

A COMPARATIVE STUDY OF SUGARCANE BAGASSE AND SOFT WOOD

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ABSTRACT

This article investigated properties of different lignocellulosic biomasses. Both acidified and non-acidified sodium chlorite were used to treat wood chips and sugar cane bagasse. Images were part of characterizations that included X-ray diffraction (XRD), thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FT-IR). Interestingly the results indicated that biomasses followed the similar crystallinity trend while thermal stability and functional groups on the cellulose surface seemed to differ. All the FT-IR spectra showed 8 main peaks but spectra of bagasse have an additional peak. Stretching vibrations of the O-Hand the C-H stretching group in cellulose molecules were clear for all biomasses. The treatment clearly removed most of aromatic compounds normally attributed to lignin and hemicellulose.

KEYWORDS: Sugarcane bagasse, soft wood, pre-treatment, cellulose pulp.

INTRODUCTION

Natural resources had ecological limits and both developed and developing countries need to consider ways of decoupling the meeting of economic growth targets from increasing natural resource's extraction. A transition towards a green economy was seen as a means to drive and implement sustainability (Brinchi et al. 2013, Sun et al. 2004, Wang et al. 2001, Entwistle et al. 2000, Moran-Maribal et al. 2013). South Africa is now taking a continental lead in the integration and implementation of a green economy, as well as putting initiatives in place to achieve the targets set out in the Millennium Development Goal (MDG) to ensure environmental sustainability. However, the concept is relatively new and there are significant capacities and knowledge gaps in this field. Since, this is a new emerging area in South Africa as a whole, growing global pressure is driving accelerated research and development (Motaung and Mokhothu 2016, Lekha et al. 2016).

The University of Zululand is making an effort to establish itself as South African leader in implementation of green economy and working hand in hand with the Department of Environmental Affairs to fast track government's initiatives to achieve this concept. Cellulose-derived from crop residues can be used as reinforcing elements in green composites because green composites have the greatest market growth potential in industries where biocompatibility and environmentally responsible design and constructions are required (Lekha et al. 2016, Silvério et al. 2013). Policies and regulations in South Africa are now conceptualized to support the development of renewable products from agro-waste. In the South African economic context an effective utilization of sugarcane bagasse for bio production is very important. The centre of the sugar industry is in KwaZulu-Natal, where it contributes between 0.5% and 0.7% of the national gross domestic production, 0.5% of total income tax, 0.9% of merchandise exports by value and about 0.3% of salaries and wages (Mohomane et al. 2017a). The demand for sugarcane in sugar industry has been increasing as a consequence in 2016; the KwaZulu-Natal (KZN) Department of Agriculture and Rural Development have launched a R14-million Sugar Cane Plantation Project on the south coast. This has directed Engineers and Scientists to perform relevant research, adding value to sugarcane bagasse and moving South Africa towards sustainable economy. The interests in supporting South Africa's bioeconomy strategy have included the use of sugarcane bagasse to aid the country to establish a proper waste management sector and to introduce a zero waste concept. Sugarcane bagasse has outstanding applications in biofuel, biogas and green composites, respectively (Rocha et al. 2011, Kim et al. 2016, Chen et al. 2011). The South African sugar industry is a mature commodity that is faced with the reality that sugar, molasses and bagasse can no longer be regarded as the final product from a sugar mill. Value addition and diversity are increasingly being investigated as possible routes to new markets and making the industry less dependent on a single commodity. However, one of the main draw backs which must be overcome before sugarcane bagasse can be used as feed stocks is the development of appropriate chemistries which will meet process and product requirement. Because, sugarcane bagasse fibres have hydroxyl groups on the surface which produce highly polar and hydrophilic surfaces which are incompatible with many polymer matrices (in case of biocomposite development), but the fibre-surface structure can be modified using chemical and thermal treatments in order to enhance adhesion at the fiber-polymer interface (Silvério et al. 2013, Li et al. 2009). Sugarcane bagasse is mainly formed by two carbohydrate fractions (cellulose and hemicellulose) embedded in a lignin matrix.

Softwoods consist mainly of pine species; about 69% of all softwoods are for sawlog production in South Africa. KwaZulu-Natal accounted for 183,554 hectares softwood in 2016. Softwood trees are gymnosperms conifers (evergreens) with needles or scale-like foliage and which are not deciduous (Quiroga et al. 2016). Examples of softwoods include pines, spruces, firs and hemlocks. It is widely used in the development of composites due to its availability, inexpensiveness and naturally occurring. Although wood can be used as an engineering construction material, its mechanical properties are insufficient for it to be used for a long time as an engineering material. For specific application in composites, wood fibres are subjected to treatment (chemical and mechanical).

Soft wood has been studied and reported to be useful in composite materials. However, there was no a systematic comparison studied between soft wood and sugar cane bagasse under low concentration of alkali treatments, which is the core of the current study.

MATERIAL AND METHODS

Materials

Sugarcane bagasse (SCB) and eucalyptus soft wood (SW) species were obtained from Mondi paper company, Emphangeni, South Africa. Sodium hydroxide pellets (99.9%) and sulphuric acid (98%) were obtained from Merck, potassium hydroxide (85%) from Laboratory consumables and sodium chlorite (80%) was obtained from Sigma Aldrich. All chemicals were used as received without further purification.

Methodology

Sugarcane bagasse and softwood were washed with tap water and dried in the oven overnight. The materials were then treated with 2% (w/v) NaOH for 1 hour 4 times at 80°C, and washed with deionised water to neutral pH. The alkali treated fibres were dried overnight in an oven at 50°C. They were further subjected to 2% (w/v) NaClO₂ for 1 hour 4 times at 80°C, washed to obtain a neutral pH and dried at 50°C. Two types of NaClO₂ were used, acidified and non-acidified. The acidified NaClO₂ (pH = 4.2) was obtained by adding glacial acetic acid and the pH was measured using a pH meter. Lastly, the fibres were treated with 2% (w/v) KOH for 1 hour 4 times at 80°C, washed to obtain a neutral pH. The step was repeated 4 times and the fibres were dried at 50°C overnight.

Characterization techniques

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 α ($\lambda = 1.5406 \text{ \AA}$) incident radiation at 40 kV and 40 mA at room temperature. The samples were grinded into fine powder and placed on a sample holder. The samples were scanned within the high angle 2θ range (10 – 90) to get all characteristic diffractions of the materials at 0.5 scan speed and 0.01314 increments.

Thermogravimetric analysis (TGA)

TGA was carried out with a Perkin Elmer Pyris1 by using nitrogen as a purge gas and a heating rate of 10°C·min⁻¹. Samples analysed were between 10 mg - 15 mg. The TGA programmed to increase the temperature linearly from room temperature to 600°C under a flow of nitrogen. The temperature of the sample was monitored and the loss of weight of the sample was expressed in terms of percentage weight loss. The analysis was only started when isothermal condition had been obtained. This was done by allowing sample to stand at room temperature for 5 minutes. The thermal gravimetric derivative data was used to obtain the decomposition temperature.

Fourier transform infrared spectroscopy (FT-IR)

FT-IR spectroscopy analysis was carried out on a Bruker Tensor 27 FT-IR spectrometer using a standard ATR cell. The samples were analyzed in a spectral region between 4000 and 400 cm⁻¹ with a 4 cm⁻¹ resolution.

RESULTS AND DISCUSSIONS

XRD Diffractograms

X-ray diffraction analysis is used to evaluate the effect of chemical pre-treatment on crystalline structure of cellulose as shown in Fig. 1. Tab. 1 summarises the values of crystallinity index calculated by Segal empirical method (Mohomane et al. 2017a, 2017b, Segal et al. 1959).

$$CI = \left(\frac{I_{002} - I_{am}}{I_{002}} \right) \times 100 \quad (\%) \quad (1)$$

where: I_{002} - the maximum intensity of the 002 lattice reflection of cellulose,
 I_{am} - the maximum intensity.

Three peaks are observed on the diffractograms of untreated and pre-treated samples (Fig. 1). The first peak is observed at 15.9° for SCB and 16.7° for SW. The second peak is observed at 21.9° and 22.7° for SCB and SW respectively. This is a crystalline peak for 002 plane which indicated the presence of cellulose (Fang et al. 2000). At this peak the bagasse showed higher and sharper reflection than wood. The last peak is observed at 33.4° and 35.2° for SCB and SW respectively. These peak patterns are in good agreement with those reported in literature (Rocha et al. 2011, Kim et al. 2016, Chen et al. 2011). After the pre-treatment with NaClO_2 all the peaks slightly increased intensity in line with crystallinity index values as shown in Tab. 1. The observation is within literature in that mercerization dissolves lignin and hemicellulose for higher crystallinity (Silvério et al. 2013, Li et al. 2009, Quiroga et al. 2016). The peak at 22.7° for the acidified pre-treatment in wood is much more intense. The effect was even more pronounced for acidified samples which confirmed dissolved amorphous region to some extent to yield even better crystallinity, which in this case, increased almost by 30% and 40% for both SCB and SW respectively.

Tab. 1: Crystalline index of untreated and alkali treated NaOH sugarcane bagasse (SCB) and soft wood (SW).

Samples	Crystallinity index (CI%)
1. SCB	63
2. Alkali treated SCB	90
3. Acidified SCB	92
4. SW	51
5. Alkali treated SW	71
6. Acidified SW	94

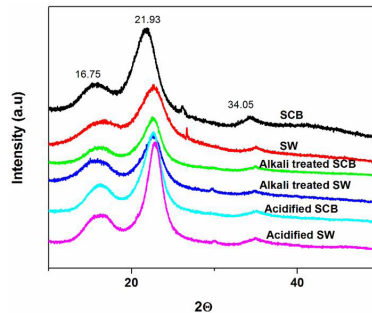


Fig. 1: XRD patterns of untreated, alkali treated and acidified sugarcane bagasse and softwood.

Fig. 2 represents the images of untreated SCB and the chemically bleached pulps. It can be seen that the pulp treated with non-acidified NaClO_2 are brownish in colour reflecting a relative incomplete delignification, while the acidified ones are milky. Coincidentally the whitish materials have highest crystallinity values than the rest as seen from XRD. Non-acidified SCB and acidified SW pulp looked more compact than the rest. The opposite is true for non-acidified SW pulp. A difference in origin of the lignocellulosic materials is more likely accountable for the interesting observations.



Fig. 2: Images of untreated SCB, SW and their respective non-acidified and acidified pulps.

The effect of treatment on the thermal behaviour of sugarcane bagasse and softwood was studied by TGA. Fig. 3 shows the TGA and DTG curves of untreated, alkali treated and acid treated sugarcane bagasse and softwood. There are three degradation stages present on the curves as confirmed by DTG. The first stage of weight loss at $\sim 30 - 100^\circ\text{C}$ normally attributed to water evaporation associated with moisture present in SCB and SW samples (Motaung and Mokhothu 2016, Mohomane et al. 2017a, 2017b). The second stage at $100 - 250^\circ\text{C}$ is the degradation of hemicellulose followed by cellulose. Apparently lignin degrades across the region of both hemicellulose and cellulose (Mohomane et al. 2017b). This proves to be correct in this study since there is no unusual peak for lignin. The thermal stability of SCB is clearly higher than of SW. The observation is consistent and more pronounced after alkali treatment, nonetheless negligible in the event of acidified counterparts. The treatments are accompanied by elimination of a the second degradation step, except in the case of SW sample which still carried a shoulder at 265°C after alkali treatment (See Fig. 3). In view of the scope of this study, the response of the samples to non-acidified alkali treatment could account for the observations.

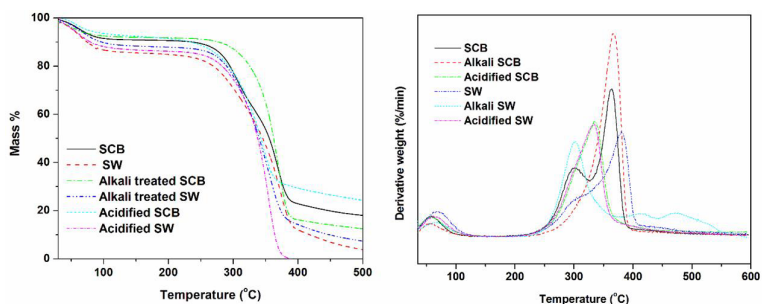


Fig. 3: TGA and DTG curves of untreated, alkali treated and acid treated sugarcane bagasse and softwood.

FTIR spectra of sugarcane bagasse, softwood and the treated counterparts are shown in Fig. 4. All the spectra show 8 main peaks but spectra of bagasse have an additional peak at 1243 cm^{-1} which will be discussed later. The absorption peaks at 3347 and 3338 cm^{-1} for SCB and SW respectively are of the stretching vibration of the OH group in cellulose molecules. The absorption bands at 2896 and 2910 cm^{-1} for bagasse and wood respectively represent the C-H stretching vibration (Motaung and Mokhothu 2016, Mohomane et al. 2017a). Peak at 1716 and 1733 cm^{-1} for SCB and SW respectively correspond to the C=O stretching vibrations of uronic and acetyl ester groups of pectin, hemicellulose or the ester linkage of the carboxylic group of p-coumaric and ferulic acids of hemicellulose and lignin. The absorption band at 1604 and 1597 cm^{-1} in the spectra of bagasse and softwood is of the aromatic C=C in plane symmetrical stretching vibration found in the lignin. The absorption peak at 1376 and 1380 cm^{-1} for SCB and SW respectively represent the bending vibration of the C-H and C-O bonds in the polysaccharide aromatic ring.

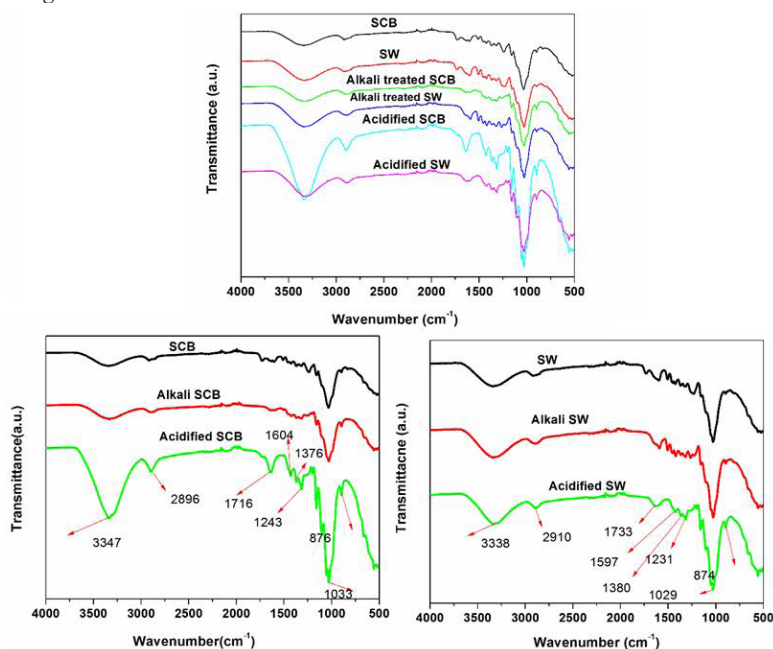


Fig. 4: FTIR spectra of SCB, SW, alkali treated and acidified sugarcane bagasse and softwood.

The peak at 1243 cm^{-1} in the spectra of bagasse only, indicates the C-O out of plane stretching vibration of the aryl group in lignin (Kim and Day 2011). The peak 874 cm^{-1} is of the β -glycosidic bond between glucose units in the cellulose. All these peaks are more intense in the acidified pulp in bagasse due to amongst other things removal of lignin and hemicellulose. In both lignocellulosic material the peaks attributed to aromatic compounds either shifts or disappear probably due to sulphate functional groups or alkali polyatomic ions trapped (Fang et al. 2000). These results confirm the variation in crystallinity from XRD and thermal stability from TGA. In fact, the morphology which led to powder may be affected by trapped polyatomic ions.

CONCLUSIONS

The preparations of modified biomasses were achieved and the effects were very reflective on the characterizations. The acidified sodium chlorite rendered powder morphology for SW and compact structure for SCB. The crystallinity of both increased with whichever treatment, while thermal stability behaved independently. The modifications are crucial and recommended for blending in biopolymers in the interests of biocomposites to address the current environmental demands.

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