INVESTIGATION OF POROSITY, WETTABILITY AND MORPHOLOGY OF THE CHEMICALLY PRETREATED SUGARCANE BAGASSE

Glauber Cruz
University of São Paulo, Engineering School of São Carlos, Mechanical Engineering Department, São Paulo, Brazil.
glauber.cruz@usp.br

Patrícia A. S. Monteiro
University of São Paulo, Physical Institute of São Carlos, São Paulo, Brazil.
pamarasantiago@gmail.com

Carlos E. M. Braz
State University Paulista "Júlio de Mesquita Filho", Chemistry Institute of Araraquara, São Paulo, Brazil.
carlosedumb@iq.unesp.br

Paulo Seleghim Júnior
University of São Paulo, Engineering School of São Carlos, Mechanical Engineering Department, São Paulo, Brazil.
seleghin@sc.usp.br

Igor Polikarpov
University of São Paulo, Physical Institute of São Carlos, São Paulo, Brazil.
ipolikarpov@ifsc.usp.br

Paula Manoel Crnkovic
State University Paulista "Júlio de Mesquita Filho", Chemistry Institute of Araraquara, São Paulo, Brazil.
paulam@sc.usp.br

Abstract. *Enzymatic hydrolysis is one of the major steps involved in the conversion from sugarcane bagasse to ethanol production. This process shows a higher potential on yields and selectivity, a lower energy costs and a milder operating conditions in comparison to conventional chemical processes. However, the presence of some factors limit the digestibility of the cellulose present in the lignocellulosic biomasses, such as lignin content, degree of crystallinity of cellulose and particle sizes. Pretreatment aims to improve the enzyme access to the substrate. Differences in BET and BJH surface area, pores diameter and volume, structural and morphological changes were investigated by SEM images, X-Ray, FTIR and Wettability for sugarcane bagasse in natura and submitted to two pretreatments: diluted sulfuric acid (1% H_2SO_4) and alkaline-solution concentrations (1, 2, 3 and 4% NaOH). Results showed that it was possible to observe morphological changes occurred after pretreatments. Acid and alkaline treatments had an increase for both BET and BJH surface areas about 9.2%, diameter and volume of pores also increased. Crystallinity index also increased about 3.6% in the amorphous cellulose and lignin regions degradation. Other experimental techniques, such as FTIR (functional groups, bands and vibrations) and wettability (hydrophobicity and hydrophilicity), were also confirmed the increase in these structural changes. In summary, the pretreatments employed were effective in chemical degradation of lignocellulosic materials for the bioenergy generation.*

Keywords: adsorption and desorption, lignocellulosic biomass, BET and BJH surface area, pore area and volume

1. INTRODUCTION

Since, the biomass is a renewable and carbon-neutral resource, it is attractive as an alternative to fossil fuel in addition, and it provides the reduction of human dependence on fossil fuels avoids the climate changes (Cornelissen *et al.*, 2012; Yoshida *et al.*, 2008).

According to Cortez *et al.* (2008) only a part of the biomass is used for bioenergy production; in the case of sugarcane, one-third of the plant for the sugar production, one-third is bagasse, which is burned for electricity production in plant power, and the other one-third remaining is left in the field, which is decomposed by microorganisms (Soccol *et al.*, 2010).

A global overview reports the extensive use of sugarcane as main feedstock for the ethanol and sugar production. Among the developing countries, Brazil, in 2011, was considered the major producer and consumer of these products in worldwide due to the harvest of sugarcane about 570 million tons (UNICA, 2012; Rezende *et al.*, 2011; Guimarães *et al.*, 2009). Sugarcane is milled for juice extraction (to produce sugar or alcohol), after this process, bagasse is obtained as a residue, which corresponds to 25% of the total weight and contains from 60 to 80% of carbohydrates (Betancur & Pereira, 2010).

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Many researches are being done to enhance the digestibility of lignocellulosic part of the biomass, especially as regards the possibility to improve the conversion of hemicellulose/cellulose to ethanol, methane and, in the last years, hydrogen. The different pretreatment methods to increase the digestibility of lignocellulosic material were cited in previous study (Shenoy *et al*., 2011; Hendriks & Zeeman, 2009; Yu *et al*., 2009).

According to Guo & Catchmark (2012) different origins and treatments are responsible for the complexity and variability of cellulosic structures. The knowledge of surface area and porosity are important parameters to understand the structure, formation and degradation of cellulose, which can contribute to be used as biofuels. For example, Fan *et al*. (1981) showed that the surface area of the biomass was very important in the enzymatic hydrolysis of the cellulose, due to the direct physical contact between cellulases and the surface of the cellulose, which was decisive to the accessibility of the cellulases into the cellulose to hydrolysis, in addition, the authors also showed that the high surface area and pore volume guarantee sufficient adsorption of the cellulases to the cellulose surface.

This study aims to evaluate the characteristics of the sugarcane bagasse samples in both *in natura* and pretreated. Different treatments were used to improve the enzyme access to the substrate: dilute sulfuric acid (1% H_2SO_4) and alkaline solution concentrations (1, 2, 3 and 4% NaOH). The characteristics observed were: BET surface area (S_{BET}) (Brunauer, Emmett and Teller) and BJH (Barrett, Joyner and Halenda) (Orr & Webb, 1997; Gregg & Sing, 1982), as well as pores diameter and volume. Morphological and structural changes were evaluated with SEM images, X-ray diffraction and FTIR spectroscopy. Contact Angle (wettability) was used to compare the interactions between substrate and the several treatments.

2. EXPERIMENTAL

2.1 Substrates

Sugarcane bagasse samples used in the experiments are from the harvest (2011/2012) and it was supplied by Raizen Group (São Paulo state, Brazil). Prior to the analysis and pretreatment, the samples were dried at 45 °C for 48 h, left at room temperature for 24 h and it is then stored in plastic containers until its use (Rabelo, 2010).

2.2 Acid and alkaline pretreatments

The dry sugarcane bagasse was initially pretreated with a solution 1% H_2SO_4 to solubilize the hemicellulose. After this step, the samples were submitted to the alkaline treatments, which consisted in using four different solutions of NaOH (1, 2, 3 and 4% w/v) to promote the delignification. The suspension containing the sugarcane bagasse was autoclaved for 40 min at 1 atm and 120 ºC. Consequently, the samples were washed with distilled water to eliminate acid or alkaline excesses until a neutral pH (Rezende *et al*., 2011).

2.3 Surface Area and Porosity Analysis (ASAP)

Nitrogen porosimetry gas adsorption at 77 K was performed in the ASAP 2020, Micromeritics porosimeter. Tests have been performed in duplicate and sample mass of (1.5 ± 0.2) g was used. The samples were previously dried in an oven by approximately 24-120 h at 110 ºC. The conditions of degas and analyses are described below:

1. Degas conditions: heating rate of 10 °C min^{-1} up to 50°C under vacuum restricted evacuation rate of 10 mmHg s^{-1} to 1 mmHg; evacuation was changed to non-restricted vacuum at the same evacuating rate until 10 µmHg, remaining under these conditions for 30 min; the heating continued at the rate of 10 °C min^{-1} up to 70 °C and the samples remaining under these conditions for 240 min.

2. Analysis conditions: the samples started in vacuum restricted at an evacuation rate of 5 mmHg s^{-1} up to 5 mmHg; the evacuation was changed to non-restricted vacuum at the same evacuation rate until 10 µmHg, remaining under these conditions for 6 min. Then P/P$_o$ programming for 33 points was applied (21 adsorption and 16 desorption points). P/P$_o$ is the pressures ratio (relative pressure) and its maximum value reached was 0.994. Where (P) is the applied pressure and (P$_o$) saturation vapor pressure of adsorbed gas (nitrogen) (Pécora *et al*., 2013).

2.4 Scanning Electron Microscopy (SEM)

Morphological and structural analysis has been obtained on a Scanning Electronic Microscope Ltd. equipment brand, LEO 440 model. The focus on this study is to evaluate the cross-section of the samples fibers, which was obtained by fracture of the fibers after to be submitted to the liquid nitrogen bath. The *in natura* studied fibers were chemically pretreated (acid and alkaline). Prior to be introduced in the microscope, samples were metalized in gold bath (Cruz *et al*., 2013; Rezende *et al*., 2011).

2.5 X-Ray Diffraction (X-Ray) Diffraction

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X-Ray diffractograms were obtained using a D 5000 model Siemens brand X-Ray Diffractometer, operating in 40 kV, 20 mA, employing radiation of CuK_α (λ = 1.541 Å) and angle 2θ with scanning between 4 ° and 80 °, under a time step of 0.020 s^{-1}.

2.6 Fourier Transform Infrared (FTIR) Spectroscopy

To obtain of the absorption spectra in the infrared region, a Shimadzu brand IR Prestige 21 model spectrophotometer (IR-TF) was used, operating in the range 4000 to 400 cm^{-1}, by Fourier Transformed, using KBr (Potassium Bromide) pellets.

2.7 Wettability or Contac Angle (CA)

Wettability measures have been obtained using an Easy Drop System – DO 4010 model (Goniometer), from Krüss German brand with DSA - Drop Shape Analysis computational program, at a room temperature and an atmospheric pressure controlled. Drop volume of 8μL with deionized water was deposited onto the substrates, by Circle Fitting method (more indicated for rough surfaces). The images were made in duplicate and save the first measure with accuracy ± 3°, immediately after the drop placement on the surface to avoid the perturbation by evaporation process (Azevedo *et al*., 2009; Krüss, 2005).

3. RESULTS AND DICUSSIONS

3.1 Analysis of the Surface Area and Porosity

The adsorption and desorption nitrogen isotherms obtained for *in natura* and chemically pretreated sugarcane bagasse samples are shown in Fig. 1.
Koo *et al*. (2011) reported that lignocellulosic materials present pores, which may also be generated by chemical and mechanical treatments. The authors state that generation of pores increase the specific surface area and consequently increasing the enzyme access into inner part of the samples.
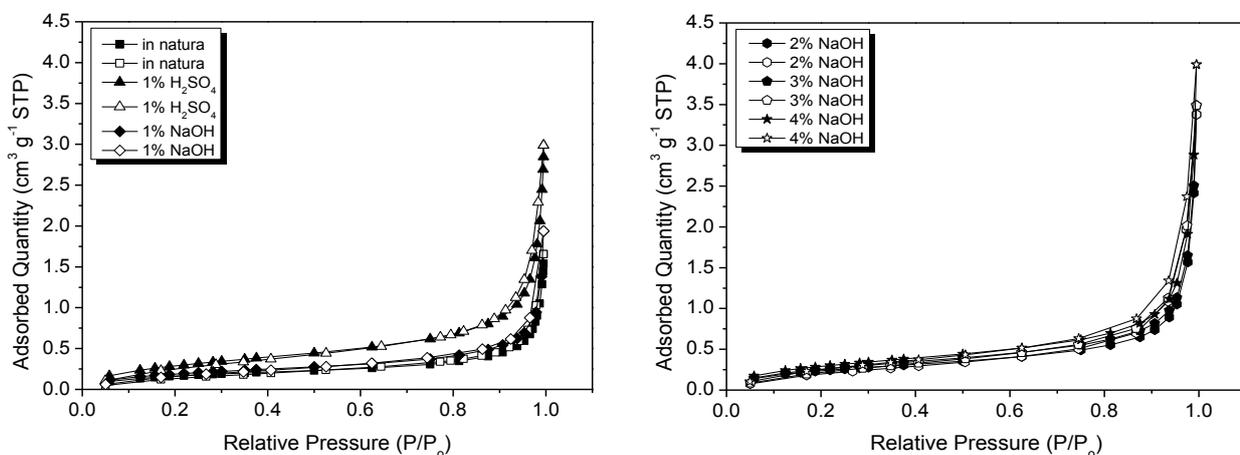

Figure 1. Adsorption and desorption isotherms in nitrogen gas for the sugarcane bagasse samples *in natura* and chemically pretreated. Full symbols indicate adsorbed and empty symbols desorbed quantity.

Figure 1 shows the nitrogen adsorption isotherms of the *in natura* and pretreated sugarcane bagasse. In all cases, there is low hysteresis and, from the profile, they have been classified as being H3 type. Hysteresis occurs due to the pores geometry and indicates the evaporation process (desorption) unlike the condensation process (adsorption) of nitrogen within of the pores (Webb & Orr, 1997).
When adsorption curves do not coincide with the desorption curves, this features hysteresis, which provides evidences about the mechanisms different that involves adsorption and desorption of nitrogen molecules in the cavities of the sample surfaces (San Miguel *et al*., 2012). Sugarcane bagasse samples presented low hysteresis compared with other biomass, such as *tucumã* seed and rice husk (Pécora *et al*., 2013; Cruz *et al*., 2012).
According to IUPAC (International Union of Pure and Applied Chemistry) this hysteresis type is observed in aggregate particles with pores in gap format (Rouquerol *et al*., 1999), that it might be explained by a higher packing and a rigid cellulose structure, resulting in less porosity (Guo & Catchmark, 2012; Gregg & Sing, 1982).
The IUPAC also classifies pores size in three categories: micropores (< 2nm), mesopores (between 2 and 50 nm) and macropores (> 50 nm) (Rouquerol *et al*., 1999).

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Specific surface areas of native cellulosic plants, such as spruce, wheat straw, flax and dried hemp free water are lower than 1.0 m^2 g^{-1} (Wiman *et al*, 2012; Yu *et al*., 2009). The sugarcane bagasse samples *in natura* presented S$_{BET}$ about 0.63 m^2 g^{-1}and smaller pores (< 10 nm).

After 1% H$_2$SO$_4$ treatment, sugarcane bagasse samples presented surface area 81% higher than *in natura*. Similar behaviors have been described by Wiman *et al*. (2012) and Koo *et al*. (2011). These authors showed that this change is due to the modification on the lignin structure. Such changes improve the degradation cellulosic matrix, generating porous and consequently facilitating the enzyme accessibility (Yu *et al*., 2009).

The limited structure of the cell wall available to the action of nitrogen gas was enhanced, due the exposition of the inner tissue by acid treatment (Yu *et al*., 2009).

Regarding the samples with alkaline pretreatments the increase in their surface areas was observed due to defibrilization, such pretreatment is important because may lead to an improvement of enzymatic accessibility (Wiman *et al*., 2012; Koo *et al*., 2011). However, no effect was noted in samples treated with 1% NaOH, which can be possibly due the migration for pore walls from water formed. Nitrogen molecules most do not enter in smallest pores during the analysis (Piccolo, *et al*., 2010).

3.1.1 Porosity analysis

Table 1 presents porosity characteristics of the *in natura* and pretreated samples of sugar cane bagasse. Although BET and BJH are usually considered for surface area evaluation, in this study we are considering the BJH

Table 1. Porosity characteristics of the sugarcane bagasse samples *in natura* and chemically pretreated determined by nitrogen gas adsorption

Biomass	S$_{BET}$ (m^2 g^{-1})	D$_{BJH.des}$ (4V/A) (Å)	V$_{BJH.des}$ x 10^3 (Å)	Q$_A$ (cm^{-3} g^{-1} STP)
in natura	0.63 ± 0.01	146.40 ± 19.10	2.08 ± 0.36	1.44 ± 0.22
1% H$_2$SO$_4$	1.14 ± 0.01	187.05 ± 21.06	4.70 ± 0.29	3.18 ± 0.19
1% NaOH	0.70 ± 0.03	185.81 ± 6.01	2.70 ± 0.13	1.85 ± 0.10
2% NaOH	0.96 ± 0.04	230.46 ± 2.54	5.26 ± 0.21	3.51 ± 0.14
3% NaOH	0.95 ± 0.07	224.92 ± 2.19	4.91 ± 0.28	3.28 ± 0.19
4% NaOH	1.14 ± 0.00	226.84 ± 1.72	6.19 ± 0.25	4.15 ± 0.15

Table 1 shows additional information for both diameter (D$_{BJH}$) and volume (V$_{BJH}$) pores using BJH desorption method. The values range from 146.4 to 230.5 Å for diameter and 2.1 to 6.2 Å for volume. According to Allen (1997), desorption relative pressure values is used because it corresponds to the more stable thermodynamical condition. A proportional increase in both the acid and alkaline treatments was also observed in the adsorbed quantity (Q$_A$) of N$_2$ atoms on the surface samples (Fig. 1 and Tab. 1).
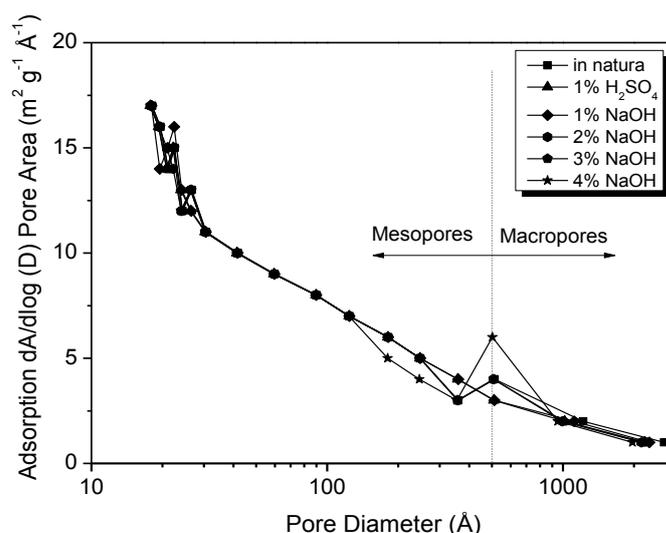

Figure 2. Distribution of pore diameter for *in natura* and chemically pretreated sugarcane bagasse samples.

Figure 2 presents the pore diameter distribution for *in natura* and chemically pretreated sugarcane bagasse samples, calculated by the BJH desorption method. For all the samples prevail mesopores, which are characterized by pores of 15 up to 30 Å. According to Yu *et al*., (2009) acid treatment samples of biomass residue there is an increase of surface area

and mesopores (around 1.14 m^2 g^{-1} and 1.8 nm, respectively). A transition region between mesopores (less than 500 Å) and macropores (greater that 500 Å) may be observed for all samples, with intensity pore area varying from 3 to 6 m^2 g^{-1} Å^{-1}(maximum peaks for the treated samples with 2, 3 and 4% NaOH). This indicates that alkaline treatment was more efficient for increasing of the specific surface area (Yu *et al*., 2009). These results described a very poorly developed pore structure in the solid particles that may be confirmed by limited surface area and pore structure of the material (San Miguel *et al*., 2012).
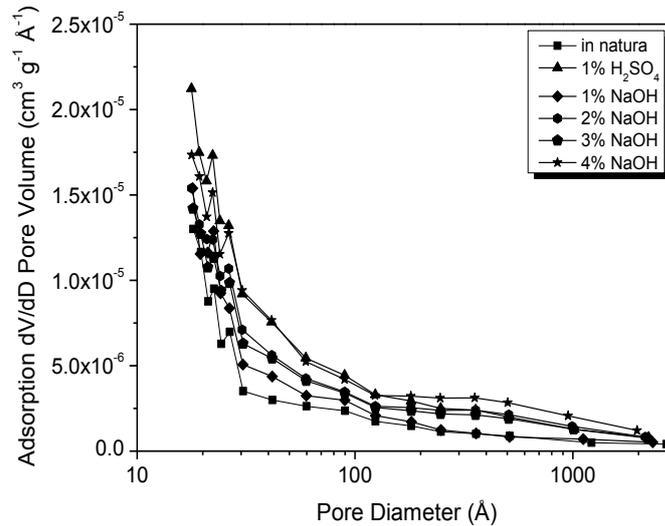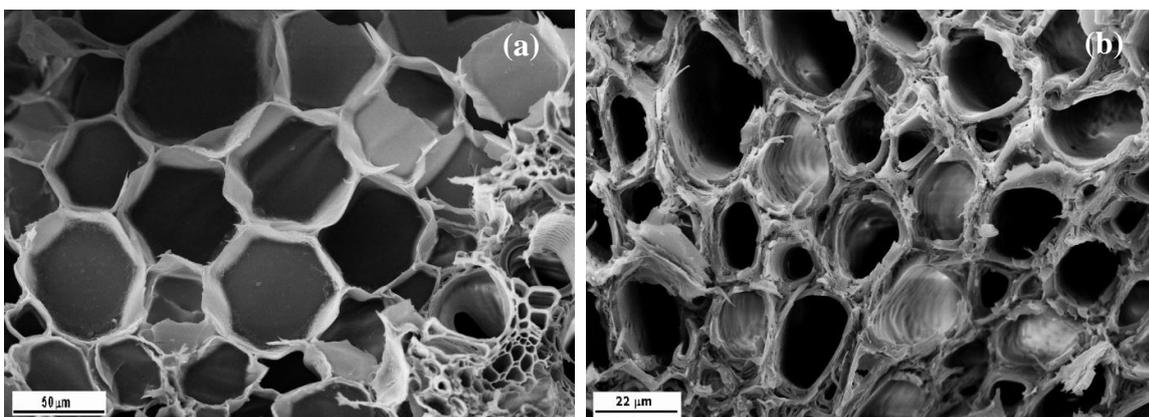

Figure 3. Distribution of pore volume for *in natura* and chemically pretreated sugarcane bagasse samples.

Figure 3 shows the pore volume distribution of sugarcane bagasse samples *in natura* and chemically pretreated, calculated by desorption BJH method. The results indicate that all analyzed samples presented a high concentration of pore volumes in their surfaces, with pore volumes in the region between 20 and 30 Å. In comparison with samples *in natura*, acid treatment was more efficient to increase pore volume, being enhanced by high exposition of the inner spaces (Yu *et al*., 2009).

Uzunov *et al*. (2012) reported that biomass samples of rice husk presented percentage of the total pore volume of 0,229 cm^3 g^{-1}. In this work by Fig. 3 for sugarcane bagasse samples these values were from 1.3x10^{-5} to 2.13x10^{-5} cm^3 g^{-1} for *in natura*, with 1% H$_2$SO$_4$ and 4% NaOH samples. Comparing these results with our finds, it can be concluded these presented a smaller order of magnitude, possibly due to the chemical pretreatments.

3.2 Scanning Electron Microscopy Images

Figure 4(a-f) shows SEM micrographics cross-section of sugarcane bagasse samples *in natura* and chemically pretreated. It was possible to observe in Fig. 4a that the samples *in natura* presented highly porous structure, which exhibits sharply the cellular structure of the fiber (Vilay *et al*., 2008), defined in the literature as "honeycomb" (Zabaniotu *et al*., 2008).

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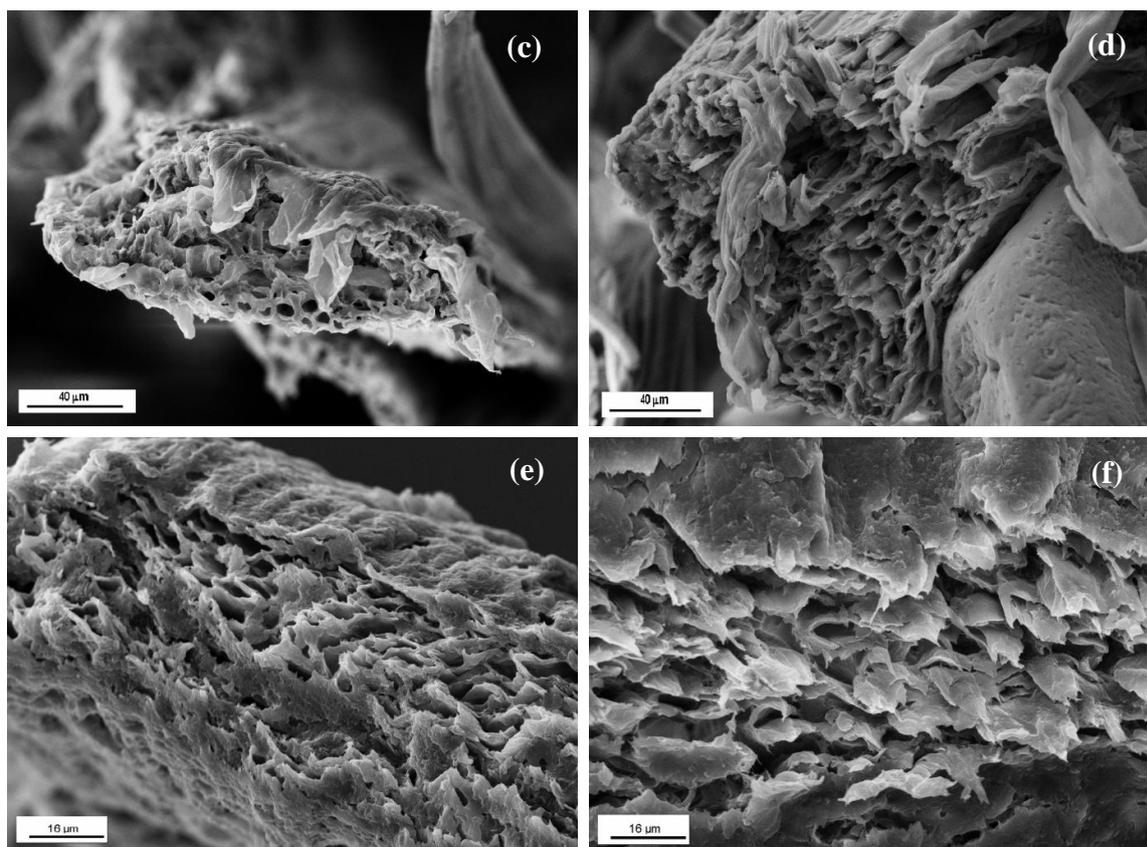

Figure 4. SEM micrographics of the cross-section of sugarcane bagasse fibers: (a) *in natura* (750 x) and chemically pretreated: (b) 1% H_2SO_4 (1,500 x); (c) 1% NaOH (1,000 x); (d) 2% NaOH (1,000 x); (e) 3% NaOH (2,000 x), and (f) 4% NaOH (2,000 x).

According to Reddy & Yang (2005), in general, all natural cellulose fibers are multi cellular structure, in which bundles of individual cells are bonded by natural polymers, such as lignin and pectin. The empty cavity in samples is known as lumen and exists in the cell unit of biofibers. The presence of this lumen decreases bulk density of the fiber and acts like acoustic and thermal insulators (Vilay *et al*., 2008).

In the 1% H_2SO_4 treatment (Fig. 4b), the fibers presented collapsed and distorted cell wall structure, but the tissue integrity is still maintained to some extent, the degradation signals are evident on the surface of the wall (Rezende *et al*., 2011; Yu *et al*., 2009), it was also observed that acid hydrolysis occurred with loss weight due to the reduction in the polymerization degree, which is responsible by rounding of the ends of cellulose fibrils (Guo & Catchmark, 2012).

For the samples treated with 1 and 2% NaOH (Fig. 4c and d), an effect of the compressed cell structure with some small pores in fibers was observed (Vilay *et al*., 2008).

Figures 4e and f, samples treated with 3 and 4% NaOH, it can be noted that occurred a melting and peeling of the structure (Fig. 4f). These effects occurred due to the increase in the alkaline-solution concentrations in the treatment (Koo *et al*., 2011; Cao *et al*., 2006). At strong-alkali concentration solutions, peeling of end-groups, alkaline hydrolysis, degradation and decomposition of dissolved polysaccharides can occur. This peeling is an advantage for later conversion, because lower molecular compounds are formed as result of the high alkali concentration, the risk on degradation and carbon loss, in form carbon dioxide, also increases (Hendriks & Zeeman, 2009).

Delignification results in the role formation in the cell wall structure, thereby its surface appears more fragile in comparison to the samples *in natura* (Rezende *et al*., 2011; Yu *et al*., 2009). However, this fragile appearance is questionable, because the important aspect of alkaline pretreatment is the change of the cellulose structure to a denser and thermodynamically more stable form than that of the native cellulose (Hendriks & Zeeman, 2009).

3.3 X-Ray Diffractograms

Vandenbrink *et al*. (2012) reported that crystallinity index (CI) of cellulosic materials is an important factor for enhancing cellulose digestibility, which is a measure of the fraction of crystalline cellulose and amorphous regions (lignin and hemicelluloses) and has shown to be inversely correlated with enzymatic hydrolysis rate in microcrystalline cellulose powder and corn stove. It believes that samples with a high CI can have a larger fraction of crystalline cellulose, hence they are less efficient for hydrolyzation with cellulase (Vandenbrink *et al*., 2012).

Some factors can affect the CI, such as chemical, physical and thermal treatments. Liu *et al.* (2005) showed that in the case of wheat, the CI value presented is similar to the different tissue types, such as leaf, node, epidermis, and parenchyma. Yoshida *et al.*, (2008) also related that the CI is correlated to the particle size samples, small particles presented lower CI. Study has compared the CI of several plant species, but some works have been done to understand natural variation in CI of species that might be directly utilized in crop improvement (Vandenbrink *et al.*, 2012).

Previous study indicated that the biomass pretreatment can modify the CI. Liu *et al.*, (2005) investigated the pretreatment of corn stover (cellulosic biomass) with H_2SO_4, it is showed an increase in the CI. Pretreatment of corn stover with NaOH also resulted in increase of CI, which was attributed to the removal of amorphous substances, such as lignin and hemicellulose leaving large glucan component. The uses of corn stover with other pretreatments similarly also increased the CI and hydrolysis rate, *e. g.*, lime and $FeCl_3$.

Removal of amorphous fraction part, including "lignin barrier" (Himmel *et al.*, 2007), by means pretreatments, an increase in CI is observed. However, this increase in CI does not contribute for overall decrease in the hydrolysis rate, such positive effect on hydrolysis by "lignin barrier" removal from biomass outweighs the negative effect of an increased CI (Vandenbrink *et al.*, 2012).

In order to compare the changes of phase structures of cellulose before and after pretreatment, the CI of both samples *in natura* and chemically pretreated were calculated with reference to the peak diffraction intensities of crystalline cellulose area (002) plan and amorphous region (100) plan by equation (1) (Vandenbrink *et al.*, 2012; Yu *et al.*, 2009; Yoshida *et al.*, 2008).

$$CI = \frac{(I_{002} - I_{am})}{I_{002}}.100 \qquad (1)$$

where I_{002} is intensity of crystalline area of (002) plane at $2\theta = 22.5º$, I_{am} is intensity of amorphous region at $2\theta = 18.0º$. I_{002} means both crystalline and amorphous intensity (background) while I_{am} represents background intensity only (Yu *et al.*, 2009).

Table 2. Crystallinity Index for the sugarcane bagasse samples *in natura* and chemically pretreated

Biomass	Crystallinity Index (%)
in natura	73.5 ± 1.5
1% H_2SO_4	77.4 ± 1.6
1% NaOH	77.6 ± 0.1
2% NaOH	81.0 ± 0.3
3% NaOH	80.0 ± 0.2
4% NaOH	82.6± 0.6

Table 2 shows crystalline index (CI) for the sugarcane bagasse samples *in natura* and chemically pretreated with diluted acid (1% H_2SO_4) and alkaline solutions concentrations (1, 2, 3, and 4%NaOH). For sample *in natura* a CI from 73% was observed, confirming the range from 70 to 80% for raw feedstock, which depends of the cellulose quantity present in samples (Guo & Catchmark, 2012) and also complex nature bonding (Yu *et al.*, 2009). During the acid pretreatment occurred an increase of 5% in CI, which can be attributed to the lignin removal, due to the reduction of the amorphous content (Guo & Catchmark, 2012; Vandenbrink *et al.*, 2012, Rezende *et al.*, 2011). This change in the structure can facilitate the accessibility of the enzymes to the inner part of the biomass (Yu *et al.*, 2009). For all samples with alkaline solutions was noted an increase on average of 3.6% in relation to the acid pretreatment, which could also be a consequence of the removal of amorphous substances (lignin and hemicellulose) (Kim *et al.*, 2003).

3.4 Fourier Transform Infrared Spectra

Rezende *et al.* (2011) reported that FTIR is an analytical technical that can be used to determine the changes in cell wall components (particularly cellulose, hemicellulose and lignin), characteristics of natural fibers, as consequence of different pretreatment conditions. The authors also showed that occurred lignin removal from sugarcane bagasse and cellulose enrichment in samples pretreated with increase NaOH concentrations.

According to Hendriks & Zeeman (2009), the acid pretreatment can be made with dilute or strong acid. The main reaction in the acid pretreatment is the hydrolysis of hemicellulose, especially xylan as glucomannan, which is relatively acid stable. The solubilized hemicelluloses (oligomers) can be subjected to hydrolytic reactions producing monomers such as, furfural, HMF (Hydroxide Methyl Furfural) and other volatiles.

Figure 5 shows the FTIR spectra of the *in natura* and pretreated sugarcane bagasse samples. FTIR technique shows functional groups and main components present in their surfaces

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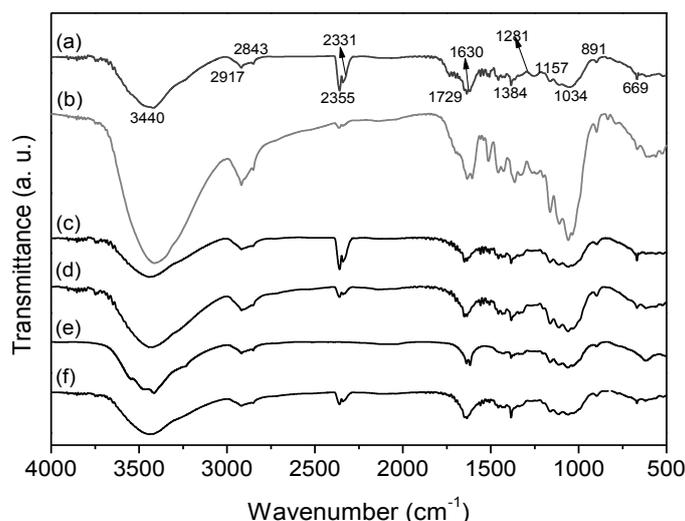*Investigation of porosity, wettability and morphological from sugarcane bagasse chemically pretreated*

Figure 5. FTIR spectra of the sugarcane bagasse samples: (a) *in natura* and chemically pretreated: (b) 1% H_2SO_4; (c) 1% NaOH; (d) 2% NaOH; (e) 3% NaOH, and (f) 4% NaOH.

The axial deformation of O-H groups is attributed to the large band, which identifies the hydrogen bonded stretching bands of O-H groups in the region of 3400 and 1030–1150 cm^{-1}. The absorptions can be attributed mainly to the carbohydrates (cellulose and lignin). Including C–O–C and C–O stretch (primary and secondary hydroxide groups) and bonds related to the glucoside linkage and possibly to lignin, that have hydroxyphenyl, guaiacyl and syringyl groups, which are aromatic compounds (Sasmal *et al*., 2012; Guimarães *et al*., 2009). Stretching bands with -CH_2 and -CH_3 at approximately 2850 and 2920 cm^{-1} are reduced by pretreated samples, signifying reduction in amount of aliphatic fractions of waxes (Kristensen *et al*., 2008).

The bands in the region of 1729 cm^{-1} can be attributed to non-conjugated C=O stretching (vibration of aliphatic carboxylic acids and ketones, mainly due to the hemicellulose and conjugated carbonyl in lignin groups close to 1650 cm^{-1}. Despite the protein amount be negligible, this can also be associated to proteins, and these can produce a broad band when there is no presence of water due to amino groups (Guimarães *et al*., 2009).

In addition, the presence of moisture may contribute for deformation of water molecules in 1630 cm^{-1} and also for the intensity of the broad band in the region of 3400 cm^{-1}. The band of vibration of skeletal bond C=C appears at 1500–1600 cm^{-1} in lignin. The band at 2917 cm^{-1} can be due to a symmetric and asymmetric stretching of C–H (Wiman *et al*., 2012; Guimarães *et al*., 2009).

All samples of this study presented the vibrations and bands cited above and were possible to identify with FTIR technique the pretreatments used. The large differences were found between the samples *in natura* and with dilute acid treatment (some bands displacement in spectra were verified); among the samples pretreated with alkaline solutions were not observed significant changes in FTIR spectra.

3.5 Wettability or Contact Angle

Wettability measurement provides informations on crystallographic structure of the surface, which is associated with variations of their contact with different types of liquids (Azevedo *et al*., 2009). This technique is commonly used in carbon films characterization or carbonaceous materials (micro, nano, boron doped diamond and carbon nanotubes, and others) (Ostrovskaya *et al*., 2007; Zhou *et al*., 2006; Kaibara *et al*., 2003; Pinzari *et al*., 2001). In this work, wettability has been applied to evaluate interactions of the surfaces of lignocellulosic materials with acid and alkaline solutions.

Baharoğlu *et al*. (2012) defined wettability, as a surface condition that determines either how fast a liquid will wet and spread on the surface or whether it will be repelled and not spread on the surface. Wettability is important to evaluate a good adhesion in the bonding between solid and liquid. Liquid have wet the surface or adhesives coatings and penetrates the cellular structure of lignocellulosic materials in order to establish an intimate contact between the substrate surface and molecules liquid. When CA (contact angle) value is equal or closer to zero, it occurs a perfect wetting of the surface. Liquids no wet surfaces with CA higher than 90º (Baharoğlu *et al*., 2012; Azevedo *et al*., 2009).

According to Heiss-Blanquet *et al*. (2011), some biomass samples *in natura* present CA values between 90º and 100º (hydrophobic). This behavior indicates weaker interactions among cellulose sheets and the liquid (Himmel *et al*., 2007).

Some biomasses present in their sheets a superhydrophobic or hydrophobic character (known as Lotus effect), resulting in a crystalline cellulose, which is resistant to acid hydrolysis. The resistance is due to formation of a dense

water layer near the hydrated cellulose surface (Himmel *et al*., 2007). Roughness may also influence to the wettability (Baharoğlu *et al*., 2012; Azevedo *et al*., 2009).

Table 3. Contact angles of the *in natura* and chemically pretreated sugarcane bagasse samples

Biomass	Contact Angle (º)	Wettability Degree	Interactions solid-liquid	Interactions liquid-liquid
in natura	(90 ± 3)	hydrophobic	weak	strong
1% H$_2$SO$_4$	(112 ± 0)	hydrophobic	weak	strong
1% NaOH	(0 ± 0)	superhydrophilic	strong	weak
2% NaOH	(102 ± 3)	hydrophobic	weak	strong
3% NaOH	(124 ± 3)	hydrophobic	weak	strong
4% NaOH	(0 ± 0)	superhydrophilic	strong	weak

Table 3 presents the contact angle values obtained for *in natura* and chemically pretreated sugarcane bagasse samples. These adhesive forces between a liquid and a solid cause the liquid drop to spread on the surfaces and cohesive forces within the liquid contributes to forming a drop ball, avoiding contact with the surfaces (Eustathopoulos, 1999; Novikov *et al*., 1998).
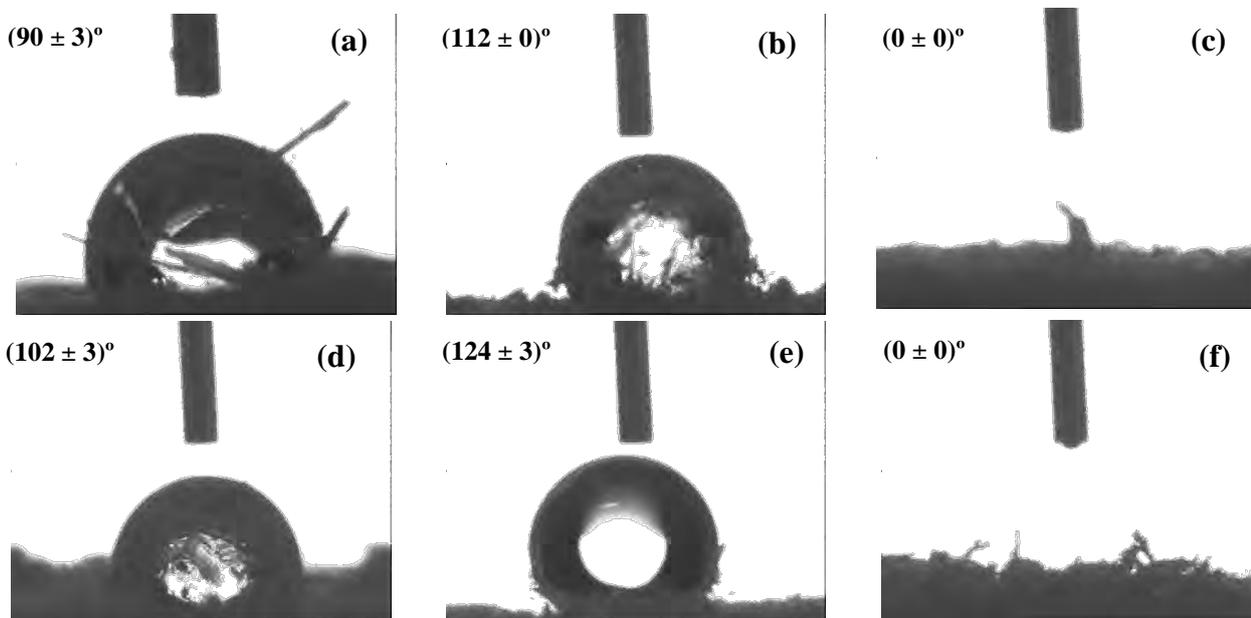

Figure 6. Contact angles of the sugarcane bagasse samples (a) *in natura* and chemically pretreated: (b) 1% H$_2$SO$_4$; (c) 1% NaOH; (d) 2% NaOH; (e) 3% NaOH, and (f) 4% NaOH.

Figure 6 (a-f) shows the images obtained by wettability technique. For *in natura* samples (Fig. 6a) the measured CA values measured (around 90º) confirm the expected value for lignocellulosic materials. For the sample treatment with 1% H$_2$SO$_4$ (Fig. 6b) was observed an increase of 24% of the CA value ($\theta = 112$º).

For samples treated with 1% and 4% of NaOH (Figs. 6c and f) the CA values were $\theta = 0$º, which presented a fully character superhydrophilic with samples wetted completely by liquid was observed, hence it can be the dominator effect in the surfaces (Himmel *et al*., 2007). Alkaline treatments, 2% and 3% (Figs. 6d and e), were presented hydrophobic character with ($\theta = 102$º and $\theta = 124$º, respectively). This behavior possibly is due to the destruction of the cellular structure (lignin), by reducing the void content of the fiber and decreasing roughness, producing a poor wet surface out (Vilay *et al*., 2008).

4. CONCLUSIONS

Regarding SEM images of the cross-section of sugarcane bagasse fibers it was possible to observe morphological changes of the surfaces after acid and alkaline treatments. Such changes are: swelling, and deformation, melting and peeling pores. Related to the porosity, an average increase about 9.2% was observed after chemical treatments.

Crystallinity index (CI) an increased about 3.6% in relation to the samples *in natura*. No significant changes have been observed in the FTIR spectra of the alkaline pretreatment in comparison to the *in natura* samples. From wettability

results, it was noted that *in natura* sample and samples treated with of 1% H_2SO_4, 2 and 3% NaOH presents hydrophobic character and samples treated with 1 and 4% NaOH presented superhydrophilic character, the effects of the wettability on the surfaces is in accordance to contact angle formed.

Results illustrate the importance of understanding the surface structure of the chemically treated samples, because it forms the basis for next stage of this work that is enzymatic hydrolysis.

5. ACKNOWLEDGEMENTS

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