EFFECT OF ANTHRAQUINONE ON PULPING OF PRETREATED SUGARCANE BAGASSE BY STEAM EXPLOSION FOR APPLICATION IN CELLULOSE DERIVATIVES


* Brazilian Bioethanol Science and Technology National Laboratory – CTBE, P.O. Box 6170, CEP 13083-970, Campinas, SP, Brazil.
** Instituto de Química – Universidade Estadual Paulista “Júlio de Mesquita Filho” – CEP 14800-900, Araraquara, SP, Brazil.
*** Departamento de Biotecnologia, Escola de Engenharia de Lorena, Universidade de São Paulo, CEP 12.602-810, Lorena, SP, Brazil.

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Abstract: The aim of this work is the production of dissolving pulps from sugarcane bagasse, for cellulose derivatives production. The pulps were produced by soda delignification process, with or without anthraquinone, of sugarcane bagasse pretreated by steam explosion. The soda-anthraquinone process showed to be more advantageous, with 32.17% less cellulose degradation than for soda pulping. The best pulp yield was reached at lower temperatures, where the process provides a reduction in the recalcitrance of lignocellulosic material with a solubilization of lignin fragments of low molecular weight without high cellulose degradation. A future goal is to use these cellulosic pulps as precursors in cellulosic derivatives.

Keywords: Alkaline delignification, steam explosion, cellulosic pulp, dissolving pulp.
1. INTRODUCTION

The production of sugarcane bagasse in Brazil has increased dramatically (CONAB, 2012), their renewable and recyclable properties make the integral use of its components an economically and environmentally desirable procedure.

Although the majority of the use of sugarcane bagasse is in fuels, the excess is very significative (Caraschi, 1996). Inside of that context, many pulping processes have been studied to sugarcane bagasse; most of these processes are based in optimized methods to the wood pulping. The application with more aggregate value is the dissolving pulp.

Dissolving pulp refers to the pulp with the cellulose content above 90%, including different types of sources. In the world, the dissolving pulp capacity concentrates in regions with abundant forest resources such as North America, South Africa and Brazil. The considerable demand for dissolving pulp encouraged many companies to build new dissolving pulp projects, leading to the substantial rise in capacity to 937.500 tons by 2012 (Reports, 2013). A wide range of products can be produced from dissolving pulp, including viscose rayon, cellophane and a variety of plastic films, cellulose esters, and cellulose ethers (Ibarra et al., 2010; Christov et al., 1998). The downstream application of dissolving pulp, with the raw materials of wood, concentrates in viscose industry (Reports, 2013).

Nevertheless the biomass structure limits the alteration of lignocellulosic fractions. The interconjunction of the cellulose-polyoses-lignin complex makes the biomass extremely resistant to the chemist reagents and to the enzymes and microorganisms. Generally it is necessary the cleavage of the complex or the removal of each fraction by pretreatment and delignification techniques. Most recently research into cellulose dissolution has been focused on new classes of solvents, such as various aqueous alkaline solvent systems, which are inexpensive, renewable, and seen as “green” chemicals (Kihlman et al., 2011). Also combining with anthraquinone it leads to better delignification, increased carbohydrate stabilization, higher yield, better strength properties, lower alkali consumption and decreased cooking chemical charge (Francis et al., 2008).

The main factor that determines a pulp application for cellulose pulp and its derivatives is the purity and cellulose content.

So the aim of this work is the evaluation of cellulose degradation, lignin solubilization, and temperature and anthraquinone effect, in the soda delignification process of sugarcane bagasse pretreated by steam explosion, for a rich cellulosic pulp obtention. In addition MEV was used to determine further structural and morphological information.

2. MATERIALS AND METHODS

2.1. Raw material

The in natura sugarcane bagasse was kindly provided by Nova America mill, located in Taruma, Sao Paulo, Brazil.

The material was washed with water until neutral in pH and dried at room temperature, until 10% of moisture content.

2.2. Steam explosion process

These procedures are designed to separate by hydrolysis the hemicelluloses present in the biomass.

The pretreatment was performed in a 250L reactor, located in the School of Engineering of Lorena (EEL – USP). The steam injection occurred until reached 190°C for a period of 15 minutes. Sequentially the reactor was suddenly depressurized and the pretreated bagasse was submitted in a 2.5 m³ cyclone and washed in a Crisante semi-industrial centrifuge with a capacity of 100 L (Rocha et al., 2011). The cellulignin was thoroughly washed by resuspending it until the yellow color of the effluent was totally removed.

2.3. Alkaline delignification process

After the pretreatment the material was delignified with NaOH, with or without
anthraquinone addition. Cellulose degradation, lignin solubilization, temperature and anthraquinone effect were evaluated for each experiments conditions (Table 1).

The bagasse pretreated (30g) was treated by NaOH 1.0% (w/v) in presence of 0.15% (w/w) anthraquinone, 1:10 (w/v) solid-to-liquid ration, for 1h in a 1L shaking autoclave with the mixing been carried out by means of vibratory movements of a vessel in a horizontal plane with amplitude of fluctuations of 20 centimeters and 60 cycles/min. The pulpings were performed at six different temperatures: 80, 90, 100, 120, 140 and 160°C.

The delignification reactions without anthraquinone, were performed in 350L iron -carbon reactor, with stirring and heating control system. The pulpings were performed at 100°C, 1h with 1:10 (w/v) solid-to-liquid ratio. (Rocha and Silva, 2005).

Table 1. Identification of each experimental condition

<table>
<thead>
<tr>
<th>Samples</th>
<th>Conditions *</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>T=80°C</td>
</tr>
<tr>
<td>2</td>
<td>T=90°C</td>
</tr>
<tr>
<td>3</td>
<td>T=100°C</td>
</tr>
<tr>
<td>4</td>
<td>T=120°C</td>
</tr>
<tr>
<td>5</td>
<td>T=140°C</td>
</tr>
<tr>
<td>6</td>
<td>T=160°C</td>
</tr>
</tbody>
</table>

*All samples were treated with NaOH 1% (w/v) + 0.15% anthraquinone (w/w), for 1 hour.

2.4. Chemical Analysis of bagasse samples

Samples of the in natura, pretreated and delignified sucarcane bagasse were milled to pass through 0.50mm screen. The in natura sample was extracted with cyclohexane/ethanol 2:1, after wash with water for 3 days in a soxhlet apparatus, for extractives content determination.

The extracted in natura sugarcane bagasse and the other samples were hydrolyzed with 72% H₂SO₄ at 45°C for 7 min. The acid was diluted to final concentration of 3% (addition of 275 mL of water) and the mixture was heated at 121°C for 30 min, in an oil bath. The residual mixture was filtered and the insoluble and soluble fractions were separated. The soluble lignin were quantified by gravimeter and UV at 280 nm (Gouveia et al., 2009) and the solids were dried to constant weight at 105°C and quantified as insoluble lignin.

The concentration of sugars in soluble fraction was determined by HPLC using an Aminex column (HPX-87H BIO-RAD, refractive index detector RID 6A model) at 45°C, with 0.005 mol.L⁻¹ sulfuric acid as mobile phase at 0.6 mL.min⁻¹ flow rate (SHIMADZU CR 7A model Chromatograph).

An aliquot of 5 mL of the hydrolyzed was eluted through a SEP-PAK C18 membrane before the chromatographic quantification. The factors used to convert monomers to cellulose and glucose were 0.90 for glucose, 0.88 for xylose and arabinose, 0.7 for acetic acid and 3.09 for formic acid. The concentration of the compounds was determined from calibration curves plotted to each component (Gouveia et al., 2009).

The concentration of hydroxymethylfurfural and furfural in soluble fraction was determined by HPLC using a RP-18 HEWLETT-PACKARD column at 25°C, with 1:8 acetonitrile/water 1:8 and 1% of acetic acid mixture as mobile phase at of 0.8 mL.min⁻¹ flow rate (Rocha et al., 1997). The conversion factors were 1.29 and 1.37 for hydroxymethylfurful and furfural respectively.

2.5. Scanning electron microscopy

The ZEISS DSM-960 model of SEM was used to observe the structure modification of the pretreated sample and the delignified material.

Samples to be observed were mounted on conductive adhesive tape, sputter coated with gold, and observed in the microscope using a voltage of 15 kV. (Martin et al., 2012).

3. RESULTS AND DISCUSSION

The chemical composition of in natura, pretreated, and pretreated and delignified sugarcane bagasse is presented in the table 2.
Table 2. Chemical Composition of in natura, pretreated and pretreated and delignified sugarcane bagasse samples

<table>
<thead>
<tr>
<th>Components</th>
<th>in natura (%)</th>
<th>Pretreated (%)</th>
<th>Pretreated and delignified samples (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>44.6 ± 1.50</td>
<td>57.60 ± 1.85</td>
<td>84.0 85.6 88.5 87.5 87.0 86.0</td>
</tr>
<tr>
<td>Hemicelluloses</td>
<td>27.3 ± 0.50</td>
<td>4.51 ± 0.65</td>
<td>5.1 4.9 4.5 4.8 4.7 4.6</td>
</tr>
<tr>
<td>Lignin</td>
<td>21.0 ± 0.50</td>
<td>34.5 ± 0.17</td>
<td>6.7 6.1 4.3 4.5 4.7 4.9</td>
</tr>
<tr>
<td>Ashes</td>
<td>1.0 ± 0.10</td>
<td>2.51 ± 0.07</td>
<td>2.7 2.2 2.1 2.0 1.9 2.3</td>
</tr>
<tr>
<td>Extractives</td>
<td>5.2 ± 0.20</td>
<td>--</td>
<td>-- -- -- -- --</td>
</tr>
<tr>
<td>Total</td>
<td>98.2</td>
<td>99.1</td>
<td>98.5 99.0 99.5 99.0 98.4 98.0</td>
</tr>
</tbody>
</table>

The influence of different pretreatment conditions on cellulose, hemicellulose and lignin degradation was investigated to determine the most efficient method for cellulosic pulp production under moderate conditions. In order to compare the contents of these materials generated by different process conditions is necessary to normalize each chemical composition by your own pretreatment or delignification mass yield, which uses the equation

$$PMY \text{ or } DMY = \frac{M_f}{M_i} \times 100$$  (1)

Where $PMY$, $DMY$, $M_f$ and $M_i$ represent the pretreatment mass yield, the delignification mass yield, the final mass and the initial mass, respectively.

The chemical composition of pretreated, and pretreated and delignified sugarcane bagasse samples corrected by PMY and DMY, in addition the solubilization of hemicellulose, cellulose and lignin after the pretreatment and the delignification process in all condition are presented also in Table 3.

The steam explosion is the most commonly used method for biomass pretreatment. The suddenly depressurization in this procedure, improves the sugarcane bagasse accessibility and surface area, by removing mainly hemicelluloses. (Sun and Cheng 2002).

Table 3. Chemical Composition of sugarcane bagasse pretreated and delignified samples corrected by PMY and DMY respectively and the contents solubilization during each process.

<table>
<thead>
<tr>
<th>Components characterization</th>
<th>Pretreated*</th>
<th>1**</th>
<th>2**</th>
<th>3**</th>
<th>4**</th>
<th>5**</th>
<th>6**</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMY (%)</td>
<td>66.0</td>
<td>56.5</td>
<td>51.3</td>
<td>45.3</td>
<td>40.6</td>
<td>36.2</td>
<td>33.0</td>
</tr>
<tr>
<td>Cell.</td>
<td>38.0</td>
<td>31.3</td>
<td>29.0</td>
<td>26.5</td>
<td>23.4</td>
<td>20.8</td>
<td>18.7</td>
</tr>
<tr>
<td>Hemic.</td>
<td>3.0</td>
<td>1.9</td>
<td>1.7</td>
<td>1.3</td>
<td>1.3</td>
<td>1.1</td>
<td>1.0</td>
</tr>
<tr>
<td>Lignin</td>
<td>22.7</td>
<td>2.5</td>
<td>2.1</td>
<td>1.3</td>
<td>1.2</td>
<td>1.1</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Components solubilisation (%)

<p>| | | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell.</td>
<td>19.29</td>
<td>17.6</td>
<td>23.7</td>
<td>30.4</td>
<td>38.3</td>
<td>45.3</td>
<td>50.7</td>
</tr>
<tr>
<td>Hemic.</td>
<td>89.6</td>
<td>36.6</td>
<td>44.7</td>
<td>55.2</td>
<td>57.1</td>
<td>62.6</td>
<td>66.6</td>
</tr>
<tr>
<td>Lignin</td>
<td>0.4</td>
<td>89.0</td>
<td>90.9</td>
<td>94.4</td>
<td>94.7</td>
<td>95.0</td>
<td>95.3</td>
</tr>
</tbody>
</table>

* corrected by the pretreatment mass yield (PMY) Calcule example (pretreatment: 57.60 x 0.66 = 38.0)
** corrected by the pretreatment mass yield (PMY) and delignification mass Yield .Calcule example (delignification: 84.0 x 0.565 x 0.66 = 31.3) Cell: cellulose; Hemic: Hemicellulose
According to Table 3, this process showed a 66% of pretreatment mass yield, due to the solubilization of 19.3% of cellulose, 89.6% of hemicellulose and 0.4% of lignin in relation to in natura contents. However, this huge hemicellulose solubilization by the steam explosion method does have its drawbacks, such as incomplete disruption of lignin, which may affect the cellulosic derivatives obtention.

The combination of different methods may yield more positive effects in cellulose obtention. The major effect of alkaline pretreatment is the removal of lignin from the biomass, but in addition, the NaOH removes acetyl and uronic acid substituted on hemicellulose chain (Chang and Holtzapple, 2000). The main alkaline hydrolysis mechanism is based on saponification of intermolecular ester bonds cross linking xylan hemicelluloses and other components such as lignin (Sun and Cheng, 2002).

The highest delignification yield of 33.0% was achieved by delignification with NaOH 1% (w/v), 0.15% anthraquinone (w/w), for 1 hour and 160°C. This indicates that soda/ anthraquinone pulping at 160°C removes most of the lignin from the sample, 95.3% of lignin solubilization, and leaves the cellulose fibers in the pulp for derivatives production.

Changes in biomass fibers occurring during pretreatment and delignification process have important impact on the fiber properties. The increase in reaction temperature during delignification process can promote more chain scission reactions increasing the delignification mass yield (Silva et al., 2010).

The literature reveals that an increase of 5 °C in the pretreatment processes results in significant changes in the chemical composition of the pretreated material. According to Figure 1 and Table 3, the solubilization of cellulose, hemicellulose and lignin are strictly connected with the PTM, DMY and temperature. High temperatures result in large openings of the packages of fiber, making the material more comminuted (Silva, 2010; Silva et al. 2010).

That effect can be explained by the occurrence of peeling reactions. Under alkaline conditions, peeling occurs as sugar units in a polymeric chain are removed one by one from the reducing ends and transformed into a carboxylic acid. This removal is accompanied by the formation of a new reducing end-group until another reaction (Borrega et al. 2013) being a cellulose extraction significant. Despite the addition of anthraquinone to the pulping liquor to minimize peeling reactions, a significant decrease in cellulose yield still occurred. Nevertheless the best set of conditions was obtained in the reaction performed at 100°C as consequence of a better compromise between cellulose preservation and lignin removal.

Furthermore, it is possible to observe a linear relation between hemicellulose, cellulose and lignin contents with the temperature. This was confirmed by plotting the experimental, temperature against the contents of hemicellulose, cellulose and lignin in the pretreated and delignified materials, which revealed a polynomial fit between these parameters, on Figure 2.
The relations between the hemicelluloses, cellulose, lignin and acetyl groups in different conditions and, followed by the Figure 3, which has the data referent of the Table 4 plotted on comparative graphs.

Table 4. Relations between the components in different experimental conditions

<table>
<thead>
<tr>
<th>Cond.</th>
<th>Cell. / Lig. (%)</th>
<th>Cell. / Hem. (%)</th>
<th>Hem. / Lig (%)</th>
<th>Hem. / A. Group (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.7</td>
<td>16.4</td>
<td>0.8</td>
<td>28.5</td>
</tr>
<tr>
<td>2</td>
<td>0.8</td>
<td>17.6</td>
<td>0.8</td>
<td>11.3</td>
</tr>
<tr>
<td>3</td>
<td>1.0</td>
<td>20.1</td>
<td>1.1</td>
<td>9.4</td>
</tr>
<tr>
<td>4</td>
<td>1.0</td>
<td>18.7</td>
<td>1.1</td>
<td>11.1</td>
</tr>
<tr>
<td>5</td>
<td>0.9</td>
<td>18.5</td>
<td>1.0</td>
<td>9.6</td>
</tr>
<tr>
<td>6</td>
<td>0.9</td>
<td>18.9</td>
<td>0.9</td>
<td>5.8</td>
</tr>
</tbody>
</table>

Fig. 2. Cellulose (A), Hemicellulose (B), and lignin (C) content of pretreated and delignified samples, corrected by DMY versus temperature.

Other important material parameters are the relationship between the monomeric components and the hemicellulose content, aiming to cellulosic derivatives synthesis.
Fig. 3. Relation between the components with the polynomial equations indicated: A-Cellulose/Lignin (Cell/Lig), B-Cellulose/Hemicellulose (Cell/Hem) and C-Hemicellulose/Lignin (Hem/Lig).

Evaluating the relationship between cellulose and hemicelluloses (Table 4), we observed that even with the increased severity of delignification, the ratio remains almost constant, which indicates a proportional loss of cellulose and hemicellulose during the experiment. It is also observed on Fig 3-B, the increase of the hemicelluloses with a slightly cellulose decay, probably because of the high availability of the polyoses with the decrease of recalcitrance of lignocellulosic material.

For the relation between cellulose and lignin (Fig 3-A) and hemicelluloses and lignin (Fig 3-C), it is observed a resembling behavior, maintaining both relations next 1%. This may indicate a similar relationship between lignin, cellulose and hemicelluloses. Nevertheless, since the used pretreatment removes a great majority of the acetyl groups, it was not possible to make a trustable comparison between lignin and hemicellulose content.

The presence of hemicelluloses enhances the formation of bonds between cellulose fibers, giving the pulp superior mechanical performance. A low hemicellulosic content is thus not desired in the production of high-quality paper pulps, whereas it is required in the production of dissolving-grade pulps (Borrega et al., 2013). Therefore for further applications it is required to obtain a pulp totally free from hemicelluloses.

It is known that cellulose, instead of hemicelluloses is crystalline, linear and consisted of glucose chains. (Fengel; WEGENER 1989). It is more resistant than hemicelluloses, owing to their high polymerization degree and the presence of crystalline fractions (Garrote et al., 1999).

However under severe extraction conditions, extensive cleavage of glycosidic bonds is observed in cellulose content. The formation of new end groups increases the susceptibility of cellulose chains towards pelling in subsequent alkaline pulping processes, despite the addition of anthraquinone, still decrease of cellulose yields occurred (Borrega et al, 2013).

On Table 5 the different characterizing data for bagasse delignified with the presence of anthraquinone at same conditions is shown.

<table>
<thead>
<tr>
<th>Conditions*</th>
<th>Cell (%)</th>
<th>Hem. (%)</th>
<th>A. Group (%)</th>
<th>Lig. (%)</th>
<th>Ash (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without AQ</td>
<td>27.2</td>
<td>0.9</td>
<td>&lt;0.1</td>
<td>1.7</td>
<td>0.5</td>
</tr>
<tr>
<td>0.15% AQ (w/w)</td>
<td>40.1</td>
<td>2.0</td>
<td>0.2</td>
<td>2.0</td>
<td>1.1</td>
</tr>
</tbody>
</table>

* 100°C, NaOH 1% (w/v), 0.15% AQ (w/w)

The formation of new reducing end-groups in cellulose chains may then promote degradation by peeling reactions during an alkaline pulping process (Alén, 2000). The stabilization of carbohydrates diminishes the extent of peeling reactions, which in turn increases the pulp yield.

Anthraquinone is an oxidant, often used in chemical pulping for carbohydrates stabilization and delignification improvement (Borrega et al., 2013). Table 5 showed the chemical composition of the delignified samples with NaOH 1% (w/v) with or without 0.15% (w/w) anthraquinone addition.

The condition performed with anthraquinone showed 40.1 of cellulose content against 27.2 for the condition with no anthraquinone addition. This oxidant results in a decrease of 32.17% in cellulose degradation, showing an advantage of the use.
4. CONCLUSION

The pretreatment is an important step, because it eases the subsequent process for lignin removal. It was observed for the experiment, the solubilization of 89.9% of hemicelluloses with the steam explosion process, producing a raw-material with high cellulose content and low hemicelluloses amount.

By analyzing the data obtained in the experiments of delignification, the best result of the process was reached with alkali delignification at 100°C with anthraquinone. Firstly because the use of anthraquinone reveals a decrease of 32.17% in degradation of cellulose and secondly, with 100°C the increase in lignin removal occurs with the reduction of the recalcitrance, but not enough to promote extensive degradation of the pulp content.

The best yield of pulp occurred only with the pretreatment followed by delignification conditions evaluated at lower temperatures, once the process provides a reduction in the recalcitrance of lignocellulosic material with a solubilization of lignin fragments of low molecular weight (Silva, 2010), which can be observed by decreased amount of insoluble lignin along increasing temperature. The reduction of recalcitrance increases the available surface area of cellulose and promotes extensive degradation of the polymer, reducing the pulp content.

The Scanning electron microphotographs of the pretreated sugarcane bagasse showed a fiber destructuring and disaggregation, resulted from the pretreatment step (Fig. 4).

Fig. 4. (A) In Natura bagasse, (B) Pretreated bagasse by steam explosion and (C) Pretreated bagasse by steam explosion and delignified.

The utilization of sugarcane bagasse for production of pulps for dissolution shows a promising result, but a best evaluation can be obtained with the application of this material as feedstock in the production of cellulose derivatives.

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REFERENCES


ABOUT THE AUTHORS

**George J. M. Rocha**

Senior Researcher in Industrial Program (PIN) at the National Laboratory of Science and Technology of Bioethanol (CTBE) in the National Center for Research in Energy and Materials (CNPEM).

**Débora Lee S. Corso**

Graduate Student in Chemical Technology from the Universidade Estadual Paulista (UNESP) and an intern at the National Laboratory of Science and Technology of Bioethanol (CTBE) at the National Center for Research in Energy and Materials (CNPEM).

**Viviane M. Nascimento**

Chemist in National Laboratory of Science and Technology of Bioethanol (CTBE) at the National Center for Research in Energy and Materials (CNPEM) and PhD in Chemical Engineering from the Universidade Estadual de Campinas (Unicamp).

**Vinicius F. N. Silva**

PhD Student at the School of Engineering of Lorena (EEL). University of São Paulo.