SUGARCANE BAGASSE PULPING AND BLEACHING: THERMAL AND CHEMICAL CHARACTERIZATION

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Cellulose fibers were isolated from sugarcane bagasse in three stages. Initially sugarcane bagasse was subjected to a pre-treatment process with hydrolyzed acid to eliminate hemicellulose. Whole cellulosic fibers thus obtained were then subjected to a two-stage delignification process and finally to a bleaching process. The chemical structure of the resulting cellulose fibers was studied by Fourier Transform Infrared (FTIR) spectroscopy. Scanning Electron Microscopy (SEM) and X-ray diffraction (XRD) were used to analyze the effects of hydrolysis, delignification, and bleaching on the structure of the fibers. Two different thermal analysis techniques were used to study the bleaching cellulose fibers. These techniques confirmed that cellulose fibers were isolated from sugarcane bagasse. A future goal is to use these fibers as reinforcement elements in composites, organic-inorganic hybrid, and membranes for nanofiltration.

Keywords: Sugarcane bagasse; Cellulose; Bleaching and Morphology

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INTRODUCTION

Sugarcane bagasse is an abundant agro-industrial by-product in Brazil and is used in many different applications (Tita et al. 2002). Sugarcane, a very tall grass with big stems, is largely grown in countries like Brazil, Cuba, Australia, South Africa, Peru, Mexico, and India (Rípoli et al. 2000). The Brazilian production of sugarcane is immense, about 425 million tons per year, and ethanol production has increased rapidly over the years, reaching 18 billion liters in 2007 (Goldemberg 2008). The transformation of sugarcane into ethanol gives rise to two main by-products, thermal energy and bagasse (Smeets et al. 2008).

Sugarcane bagasse can be considered either as a waste, affecting the environment, or as a resource when appropriate valorization technologies are implemented. In such cases, sugarcane bagasse offers possibilities for integral valorization by processing it into a set of commodities with national and international market potential (Contreras et al. 2009). For instance, Gonçalves et al. (2005) analyzed an integrated process for conversion of sugarcane bagasse and straw and concluded that almost all products obtained from the petrochemical processes can be obtained from biomass through direct, catalytic,

or aggressive conversion of cellulose, hemicellulose, and lignin.

Bagasse consists of cellulose 43.8%, hemicellulose 28.6%, lignin 23.5%, ash 1.3%, and other components 2.8% (Luz et al. 2007). The two former components are hydrophilic, and the latter is hydrophobic (Sun et al. 2004). The cellulose from sugarcane bagasse can be easily obtained by acid hydrolysis followed by an alkaline pulping process. During hydrolysis, the reagents acts on the lignin, breaking the macromolecule into units of low molecular weight, which are soluble in the liquor (Luz and Gonçalves 2001). However this reaction is not strong enough to eliminate all lignin and hemicelluloses residues; therefore an additional process can be used, bleaching. The bleaching treatment can be made with sodium chloride, which can result in cellulose degradation (Saheb 1999), and different properties and characteristics of cellulose can arise.

Thus, in this work, the sugarcane pulping and bleaching were investigated using Fourier Transformer Infrared Spectroscopy (FTIR) to determine the chemical structure of cellulose fibers. Furthermore, we used two different thermal analysis techniques to study the bleaching of cellulose fibers. Thermogravimetric analysis (TGA) and differential thermogravimetry (DTG) provide information about the nature and extent of degradation and thermal stability of the materials (Brown 1988). In differential scanning calorimetry (DSC), the heat flow rate associated with a thermal event can be measured as a function of temperature, providing quantitative information about water absorption from samples (Hatakeyama and Quinn 1999). In addition, X-ray diffraction and SEM were used to determine further structural and morphological information. These techniques will provide important information about composition, morphology, structure and thermal stability of bleached cellulose fibers, and they may be widely used for other pulp characterizations.

EXPERIMENTAL

Materials Preparation

Preparation of the bleached cellulose

Crude cellulose: To begin, natural sugarcane bagasse was pretreated with 10% (w/v) sulfuric acid solution (reactor of 350 L at 120ºC, 10 min), followed by centrifugation with the purpose of separating the rich pentosans solution. The extracted lignocellulosic fraction was delignified with 1% (w/v) solution (reactor of 350L at 100ºC, 1 h). The product was designated as the crude pulp.

Bleaching cellulose: Crude pulp was bleached with acetic acid and sodium chloride under stirring and heating, followed by filtration under vacuum, then exhaustive washing with distilled water. This technique was used to remove residual lignin. Furthermore the bleached cellulose fibers dried at 50 ºC for 12 h (Mulinari et al. 2006).

Characterization of the Materials

X-Ray diffraction (RXD)

Physical structures of the cellulose fibers from sugarcane bagasse were evaluated by X-ray diffraction technique. X-ray diffractograms were obtained with a Shimadzu

diffractometer model RXD6000. Conditions used were: radiation CuKα, voltage of 30 kV, current of 40 mA, and 0.05 (2θ/ 5 s) scanning from values of 2θ with angles of 10 to 70º (2θ). The degree of crystallinity (*CI*) was calculated as the ratio of the intensity differences in the peak positions at 18º and 22º according to Equation 1 (Segal 1959),

$$CI = \frac{I_{(22)} - I_{(18)}}{I_{(22)}} \times 100 \quad (1)$$

where I_{22} is the maximum intensity of the 002 lattice reflection of the cellulose *I*, and I_{18} is the maximum intensity of X-ray scattering broad band due to the amorphous part of the sample.

Thermal analysis (TG/DTG)

TG/DTG curves were obtained by the use of a Shimadzu thermogravimetric instrument model TGA-50. Thermal behavior of the preparations was obtained by recording the TG/DTG curves in the range 25 to 900ºC under conditions of nitrogen atmosphere using weighed samples in the range 5 to 10 mg, at 20ºC min^{-1}.

Thermal analysis (DSC)

DSC analysis was performed using a calorimetric instrument DP Union, by the heating of the 5 mg sample at temperatures in the range 25 to 550°C under nitrogen atmosphere at a rate of 10°C min^{-1}.

Scanning electron microscopy (SEM)

A JEOL JSM5310 model scanning electron microscope (SEM) was used to observe the modification on cellulose fibres, cellulose bleaching, and hydrous niobium phosphate. Samples to be observed under the SEM were mounted on conductive adhesive tape, sputter coated with gold, and observed in the SEM using a voltage of 15 kV.

RESULTS AND DISCUSSION

Sodium chloride has been widely used for bleaching of mechanical pulps under acid conditions. Currently, with the development of totally chlorine-free bleaching technologies, there is also a growing interest in the use of sodium chloride as one of the oxidants replacing chlorine-based reagents. Sugarcane bagasse, used as raw material for obtaining cellulose, was chemically characterized, and its cellulose and lignin content were, respectively, 45.4% and 23.4%.

After the bleaching of sugarcane bagasse, the extracted cellulose had a lignin content of 0.3% by according Table 1. In addition, it was possible to see that the pulping and bleaching directly affected hemicellulose and cellulose contents.

Table 1. Chemical Composition of the Fibers

Mass %	Sugarcane bagasse in nature	Crude cellulose	Bleaching cellulose
Hemicellulose	28.7±0.7	7.8±0.1	6.4±0.2
Lignin	23.4±0.2	11.5±0.2	0.3±0.0
Cellulose	45.4±0.8	79.5±0.5	91.7±0.8
Ashes	2.7±0.1	1.3±0.0	1.7±0.1

The main differences in respect to functional groups in the sugarcane bagasse and in cellulose that was extracted from it may be observed on the FTIR spectra presented in Fig. 1.

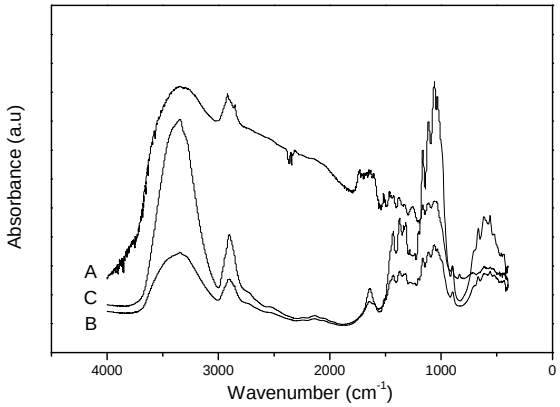


Fig. 1. FTIR spectra of sugarcane bagasse (wavenumber 4000 to 400 cm^{-1}): unmodified fibers (A), crude cellulose fibers (B), and bleached cellulose fibers (C)

The main differences in FTIR spectra can be seen in the Table 2. This table summarizes higher bands observed in the FTIR spectrum of sugarcane bagasse and their assignments to chemical group vibrations and molecules.

Table 2. Infrared Main Transitions for Sugarcane Bagasse

Wavenumber (cm^{-1})	Vibration	Source
3300	O-H linked shearing	Polysaccharides
2885	C-H symmetrical stretching	Polysaccharides
1732	C=O unconjugated stretching	Xylans
1650-1630	OH (water)	Water
1335	C-O aromatic ring	Cellulose
1162	C-O-C asymmetrical stretching	Cellulose
670	C-OH out-of-plane bending	Cellulose

The most visible differences between the spectra of unmodified sugarcane bagasse, crude cellulose fibers, and bleached cellulose fibers were found within the region from 3500 to 700 cm^{-1}. The absorption bands at 1730, 1620, 1595, and 1512 cm^{-1}

were not observed in the spectrum of the cellulose that was extracted from sugarcane bagasse (Fig. 2). These absorptions are attributed to the functional groups present in the lignin that are associated with cellulose and hemicellulose before the process of delignification and bleaching of sugarcane bagasse. Figure 2 shows two absorption bands that must be emphasized, the bands at 1512 and 1250 cm^{-1}. The band at 1512 cm^{-1} is not present and the band at 1250 cm^{-1} is drastically reduced in the spectrum from bleached cellulose fibers. These two absorption bands are important because their absence in the bleached cellulose fibers spectra indicates that most of the lignin was removed. Favorable phenomena have been found for application of such fibers as reinforcement in certain polymer matrix, due to a decrease in fibers hydrophilicity (Oliveira et al. 2010). The removal of lignin was confirmed by X-ray diffraction, which showed an increased crystallinity degree of the bleached cellulose fibers.

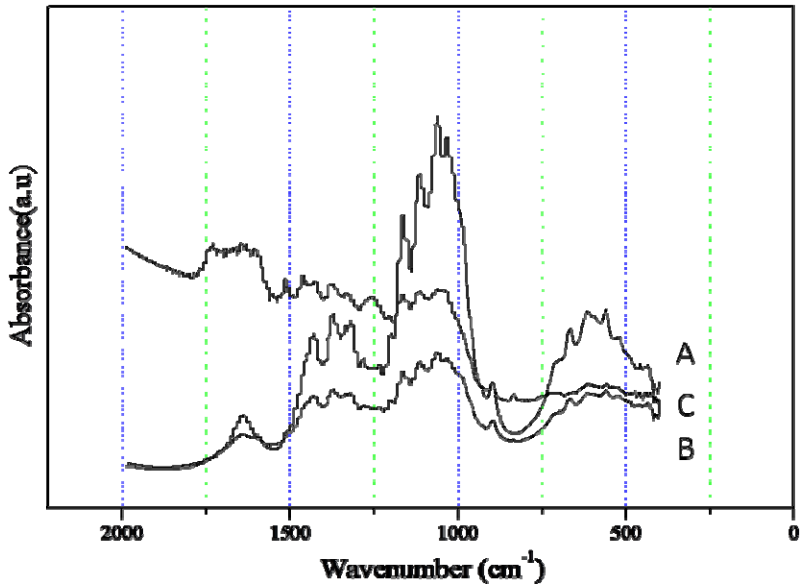


Fig. 2. FTIR spectra of sugarcane bagasse (wavenumber 2000 to 400 cm^{-1}): in unmodified fibers (A), crude cellulose fibers (B), and bleached cellulose fibers (C)

Figure 3 show diffractograms obtained from unmodified sugarcane bagasse, crude cellulose, and bleached cellulose fibers. It was possible to observe a major diffraction peak for 2θ ranging between 22° and 23°, which corresponds to cellulose (002) crystallographic planes.

X-ray diffraction peaks for both materials can be attributed to scattering by the crystalline regions, and the diffuse background can be attributed to disordered regions. Thus, the materials tested were semicrystalline.

The spectrum corresponding to the unmodified sugarcane bagasse showed diffraction peaks at the following 2θ angles: 15.9º and 22.4º. For crude cellulose fibers the same peaks could be observed at 15.9º and 23.2º. For bleached cellulose fibers the same peaks could be observed at 16.2º and 22.9º.

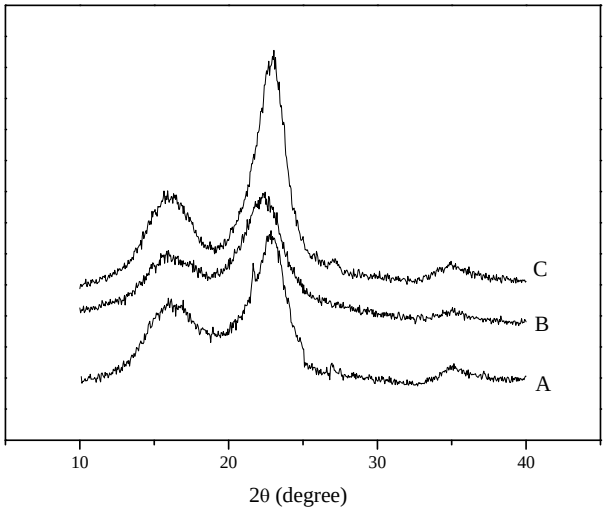


Fig. 3. X-ray diffractograms of sugarcane bagasse: Unmodified (A), Crude cellulose (B), and Bleached cellulose

The presence of the peaks at 15º and 22º provides evidence of the effects of the treatments on fibers. The position of these peaks indicates an increase of the interplanar distance in relation to the treated fibers. This behavior occurs due to the generation of disorder when fibers are treated. The projection of substituting groups along the axis is associated with an increase in the interfibrillar distance (Rodrigues Filho et al. 2006)

Patterns for both materials were similar; however unmodified sugarcane bagasse was less crystalline than the bleached cellulose fibers. Based on these results (Segal 1959), unmodified sugarcane bagasse, crude cellulose, and bleached cellulose fibers exhibited 37%, 47.5%, and 56% of crystallinity, respectively.

The effect of pulping and bleaching on the thermal behavior of sugarcane bagasse was also studied by TGA and DSC in temperature range from room temperature to 600°C at a rate of 10°C min^{-1} under nitrogen flow. Figures 4 and 5 show the TGA and DSC curves, respectively, for unmodified sugarcane bagasse, crude cellulose, and bleached cellulose fibers.

TGA curves of the fibers exhibited two degradation stages. The first stage of weight loss occurred between 30 and 100°C (both fibers), which corresponds to water vaporization heat in the sample. The second stage of weight loss for unmodified fiber presented thermal degradation peaks around 310°C. Table 3 shows the weight loss and degradation temperature peak of fibers.

Table 3. Thermal Properties of Fibers

Samples	*Weight loss (%)*						*Degradation temperature peak (°C)*
	100 °C	*200 °C*	*300 °C*	*400 °C*	*500 °C*	*600 °C*	
Unmodified sugarcane bagasse	7.9	8.2	25.2	77.1	80.6	81.9	260
Crude cellulose	4.3	5.1	6.4	81.2	88.9	93.9	324
Bleached cellulose	13.1	14.8	16.3	78.4	81.7	84.5	340

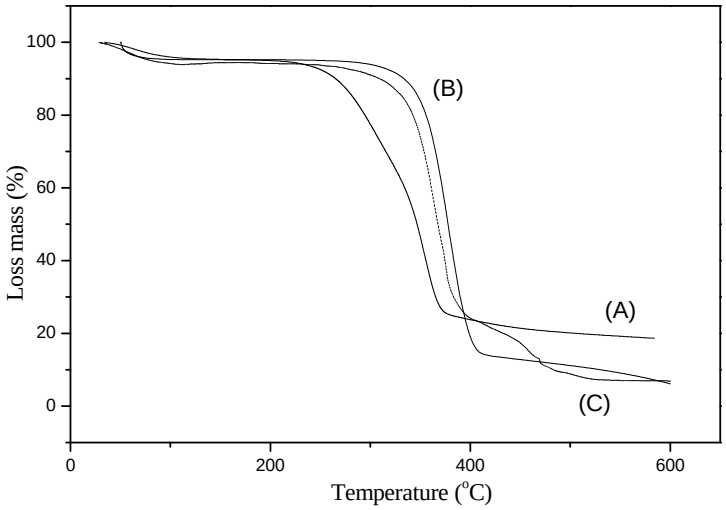


Fig. 4. Curves TGA sugarcane bagasse: unmodified fibers (A), crude cellulose fibers (B), and bleached cellulose fibers (C)

Table 3 shows different decomposition temperatures for each type of cellulosic fiber. Unmodified sugarcane bagasse started to decompose at 300 ºC. On the other hand, crude cellulose and bleached cellulose fibers started to decompose at 324 ºC and 340 ºC. This increase in the decomposition temperature of cellulose fibers can be attributed to the treatments.

The DSC curve in Fig. 5a (unmodified bagasse) shows an endothermic peak near 110 °C, which is attributed to the removal of moisture when the sample was heated. Two exothermal peaks appear at 310 and 385 °C, respectively, and they are attributed to charring (Yang et al. 2007), while a large endothermic peak at 365 °C is related to the cellulose fraction. This behaviour is related to the full decomposition of cellulose that might be attributed to quick devolatilization reactions, leading to very little solid residue.

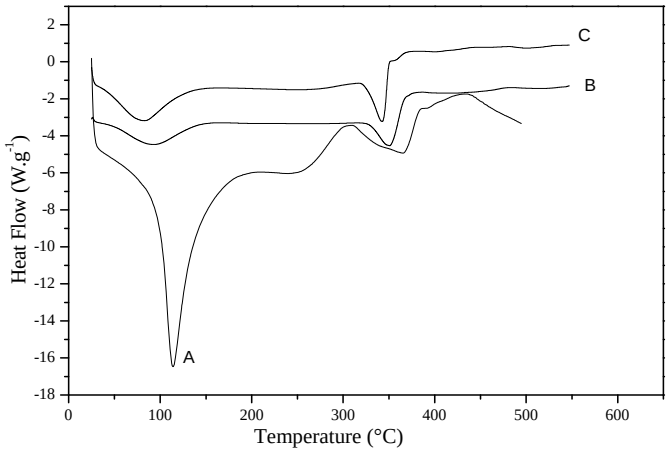
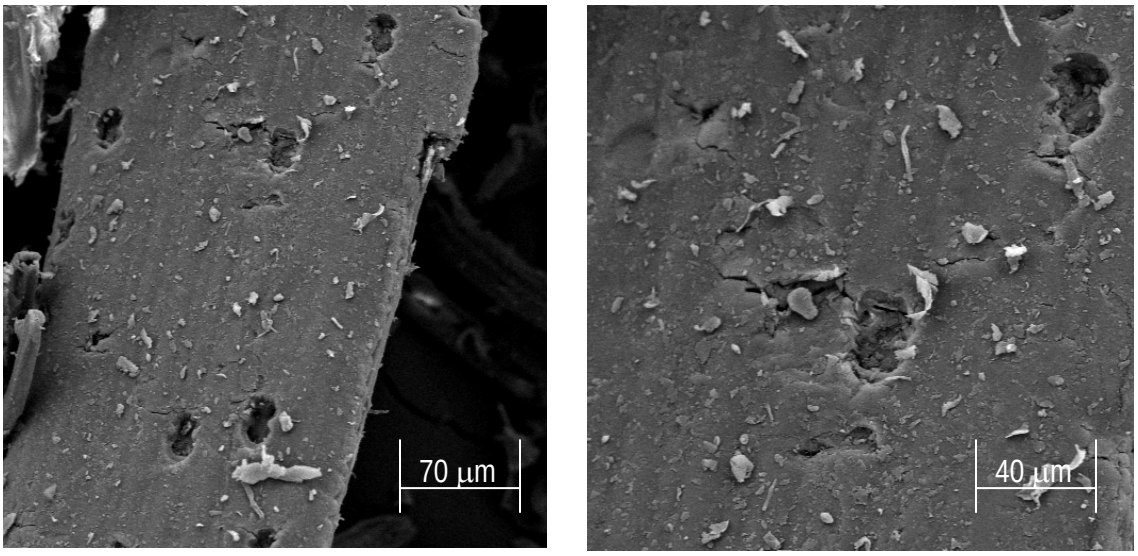


Fig. 5. Curves DSC sugarcane bagasse: unmodified fibers (A), crude cellulose fibers (B), and bleached cellulose fibers (C)

DSC curves Fig. 5 b and 5c show endothermic peaks from 25 °C to 130° C due to evaporation of water (Shaikh et al. 2009; Yang et al. 2007), and a second peak appeared at about 350 and 400°C, which is associated with the dehydration/decomposition of the cellulose.

To confirm the effects of the treatment on cellulose fibers, the samples were analyzed by scanning electron microscopy. Figure 6 shows micrographs of unmodified sugarcane bagasse fibers, providing evidence of a superficial layer with a high percentage of extractives on the fibers.



(A) (B)

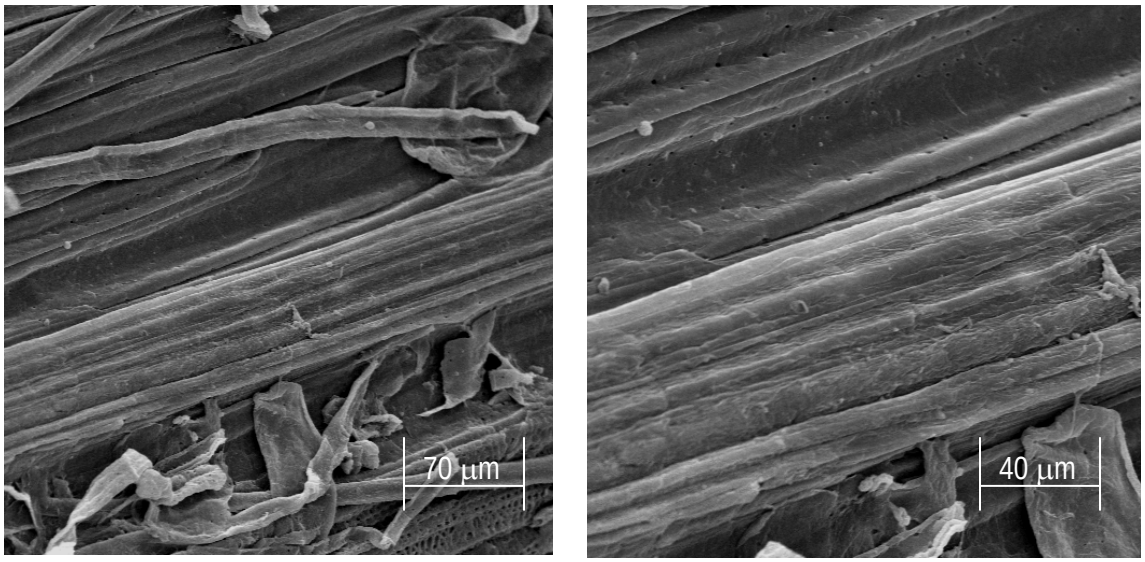
Fig. 6. Morphology of unmodified sugarcane bagasse: (A) 500X; (B) 1000X

A definitive change in the morphological structure of the sugarcane bagasse occurred after the pretreatment with 10% sulfuric acid solution and delignification with NaOH solution. Removal of the extractives from surface fibers was apparent (Fig. 7). It was verified also that elimination of superficial layer was able to increase the contact area because the fibrils became more exposed.

Chemical pulping provided relatively cleaner surfaces, which is consistent with the removal of wax, pectin, lignin, and hemicelluloses, as shown by chemical analyses. Afterwards, typical vegetable cells, parenchyma, and pits could be observed in the morphology of Fig. 7A and 7B.

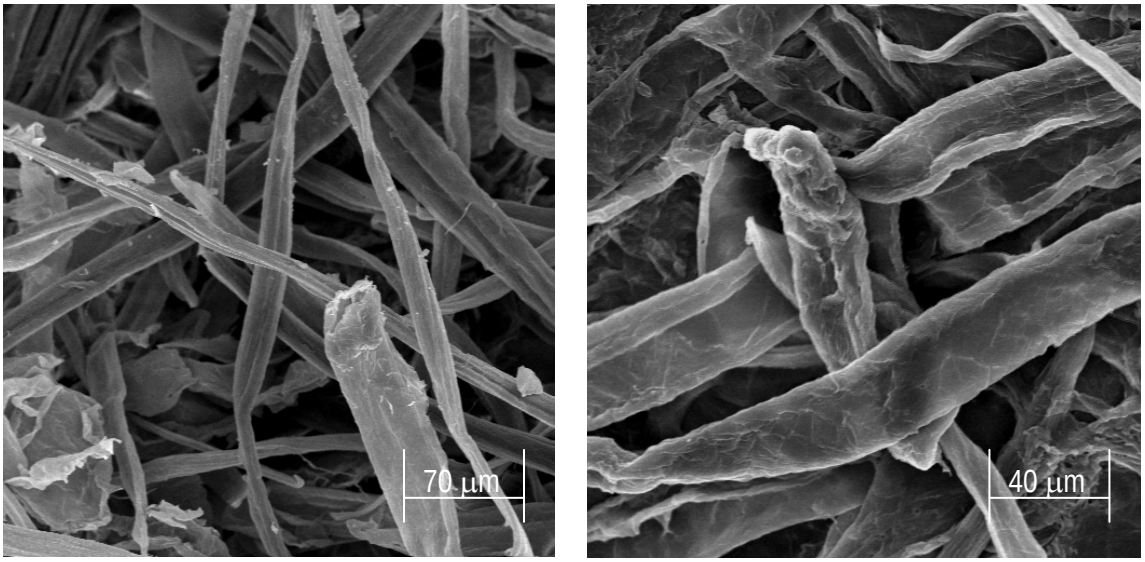
On the other hand, after bleaching the fibers exhibited flattened forms and different sizes. These findings can be observed in images of Fig. 8. Analyzing Fig. 8, the defibrillation of fibers was noted, causing a decrease in fiber length and diameter.

Table 4 shows evidence of the changes in fibers length and diameter after chemical pulping.



(A) (B)

Fig. 7. Morphology of crude cellulose: (A) 500X; (B) 1000X



(A) (B)

Fig. 8. Morphology of bleached cellulose: (A) 500X; (B) 1000X

Table 4. Fibers Length and Diameter after Chemical Pulping

Material	Lenght (µm)	Diameter (µm)
Unmodified sugarcane bagasse	500 – 2000	50 - 400
Crude cellulose fibers	500 – 2000	50 –400
Bleached cellulose fibers	100 - 500	10 – 30

CONCLUSIONS

The general observations of this work can be attributed to structural, thermal, and morphological changes on fibers after chemical modifications. It is evident that the treatments cause different changes in properties and because of that it can be applied in many applications. Chemical pulping in sugarcane bagasse caused removal of wax, pectin, lignin, and hemicelluloses, and these changes were made evident by FTIR and chemical analyses. After bleaching, cellulosic fibers were obtained (rich in cellulose content). It was observed that the bleached cellulose fibers demonstrated higher thermal stability, crystallinity content increase, and flattened morphology when compared to crude cellulose fibers.

Nowadays, cellulose can be applied in many products, for example, composites, chemical derivatives, and others. For this reason, the sugarcane bagasse in this work can serve as an excellent renewable alternative for manufacturing a variety of products.

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