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# Hydrothermal Treatment Of Sisal Bagasse

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Sisal (*Agave sisalana*) is cultivated in semi-arid regions because it is resistant to drought, presenting great potential for use in regions with low rainfall. From the sisal leaves, 3 to 5% of their fiber weight is used, and the rest, on the average, is 16% of bagasse and 81% of juice, which are discarded. Sisal residues are characterized as lignocellulosic residues since they mainly contain cellulose, lignin, and hemicellulose. Lignocellulosic materials have been studied as a source of fermentable sugars for the production of ethanol due to their high availability and low cost and for the construction of integrated biorefineries. Many types of research are being carried out to improve the chemical and enzymatic digestibility of the lignocellulosic biomass for the efficient conversion of cellulose into ethanol, among these technologies the pre-treatments can be highlighted. The hydrothermal treatment consists of the use of water under high temperature and pressure, being considered as one of the promising methods of pre-treatment of lignocellulosic materials due to the non-use of reagents. In this way, this work aimed to evaluate the potential of the sisal bagasse submitted to hydrothermal treatment for the production of cellulosic ethanol. The lignocellulosic composition analyses were performed before and after hydrothermal treatment using the methodology developed by Brazilian Agricultural Research Corporation, which follows the determination of moisture, ash, extractives, lignin, holocellulose and alfa cellulose. The bagasse of sisal in nature had a high content of cellulose (36.4%) and hemicellulose (19.8%), and lower lignin content (13.4%), compared to traditional biomasses. The X-ray diffraction of the in natura sisal bagasse indicated the presence of the characteristic peaks of cellulose. The thermogravimetric curves of in natura sisal bagasse presented four stages of mass loss attributed to the dehydration and decomposition of cellulose, hemicellulose, and lignin. For the hydrothermal treatment, a Parr stainless steel reactor was used at 1 atm pressure, testing different temperatures (150 and 200 $^{o}$C) and times (90, 100 and 110 min.) in the proportion 1/10 bagasse/water. The hydrothermal treatment was efficient in the solubilization of cellulose and hemicellulose, as evidenced by the reduction of cellulose and hemicellulose determined in the solid residue and confirmed by spectroscopic techniques. Thus the temperature of 200 °C for 90 min. was the most efficient condition in the solubilization of cellulose and hemicellulose, whose sugars contained in the hydrolysate can be converted to ethanol. The sisal bagasse is a promising alternative for the production of second-generation ethanol.

## 1. Introduction

Currently, large amounts of waste resulting from agro-industrial processes are generated and discarded in inappropriate places. This practice leads to environmental problems, and some of this waste represents loss of raw material and energy (Bento and Casaril, 2012). The use of waste from various processes, whether urban or agro-industrial, is underscored by the fact that society has become more concerned about the development of renewable and sustainable products. In addition to the agroindustrial lignocellulosic residues present a considerable amount of sugars (xylose, glucose, arabinose, among others) in its composition (Lima et al, 2014).

Sisal, or *Agave sisalana*, originated in Mexico and is considered the main hard fiber produced in the world. In Brazil, production is concentrated in the northeast, mainly in the states of Bahia and Paraíba. Sisal is cultivated in areas where climate and soil conditions are not conducive to the cultivation of other crops (Embrapa, 2011). According to data from the National Supply Company, in 2016 the production of sisal was approximately 84.6 thousand tons, a volume that was 7.9% lower than the harvest of 2015.A large part of this production was destined for the external market; in the case of fibers, the export was 34.4 thousand tons in 2016 (Conab, 2017). The sisal bagasse is characterized as a residue from the processing of sisal fiber and is discarded in the environment (Valentini et al., 2011).
Bagasse and sugarcane straw have been studied as sources of fermentable sugars for the production of biofuels (Valentini et al., 2011). Sisal is an alternative raw material for the production of these compounds, due to its low cost of biomass, its inability to be used as a food source, and the presence of high cellulose content (Neto et al., 2016).
The production of ethanol using lignocellulosic materials has been studied for two fundamental reasons: they will not compete with food crops, and they are less expensive than conventional ones. In addition, the use of these biomasses will add value to crops that are still rarely used for energy purposes (Neto et al., 2016). Second-generation industrial processing may improve ethanol production throughout the year, as the supply of lignocellulosic crops is less seasonal than sugarcane (Chovau et al., 2013).While first-generation technologies are based on the alcoholic fermentation of the carbohydrates present(in sugarcane juice, for example), the second generation consists of producing cellulosic ethanol from the breakdown of the polysaccharides that are present in the vegetal cell wall of the lignocellulosic residues (Pitarelo et al., 2012).
One of the major challenges for obtaining ethanol from lignocellulosic materials is the fractionation of the chemical components (cellulose, hemicellulose and lignin) that make up the structure of the plant biomass; a resolution must ensure that the polysaccharides, which will be used in the fermentation process, are not degraded during this fractionation. Thus, many studies are being conducted to improve the chemical and enzymatic digestibility of lignocellulosic biomass for the efficient conversion of cellulose and hemicellulose to ethanol (Barcelos et al., 2006).
Pretreatment is one of the most expensive steps in the conversion process of lignocellulosic materials (Galbe and Zacchi, 2012).There are several pretreatment methods, and each of them has an effect on lignocellulosic biomass. Physical treatments, such as milling, make use of conditions and reagents that affect the physical and chemical properties of biomass (Mathew et al., 2016). In this group of techniques, the hydrothermal treatment has presented effective solubilization of the hemicellulose and the non-production of inhibitors (Vallejos et al, 2016).The hydrothermal process is considered one of the most promising methods of pretreatment of lignocellulosic materials, since it does not cause damages to the environment; it works through the use of water at high temperature and pressure, increasing its ionic strength (Vallejos et al., 2015).
The use of hydrothermal pretreatment has its benefits. The process does not use chemical reagents, which is interesting from an environmental and economic point of view; futhermore, it does not need to work with highly corrosion resistant reactors, thus reducing the cost of the process. As a result, it is necessary to define the conditions for each raw material that favor the greatest hydrolysis efficiency. For this purpose, the current work aimed to evaluate the potential of the sisal bagasse submitted to hydrothermal treatment for the production of cellulosic ethanol.

## 2. Materials and methods

The raw material was supplied by farmers in the municipality of Nova Floresta - Paraíba. The sisal bagasse was dried in a SOLAB SL-102 greenhouse at 75 °C for 24 hours, then ground in a SOLAB SL-31 knife mill.

### 2.1 Lignocellulose Composition

The lignocellulosic composition was determined before and after hydrothermal treatment through moisture, ash, extractive, lignin, holocellulose, and alfacelulose analyses, according to methodology developed by Brazilian Agricultural Research Corporation (Embrapa, 2010).

### 2.2 Characterization Of Sisal Bagasse

The X-ray diffraction analyses were performed in a Shimadzu diffractometer, model XRD 6000, with CuKα radiation source, 40 kV voltage, 30 mA current, 2 $min^{-1}$ speed, and 2θ scan range = 10 to 80°.
The thermogravimetric curves were obtained in a Shimadzu Thermal Analyzer, model DTG 60, 7 mg mass, alumina crucible, heating rate of 10 $°C.min^{-1}$, in nitrogen atmosphere, flow of 100 mL, and ambient temperature range up to 900 °C.

### 2.3 Hydrothermal Treatment

The hydrothermal treatment was performed in a Parr model 4848 stainless steel reactor. In each experiment, the ratio 1/10 for sisal/water bagasse was used according to the temperature and reaction time evaluated (Table 1). Then, the hydrolysate was analyzed by High Performance Liquid Chromatography, and the solid residue was analyzed by absorption spectroscopy in the infrared region.

*Table 1 - Hydrothermal treatment*

| **Experiment** | **Temperature ($^oC$)** | **Time (min.)** |
|---|---|---|
| 1 | 200 | 90 |
| 2 | 200 | 100 |
| 3 | 200 | 110 |
| 4 | 150 | 90 |

The chromatographic analyses were performed in a VARIAN Chromatograph (Waters, California, USA), equipped with isocratic solvent system, Rheodyne valve with 20 µl loop, coupled with an Agilent Hi-Plex Ca column (7.7 x 300mm, 8 µ), at 65 ° C, VARIAN refractive index detector and GALAXIE Chromatography Data System processing software. Mobile phase was ultra-pure water and flow of 0.6 mL.min$^{-1}$.

Absorption spectra in the infrared region were obtained from a Shimadzu Spectrophotometer, IR Prestige model, using KBr pellets in the range of 4000-400 cm$^{-1}$.

## 3. Results and discussion

When the lignocellulosic characterization of the sisal bagasse in natura (Table 2) is compared with the results of LIMA et al. (2013), it is verified that the sisal bagasse of this study presented higher levels of holocellulose (56.2%) and alfacellulose (36.4%) and lower content of lignin (13.4%) and extractives (10.2% of organo-soluble compounds). These differences can be attributed to the time of harvest of the material, the procedures used, and the age of the plant.

*Table 2 - Lignocellulosic composition of sisal bagasse in natura*

| **Analysis** | **%** |
|---|---|
| Moisture | 9.2 ± 0.10 |
| Ash | 11.8 ± 0.07 |
| Extractives | 10.2 ± 0.09 |
| Lignin | 13.4 ± 0.30 |
| Alfacellulose | 36.4 ± 0.90 |
| Hemicellulose | 19.8 ± 0.90 |

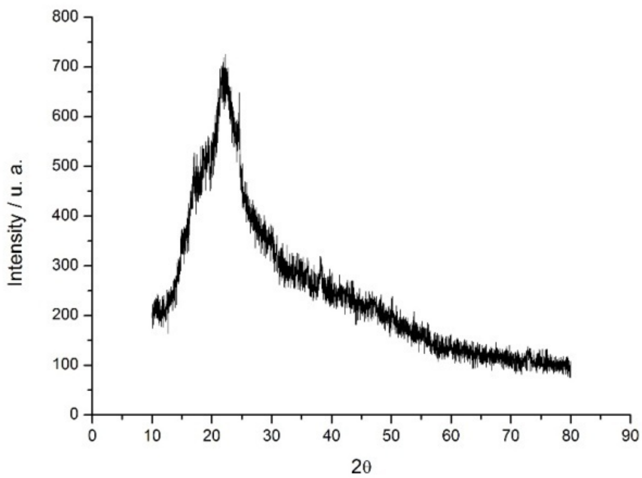


*Figure 1 - Diffractogram of sisal bagasse in natura*

The diffractogram of the sisal bagasse *in natura* (Figure 1) showed a peak of greatest intensity at 22º, assigned to the crystalline part of the lignocellulosic material and reflection plane (002) according to ICDD 00-060-1502, which indicates that this plane is characteristic of β-cellulose. Peaks at the angle of 18º were observed, assigned to the amorphous region according to LEGOWSKI et al. (2013). Thus, the sisal bagasse showed peaks that indicate the presence of crystalline cellulose and amorphous components, such as hemicellulose and lignin. Cellulose is the only polymer responsible for the crystalline characteristic in biomass, due to the high ordering of its repeating units.
The thermogravimetric curve of the *in natura* sisal bagasse presented four steps of mass loss, related to the dehydration and decomposition of the lignocellulosic components (Figure 2). The first step of mass loss occurred from 30-110°C and was attributed to dehydration; the second step occurred in the temperature range of 110-370°C and was attributed to degradation of cellulose and hemicellulose. The cellulose can decompose at higher temperatures, overlapping the lignin decomposition. Thus, the second step was attributed to the decomposition of carbohydrates, mainly hemicellulose, while the third and fourth steps were attributed to the degradation of the remaining cellulose and lignin.

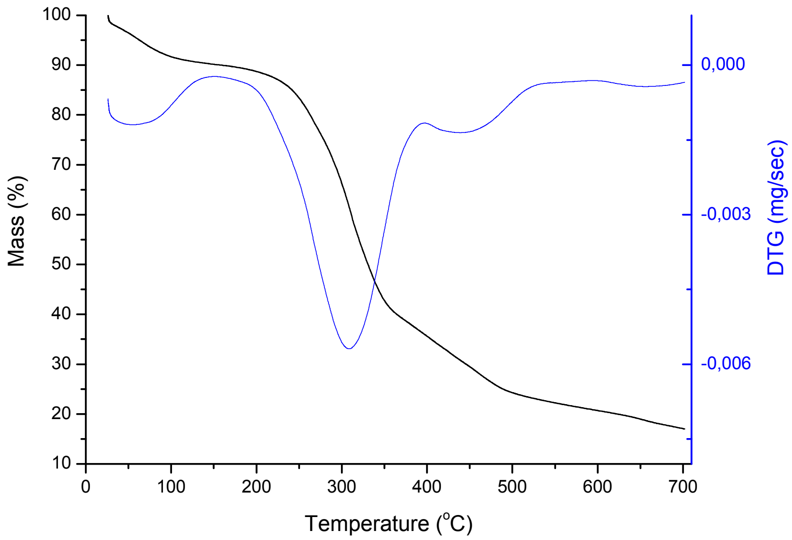


*Figure 2 - TG / DTG curves of sisal bagasse in natura*

The lignocellulosic characterization of sisal bagasse after hydrothermal treatment was also performed (Table 3). The composition of the sisal bagasse after hydrothermal treatment presented smaller amounts of cellulose and hemicellulose.

*Table 3 - Lignocellulosic composition of sisal bagasse after hydrothermal treatment*

| **Analysis** | **Experiment 1/%** | **Experiment 2/%** | **Experiment 3/%** | **Experiment 4/%** |
|---|---|---|---|---|
| Holocellulose | 39.8 | 51.2 | 46.9 | 41.2 |
| Alfacellulose | 25.6 | 30.4 | 26.0 | 24.2 |
| Hemicellulose | 14.2 | 20.8 | 20.9 | 17.0 |

The highest removal of hemicellulose occurred in experiment 1, with the highest temperature and the shortest time, at 200 °C and 90 min. Similar results were found by SANTOS (2013), the concentration of hemicellulose (31.51%) present in the *in natura* straw was higher in relation to the straw submitted to the hydrothermal pretreatment (17.06%).
The hydrolyzate was analyzed by High Performance Liquid Chromatography indicated highest content of sugars, mainly celobiose (Table 4) and absence of HMF and furfural inhibitors. Analyzing Table 4, it is possible to corroborate the data presented in Table 3, where the sample with the highest amount of sugars recovered was experiment 1 (total of 15.61 $gL^{-1}$). These sugars are derived from the cellulose and hemicellulose fractions where the hydrothermal treatment acted by cleaving the bonds of the polymer chains.

The presence of a considerable amount of cellobiose is highlighted, indicating that the condition used could not cleave this component in glucose monomers.

*Table 4 – Sugars content of sisal bagasse hydrolysate*

| Experiment | Cellobiose ($gL^{-1}$) | Others sugars ($gL^{-1}$) |
|---|---|---|
| 1 | 13.52 | 2.09 |
| 2 | 9.81 | 1.91 |
| 3 | 8.91 | 1.65 |
| 4 | 5.26 | 0.40 |

The infrared spectra (Figure 3) of treated samples (E1 to E4) presented lower intensity in band at 1740 $cm^{-1}$ in relation to sisal bagasse in natura (BN) attributed to the partial removal of hemicellulose components. In the in natura bagasse these band may be attributed to the stretching of C=O bonds present in the ester bonds and/or in the carboxylic acids of the hemicellulose fraction (Xavier et al., 2018).

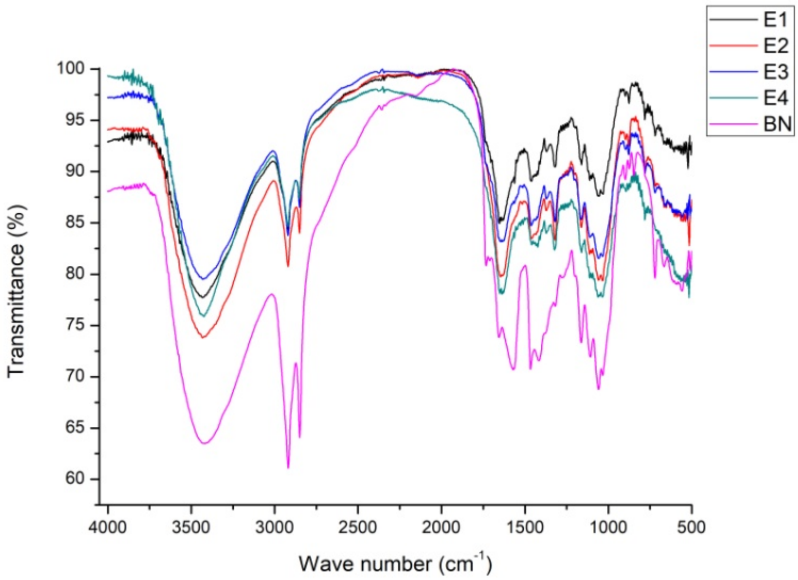


*Figure 3 – Infrared spectra of sisal bagasse*

## 4. Conclusions

The bagasse of sisal *in natura* presented high content of cellulose and hemicellulose. The hydrothermal treatment was efficient in the solubilization of cellulose and hemicellulose, as evidenced by the reduction of these components in the lignocellulosic composition of the bagasse after the treatment. The sugar content, as quantified in the hydrolysate of the sisal bagasse after treatment, indicated that the temperature of 200 °C and the time of 90 minutes is the most efficient condition in the removal of sugars, which can be converted to ethanol. In addition, the formation of hmf and furfural inhibitors did not occur.

Sisal bagasse is a promising alternative for the production of second generation ethanol.

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