, carbonyl carbon of acetic anhydride will be activated by iodine; subsequently, the oxygen from the hydroxyl group of cellulose will attack this carbonyl carbon resulting in sp^3 hybridization (Das et al. 2014; Biswas, et al. 2005). The yield of CA represents the weight of the product compared with that of initial cellulose. It showed that yields were high for both CT and SB acetylated celluloses. Compared with a previous study by Das et al. (2014), the DS for CT and SB were lower than that for RH. However, the yield of RH acetylated cellulose was lower than those of CT

and SB. The temperature reaction for CT and SB was 100°C that could result in a too fast acetylation rate when compared with 80°C for RH, and the CA nucleus cannot be formed further. Based on the DS value, the products for CT and SB were suggested to contain not only CA but also remaining cellulose that cannot be converted completely.

Spectral studies of proton NMR (^1H NMR) on CT CA and SB CA were conducted and are shown in Figure 2. In the CT CA spectra with DS 1.9, two dominant chemical shifts that refer to acetyl- CH_3 protons appeared (δ 2.071 and 2.040). Meanwhile, for SB CA spectra, only one acetyl- CH_3 chemical shift was observed (δ 2.029). These results confirm that CA was formed from each material. Moreover, chemical shifts of CT CA could be contains di-acetate because it has two chemical shifts. Meanwhile SB CA could be dominated by mono-acetate and contain small portion of di-acetate. These results corresponded to its DS values that CT was higher than SB.

Figure 3 presents the thermographic analysis of acetylated cellulose. Based on the TGA thermogram obtained for CT CA and SB CA, there is a slight mass loss of approximately 5% up to 200°C, corresponding to the loss of volatile compounds and H_2O bound to the hydrophilic (OH) groups of CA chains and, subsequently, to CA deacetylation. Furthermore, another stage of thermal decomposition was between 300°C and 400°C. In this stage, mass loss was between 70% and 80%, which was suggested to CA chain degradation due to the breakdown of glycosidic bonds followed by the primary decomposition in volatile and dehydrated compounds. This stage was the main thermal decomposition of CA.

The crystalline nature of the CT CA and SB CA was compared with those of commercial cellulose and CA. The crystallinity index (Crl) was calculated using the following equation: **see equation 1 in the supplementary files.**

In Figure 4, the sharp high-intensity peak at $2\theta = 22^\circ$ describes the crystalline nature of cellulose; the Crl of cellulose was 86.6. After the acetylation, the Crl of the SB CA and CT CA was 75.6 and 60.2, respectively. Meanwhile, there was no peak detected at $2\theta = 22^\circ$ for commercial CA. It can be assumed that during the acetylation process, the crystallinity of cellulose decreased. However, because there was still remaining cellulose in the CA, the crystallinity was still detected for the acetylated cellulose. Moreover, the Crl of bagasse CA was higher than those of cajuput CA, which negatively correlated with the DS of the products.

The surface morphologies of CT CA and SB CA were compared with those of cellulose. Figure 5 shows that the fiber diameter of acetylated decreased compared with commercial cellulose, its diameter ranging from 26 to 29.9 μm . Meanwhile, CT CA diameter was approximately 10 μm and for most of the bagasse CA, the fiber diameter was 20 to 30 μm . It was observed that the cellulose diameter decreased during the acetylation. Therefore, the acetylation process influences the surface structure of cellulose fibers.

4. Conclusions

- The mixture of cellulose mono-acetate and di-acetate successfully synthesized from CT and SB were confirmed from its FTIR and ^1H NMR spectra. Pretreatment by using NaOH and two-step bleaching by using NaClO_2 and H_2O_2 was suitable to prepare the cellulose before the acetylation process. The iodine that is more environmentally friendly than H_2SO_4 was used as a catalyst. This study found that cajuput twig is easier to be acetylated than SB, which was indicated by higher DS value. It was showed that CT and SB are potential alternative sources for CA production in the near future.

Declarations

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Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Contributions

R.M. is main contributor and corresponding author, conceptualized the study, performed pretreatment and study analysis result for HNMR and SEM, while M, ET and HP performed the other experiments. O.O. and A.K.D. had revised and finalized it. YS supervised the study.

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Figures

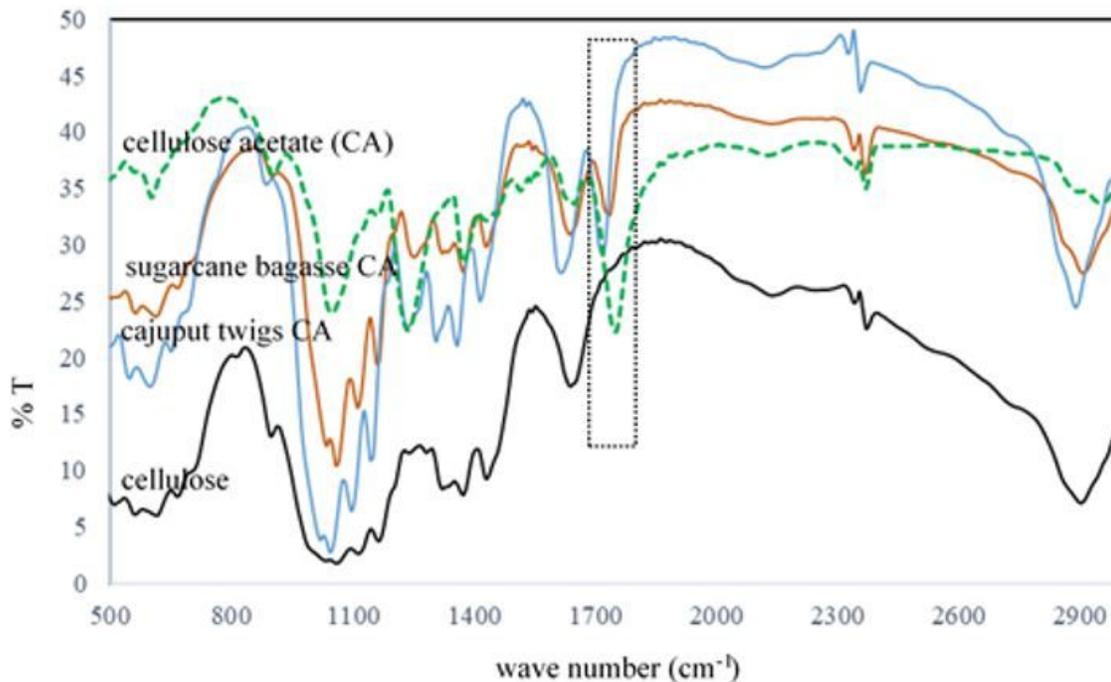


Figure 1

IR spectra of cellulose, cajuput twigs CA, sugarcane bagasse CA, and commercial CA

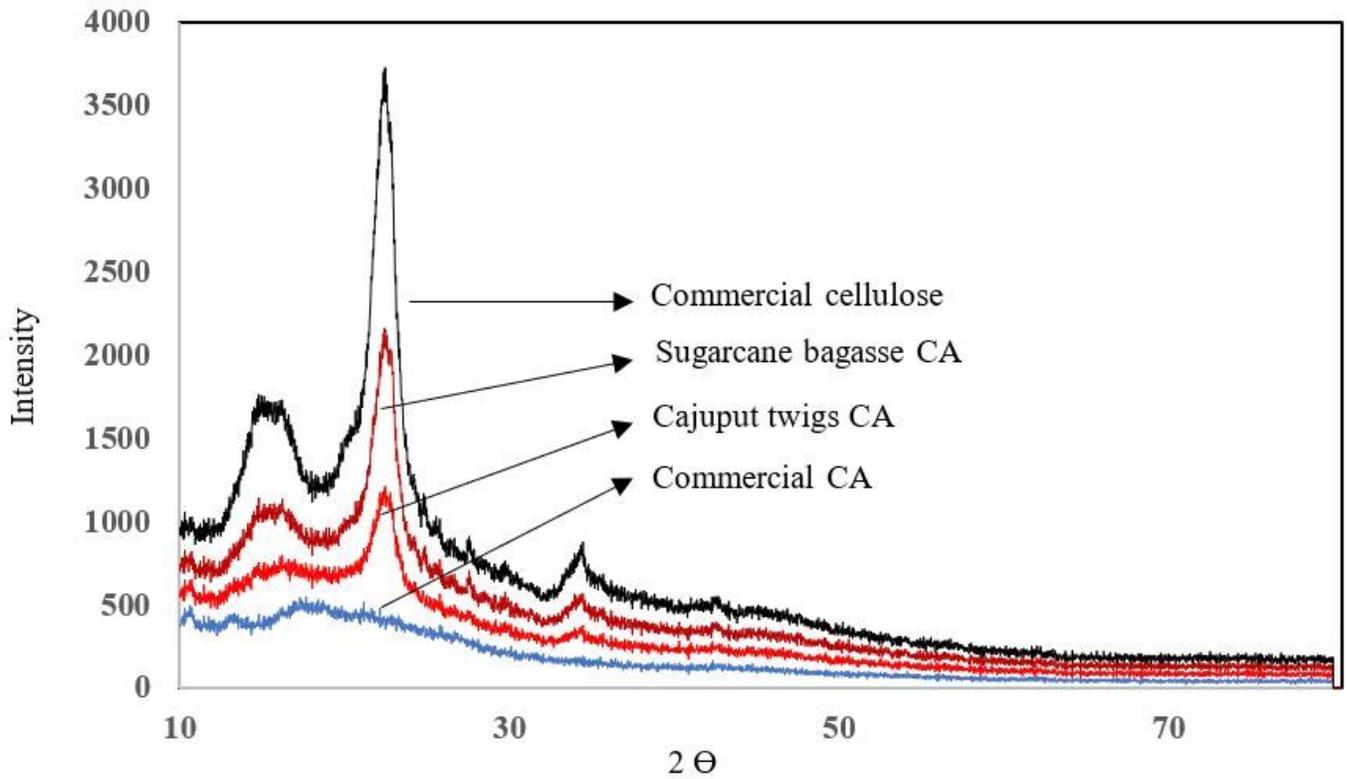


Figure 4

X-ray diffraction spectra for commercial cellulose, sugarcane bagasse CA, cajuput CA, and commercial CA

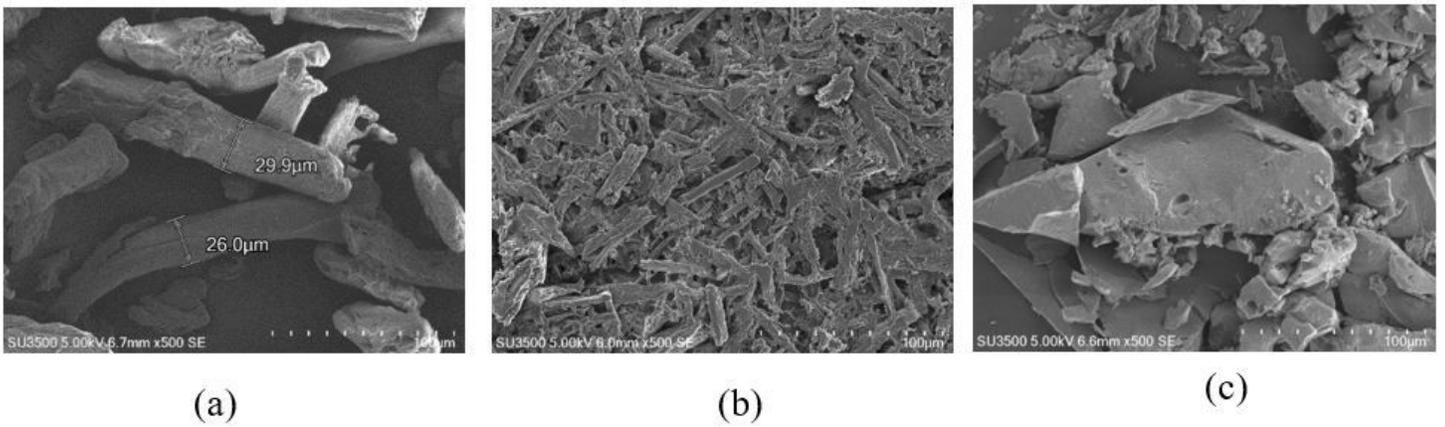


Figure 5

SEM micrograph for commercial cellulose (a), cajuput twigs CA (b), and sugarcane bagasse CA (c)

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