

## **EFFECT OF EXTRACTION PERIOD ON PROPERTIES OF SUGARCANE BAGASSE AND SOFTWOOD CHIPS CELLULOSE**

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### **ABSTRACT**

This work evaluates the extraction of sugarcane bagasse (SCB) and soft wood (SW) celluloses with alkali treatment followed by bleaching process using sodium chlorite at different time. The influence of extraction time (2 hrs and 4 hrs) on the thermal, crystallinity and morphological properties was investigated. The extracted celluloses were analysed by scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transmission infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA). The aromatic skeletal vibrations of lignin and hemicellulose confirmed the extraction of cellulose which varied extraction time. TGA analysis shows that the untreated SCB degrade earlier than their respective celluloses and the prolonged treatment affects the onset of main degradation. XRD results showed that extracted celluloses had greater crystallinity index, and was affected at prolonged time due to long range destruction of cellulose crystals. The SW revealed a complex behaviour due to the dominated lignin content as revealed from chemical composition analyses.

**KEYWORDS:** Sugarcane bagasse, soft wood, cellulose, extraction time.

### **INTRODUCTION**

There has been an increasing interest towards more sustainable usage of lignocellulosic biomass such as sugarcane bagasse and softwood as raw materials for industrial applications (Suna et al. 2004, de Carvalho et al.2017, Gellerstedt et al. 2015). Sugarcane bagasse (SCB) is a by-product of cane from the alcohol and sugar industries that is mainly used in pulp and electricity generation. Chemically, sugarcane bagasse contains approximately cellulose (46.0%), hemicellulose (24.5%), lignin (19.95%), fat, waxes (3.5%), ash (2.4%), silica (2.0%) and other

trace elements (1.7%) (Cotona et al. 2013, Sun et al. 2004, Wang et al. 2001). Soft wood (SW) is increasingly becoming a renewable alternative to fossil fuels due to the high abundance, particularly in areas, such as Mhlathuze in South Africa, where industries abandon soft wood dust in an open space as a waste. SW has a wide range of applications in fibre, pulp, and polymer industries. Structurally, this complex biomass material constitute mainly of cellulose (40-50%), hemicelluloses (15-25%), lignin (20-30%) and variable amounts of extractives. SW is characteristically known for its high lignin content, which results in its reluctances to chemical treatment (Silvério et al. 2013).

The process of pure cellulose isolation has become the subject of extensive research work for many decades due to the cell wall structure complexity. Cellulose is the main constituent of biomass, forming approximately 40% to 45% of the dry substance in most lignocellulosic materials. Cellulose is a linear, unbranched homopolysaccharide composed of anhydroglucose units which are linked together by  $\beta$ -1,4-glycosidic bonds to form a crystalline material (Abdel-Halim et al. 2014, Mittal et al. 2011). This is confirmed by the presence of three hydroxyl groups (secondary OH at the C-2, and at the C-3 and primary OH at the C-6 position) with different reactivities. These hydroxyl groups and their ability to form hydrogen bonds play a major role in directing the crystal packing and also governing the physical properties of cellulose (Silvério et al. 2013, Mandal et al. 2011).

Alkaline treatment or mercerization is one of the most used chemical methods for isolation of cellulose in natural fibers as well as agro-waste. The important modification achieved with alkaline treatment is the disruption of the hydrogen bonding in the network structure (La Mantia et al. 2011, Tran et al. 2014, Shukla et al. 2014, Ye et al. 2012, Gao et al. 2013). This treatment is generally followed by delignification process, since alkali treatment may not completely remove lignin contents. Acidified- $\text{NaClO}_2$  is an established laboratory method for lignin removal. In the presence of acetic acid, aqueous sodium chlorite solutions dissociates into highly reactive chlorine anion ( $\text{ClO}_2^-$ ) and chloride anion ( $\text{Cl}^-$ ) to destroy lignin to simpler compounds, which are dissolved and washed out, resulting in permanent whiteness (Abdel-Halim et al. 2014, Yue et al. 2015). There is a little information or no information in literature which test the same treatment against time. In most studies concentration of chemicals were varied. The aim of this study was to investigate the influence of extraction time (2 and 4 hours) on the morphology, crystallinity and thermal stability of the resulting cellulose extracted from SCB and SW.

## MATERIAL AND METHODS

### Materials

Sugarcane bagasse and soft wood were obtained from local sugar and wood factories (Empangeni, South Africa). Sodium hydroxide pellets (99.9%) were supplied by Merck, India, Sodium chlorite by Capital lab Suppliers CC, Germany. All chemicals were used as received without further purification.

### Methods

The washed and room temperature dried SCB and SW were initially treated 4 times with 2% (w/v) NaOH for 2 hours respectively and washed with deionised water to neutral pH. Secondly, the alkali treated SCB and SW were further subjected to 4 times treatment of 2% (w/v)  $\text{NaClO}_2$  treatment for a further 2 and 4 hours and washed to obtain neutral pH and dried. The celluloses extracted from that were named cell 2 and cell 4, respectively.

## Chemical composition

The untreated SCB and SW raw samples were used to determine their respective chemical composition. The lignin, cellulose and hemicellulose of the untreated materials SCB and SW were determined according to the TAPPI Standard T222 om-88, and TAPPI T19m-54 standards.

## Characterization techniques

### *Scanning electron microscopy (SEM)*

The SEM and EDX measurements of the as-deposited thin films were performed on a Philips XL 30 FEG (at 10 kV) and DX4 detector (at 20 kV), respectively. The films were carbon-coated by using Edward's E306A coating system, prior to the analyses.

### *Fourier transmission infrared spectroscopy (FTIR)*

FT-IR spectroscopy analysis was carried out on a Bruker Tensor 27 FT-IR spectrometer using a standard ATR cell; the catalysts were analysed as-synthesised with no prior preparation required. The force was adjusted to 90 gauges for sufficient contact between the surfaces. The catalysts were scanned over the mid-IR region (450- 4000  $\text{cm}^{-1}$ ).

### *Powder X-ray diffraction (XRD)*

The XRD characterization of all samples was performed on Powder X-Ray Diffraction spectroscopy (Bruker AXS Advance D8 diffractometer) with monochromatic Cu  $K\alpha$  ( $\lambda = 1.5406 \text{ \AA}$ ) incident radiation at 40 kV and 40 mA at room temperature. The samples were scanned within the high angle  $2\theta$  range to get all characteristic diffractions of the materials at 0.5 scan speed and 0.01314 increments. The crystallinity index (CI) was obtained from:

### *The height peak method*

The CI was calculated from the ratio of the maximum peak intensity 002 ( $I_{002}$ ,  $2\theta = 22.5$ ) and minimal depression ( $I_{\text{am}}$ ,  $2\theta = 18.5$ ) between peaks 001 and 002 according to Eq. 1.

$$\text{CI} = (I_{002} - I_{\text{am}})/I_{\text{am}} \times 100, \quad (\%) \quad (1)$$

where:  $I_{002}$  - maximum intensity of the 002 peak,  
 $I_{\text{am}}$  - minimal depression of the amorphous structure.

### *The deconvolution method*

The CI was determined using Eq. 2, by comparing the corresponding areas of the crystalline and amorphous fractions, obtained by deconvolution of the diffractogram, where  $A_A$  is the area of the amorphous phase and  $A_t$  the total area of the diffractogram.

$$\text{CI} = (1 - A_a/A_t) \times 100 \quad (\%) \quad (2)$$

### *Thermal gravimetric analysis (TGA)*

Thermogravimetric analyses were performed using TGA analyser unit (Perkin Elmer), under flowing nitrogen atmosphere at flow rate of 20  $\text{ml min}^{-1}$ . Approximately 10-15 mg of sample was heated from 25°C to 600°C at a heating rates rate of 10°C·min<sup>-1</sup>. The sample weight loss and rate of weight loss were recorded continuously as functions of temperature. The analysis was only started when isothermal condition had been obtained.

## RESULTS AND DISCUSSION

**Chemical composition**

Chemical composition analysis was conducted to ascertain various contents of biopolymers from untreated SCB and SW in Tab. 1. The cellulose content is highest in both materials than hemicellulose and lignin. There is no common trend exhibited by hemicellulose and lignin in both materials, however a first trend shown by SCB, in which hemicellulose is more than lignin in a natural fibre, is abundant in literature and appeared acceptable. However, in this study a second trend by SW showed the opposites. The phenomenon which is infrequent in literature but not ruled and/or impossible due to various factors affecting the contents of the components such as the origin and a part in a plant (Gellersterdt et al. 2015).

Tab. 1: Chemical compositions of SCB and SW fibres.

Sample	Cellulose (%)	Hemicellulose (%)	Lignin (%)
SCB	39.75 ± 0.7	38.03 ± 0.1	22.01 ± 0.6
SW	40.00 ± 0.5	24.00 ± 0.1	37.00 ± 0.5

**Surface analysis**

Fig. 1 represents the SEM images of extracted cellulose from SCB and SW. It is clear that the untreated SB and SW (Figs. 1 a, and b, respectively) have particles, probably waxes and pectin, on the surfaces which were removed after treatments to obtain cellulose. In fact, the removal of particles for SCB Cell 2 and SW cell 2 was accompanied by a decrease in diameter from approximately 45 to 10 and 60 to 20 µm respectively (Figs. 1 c, and e). The SCB Cell4 and SW Cell 4 revealed even smaller average diameter, which is approximately smaller than 5 µm and 10 µm respectively, than both Cell 2 samples. This suggests that further defibrillation occurred during 4 hours treatment and it seems as though SCB has a weak cell wall which rendered little resistance to defibrillation. This also explains why SCB Cell 4 contained what arguably looked like nanofibrils compared to SW Cell 4, which contained almost none.

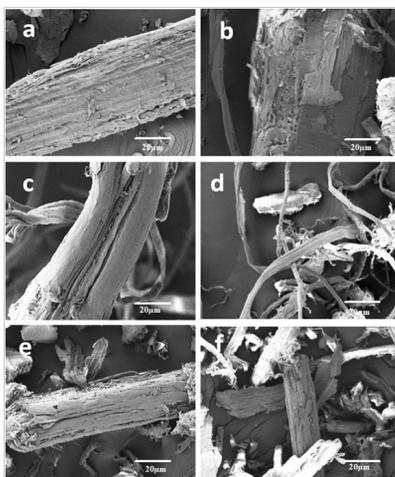


Fig. 1: SEM images of untreated SCB (a), SW (b), SBC Cell 2 (c), SW Cell 4 (d), SW Cell 2 (e) and SW Cell 4 (f).

## Spectral analysis

FTIR of untreated SCB and SW and their corresponding celluloses are shown in Fig. 2. The FTIR spectra of SCB showed more intense peaks than SW. Both spectra showed similar patterns with the dominant peaks observed around  $3336\text{ cm}^{-1}$  (O–H stretch),  $2901\text{ cm}^{-1}$  (C–H vibrations),  $1593\text{ cm}^{-1}$  (C=C aromatic),  $1319\text{ cm}^{-1}$  (O–H vibration of phenolic group),  $1028\text{ cm}^{-1}$  (O–H stretching),  $897\text{ cm}^{-1}$  ( $\beta$ -glycosidic linkage), and  $558\text{ cm}^{-1}$  related to C–OH out-of-plane bending. These peaks are typical for lignocellulosic materials and in agreement with those reported in the literature for both untreated SCB and SW (Sivério et al. 2013, Abdel-Halim 2014, Mandal and Chakrabarty 2011). But after the chemical treatment, the peaks observed in the range  $1750$  and  $1250\text{ cm}^{-1}$  linked to aromatic skeletal vibrations of lignin and hemicelluloses were reduced and others are almost diminished as compared to untreated materials. This indicates removal of lignin and hemicelluloses, as well as an exposure of cellulose (de Oliveira et al. 2016, Lionetto et al. 2012). The intensity of most peaks for SCB cell 2 was reduced, while an aromatic peak at  $1509\text{ cm}^{-1}$  almost disappeared. The same applied for SCB cell 4 except the intensity which was not that much affected in most peaks. Surprisingly for SW cell 2 and 4, a peak which seems to disappear is at  $1732\text{ cm}^{-1}$  with no much change with time. This might be associated to removal of the aromatic structure of lignin which seems to differ with that of SCB.

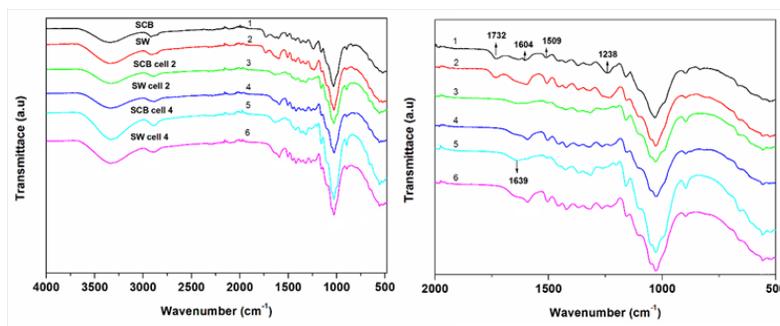


Fig. 2: FTIR spectra of untreated SCB and SW, and extracted SCB and SW cellulose at 2 and 4 hours.

## X-ray diffraction

The X-ray diffraction patterns of untreated SCB and SW and their corresponding celluloses are shown in Fig. 3 and the crystallinity index values presented in Tab. 2. The diffractograms of SCB and SW materials display dominant peaks at  $2\theta$  values corresponding to  $15.5^\circ$  and  $22.5^\circ$  of the polymorphs of cellulose I of natural fibers (Teixeira et al. 2011, Nakasone and Kobayashi 2016). The crystallinity results showed that both the SCB and SW presented the lower crystallinity when compared to celluloses. Similar results were also reported by Candido et al. (2017) who observed an increase in crystallinity index after extraction of cellulose from SCB. They ascribed the higher crystallinity index to a larger exposure of cellulose in SCB cellulose than in untreated SCB. The SCB cell 4 and SW cell 4 presented a reduced crystallinity index as compared to SCB cell 2 and SW cell 2. This observation suggests that time of 4 hours was too severe to not only remove the amorphous phase, but also destroyed parts of the crystalline cellulose. Wang et al. (2013) explained the similar observation to broken intermolecular and intra-molecular hydrogen bonds of cellulose which apparently causes the disintegrate of crystal structure. This is highly possible in this study when considering disappearance and intensity change of some peaks in the FTIR results, which reflected change in crystal structure.

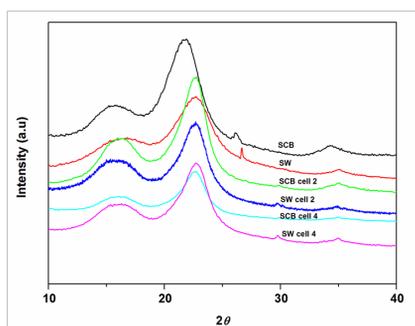


Fig. 3: XRD analysis of untreated SCB and SW, and extracted SCB and SW cellulose at 2 and 4 hours.

Tab. 2: Crystalline index of untreated SCB, SW and extracted SCB and SW cellulose.

Sample	Peak height method	Deconvolution method
SW	51.0	56.9
SW Cell 2	71.9	75.8
SW Cell 4	62.9	67.4
SCB	62.4	66.4
SCB Cell 2	78.3	80.3
SCB Cell 4	64.2	76.3

### Thermal properties

The TGA curves for SCB and SW and their respective celluloses are shown in Fig. 4. The untreated materials exhibited three degradation steps known for moisture, hemicellulose, cellulose and lignin that cuts across the thermal region of cellulose and hemicellulose (Silvério et al. 2013, Yue et al. 2015, Nakasone and Kobayashi 2016).

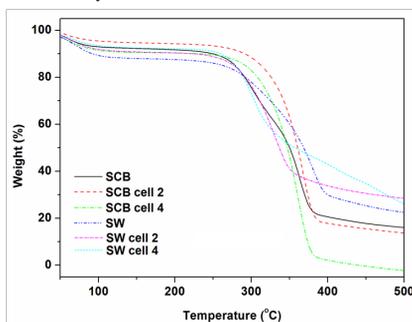


Fig. 4: TGA graphs of untreated SCB and SW, and extracted SCB and SW cellulose at 2 and 4 hours.

The SW was thermally stable than the SCB and presented the higher char content than SCB. As expected, the onset of main degradation shifted towards a higher temperature for all celluloses and SCB Cell 2 and SW Cell 2 presented the higher thermal stability than SCB Cell 4 and SW Cell 4. This clarifies the observations of XRD and FTIR that prolonged period, in fact, depolymerized cellulose to give the reduced crystallinity index values and ultimately lowered thermal stability. Interestingly, the SCB cell 2 and cell 4 decreased in char content while

the opposite occurred for SW cell 2 and cell 4. The observation is embedded in the thermal degradation mechanism which is informed by morphology observed from FTIR and XRD.

## CONCLUSIONS

Cellulose materials were successfully extracted from SCB and SW lignocellulosic materials through alkali treatment and delignification using  $\text{NaClO}_2$  bleaching agent. The chemical composition results showed that SCB had higher hemicellulose content than cellulose, and SW presents the highest lignin content. The results obtained from FTIR confirmed that both lignin and hemicellulose were removed during the chemical process with complete removal obtained at 2 hours. The crystallinity index results showed that the crystallinity was increased with chemical treatment, with the highest crystallinity values obtained at 2 hours for treated SCB and SW, respectively. The TGA further results revealed that the untreated SCB and SW materials analysed at 2 hours were thermally stable than their untreated and 4 hours treated counterparts.

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