International Congress of Science and Technology of Metallurgy and Materials, SAM - CONAMET 2013

Extraction, Addition and Characterization of Hemicelluloses from Corn Cobs to Development of Paper Properties

Juliana Cristina da Silva*, Rubens Chaves de Oliveira, Armando da Silva Neto, Vanessa Cunha Pimentel, Allan de Amorim dos Santos

*(a) Universidade Federal de Viçosa – Viçosa, Minas Gerais, 36570-000, Brazil.

Abstract

The corncob is a product found in significant amounts in the residues of agriculture, which has potential for use underexplored. This paper presents a study of the chemical characterization of corn cobs, extraction and application of hemicelluloses present in these wastes. Two fractions of hemicelluloses were obtained, the first being obtained after neutralization and precipitation of the alkaline solution and the second after addition of ethanol in the supernatant of the same solution. Handsheets were made by using bleached kraft eucalyptus pulp, and adding hemicelluloses. After that, their physical and mechanical properties were evaluated, according to TAPPI Standard. An increase in the resistance was observed to drainage and in the properties directly affected by the inter-fiber bonds with the content increase of hemicelluloses and also obtaining handsheets with lower bulk with content increase of these carbohydrates.

Keywords: Hemicelluloses; corn cob; papers properties.

1. Introduction

Hemicelluloses are polysaccharides that are different from cellulose for containing several kinds of sugar units in composition (D-xylose, D-mannose, D-glucose, L-arabinose, etc). They are branched polymers (amorphous) and
shorter chains (degree of polymerization of up to 200 sugar units) compared with cellulose (Fengel and Weneger, 1989; Salmén, and Olsson, 1998). The monosaccharides that form structures of hemicelluloses are composed by hexose sugars comprising glucose, mannose and galactose and pentose comprising arabinose and xylose, and can also provide varying amounts of uronic acids and deoxy-hexose in some types of vegetables.

In the specific case of corn cobs, it is considered that the xylans usually present a chemical structure formed by 4-O-methyl-D-glucuronic acid, L-arabinose and D-xylose in the ratio 2:07:19 (Silva et al., 1998). In recent years, evidence has emerged that the arabinoxylans (xylan which has a large number of residues in the side chains of arabinose) contained in the cereal grains are interconnected in cell wall by cross-linking occurring by esterification with the diferulic acid, and/or by formation of complexes with proteins. These structures would be responsible for the difficulty of extraction and purification of xylan and the digestion time cereal grains (Silva et al., 1998).

Several studies have been carried out showing the processes of isolation of hemicelluloses (Yllner and Enström, 1956; Yllner and Enström, 1957; Aurell, 1965; Hansson and Hartler, 1969; Henriksson and Gatenholm, 2001; Schönberg et al., 2001; Linder et al., 2003; Danielsson and Lindström, 2005; Danielsson, 2007; Köhnke and Gatenholm, 2007; Köhnke et al., 2008; Muguet et al., 2010; Silva, 2011) and the relationship between the cellulose and hemicellulose levels in paper properties (Schönberg et al., 2001; Danielsson and Lindström, 2005; Köhnke and Gatenholm, 2007; Köhnke et al., 2008; Muguet et al., 2010; Milanez et al., 1982; Molin and Teder, 2002; Anjos et al., 2005; Molina et al., 2008; Manfredi and Oliveira, 2010).

Researches to evaluate the effects of different levels of hemicelluloses in the pulp are performed through drastic variations in pulping and bleaching processes. More recently, researches were carried out by using the addition of these carbohydrates in the pulp, which requires the removal of hemicelluloses in a certain source and their introduction into the pulp. The main drawback of this approach is the difficulty of obtaining hemicelluloses in an economically viable way (Manfredi and Oliveira, 2010). The added amount of hemicellulose and the consistency of the fibrous suspension can affect treatment results. The lower the dose of hemicelluloses, faster maximum adsorption occurs (Köhnke and Gatenholm, 2007). However, at higher doses, most of the hemicelluloses tend to be kept in the pulp (Silva, 2011; Manfredi and Oliveira, 2010).

The hemicellulose content is extremely important in papermaking processes, as no other chemical component of wood has more influence on the properties of paper, since cellulose chains are not very damaged or degraded (Foelkel, 2007).

Pulps having reduced levels of hemicelluloses, such as recycled pulps are more difficult to be refined and have smaller and weaker bonds between the fibers when compared with pulps with higher levels of hemicelluloses (Silva, 2011). Hemicelluloses are responsible for most of the bonds between fibers and directly affect the properties of the influence of these links (Schönberg et al., 2001; Köhnke et al., 2008; Leopold and McIntosh, 1961; Petterson and Rydholm, 1961; Spiegelberg, 1966; Kettunen et al., 1982; Osterberg et al., 2001). One study found that the adsorption of xylan leads to an increase of negative ionic charge of the pulp, which is directly related to the tensile strength of the paper that is produced, due to the fact that negative charges promote increased swelling and thereby increase the flexibility of the fiber. Fibers that contain higher levels of hemicelluloses are able to produce papers with higher strengths, better bonds between the fibers, better surface smoothness, but lower porosity and bulk (Wang, 2006). The use of corn cobs as a source of hemicelluloses is justified by obtaining greater added value for this product that is found in significant amounts in wastes from agriculture, which has untapped potential use.

For 100 kg of corn ear, about 18 kg is formed by corn cob. World production of corn cob was about 144 million ton in 2008. Despite the large amount of this product generated, the range of use has not been shown in accordance with its potential for use (Silveira, 2010).

Thus, this study aimed to chemical characterization of corn cob, isolation of hemicelluloses present in this material and application in bleached eucalyptus kraft pulp for the development of the properties of papers.

2. Experimental procedure / methodology

Hemicelluloses were obtained following methodology described in literature (Silva et al., 1998), with adaptations. The procedure was repeated several times until the obtain desired amounts of hemicelluloses.

2.1. Hemicellulose isolation
Initially, corn cobs were exposed to sunlight for 48 hours to dry. They were then crushed in a mill and classified through a series of sieves. The fraction retained between screens 40 mesh and 60 mesh were subjected to various treatments as described below.

2.2. Quantitative chemical characterization

The carbohydrate composition of raw materials was established by High Performance Anion Exchange Chromatography with Pulse Amperometric Detection (HPAEC-PAD) after pre-treatment (30°C, 1 h) with aqueous 72% H2SO4 followed by hydrolysis with 3% H2SO4 in an autoclave (100°C, 3 h). HPAEC-PAD was carried out in a Dionex ICS-3000 system equipped with a CarboPac PA1 (250 x 4mm) analytical column. The monosaccharides were separated isocratically with 0.001 M NaOH (45 min, flowrate 1 mL/min) (Wallis et al., 1996). The solid residue after hydrolysis was considered as Klason lignin according to T222 cm⁻1 standard procedure (TAPPI, 2001). Ashes were determined by calcination according to TAPPI standard T211 om-12 (TAPPI, 2001). Acid soluble lignin was determined by measuring the UV-absorbance of the filtrate at 205 nm (Goldschmid, 1971). Total uronic acids in raw materials hydrolysates were measured by the colorimetric method involving 3,5-dimethylphenol (Scott, 1979). The content of acetyl groups was also determined (Solár et al., 1987). All results were calculated from two replicate determinations.

2.3. The aqueous extraction

The crushed material was subjected to aqueous extraction at a ratio of 30 g of powdered corn cobs to 1,000 ml of distilled water with constant stirring for 12 hours. Then the mixture was centrifuged and the solid phase was dried in climatic room at 23 °C and 50% humidity for 24 hours.

2.4. Removing lipids

After the aqueous extraction, the material of underwent lipid extraction with acetone in a Soxhlet-type apparatus, with 6 cycles per hour for 3 h. After that, it was dried under a fume hood for 3 hours to evaporate the acetone, and then remained in a desiccator for 24 hours.

2.5. Delignification

After drying the material obtained above, it was subjected to the organosolv pulping process taking into account the efficiency of removal of lignin as described by Silva et al. (1998). About 10 grams of sample was dispersed in 1,000 ml of mixture composed by 97% of 1,4-dioxane and 3% of hydrochloric acid. The system was kept under stirring at room temperature for 3 hours. At the end of the delignification, the solution was filtered and the residue containing hemicelluloses was washed several times with 1,4-dioxane and then with distilled water with a pH around 1. The residue was dispersed in distilled water and then neutralized with aqueous sodium hydroxide to 4% to reach a pH = 7.0. The solution was centrifuged and the residue was dried under vacuum.

2.6. Alkaline extraction

Solubilization of hemicelluloses was performed by alkaline treatment with 4% NaOH of corn cob powder at room temperature. A ratio of 10 grams of powder per 200 ml solution was used. The system remained in low agitation for 5 hours. After vacuum filtration, the solution was neutralized by adding glacial acetic acid to reach pH=7.0. At this stage, we observed the appearance of precipitate in the medium, which was attributed as Hemicelluloses A. After centrifugation, the fraction of hemicelluloses suffered several washings with ethanol and then dried under vacuum. The filtrate containing Hemicelluloses B was precipitated by the addition of ethyl alcohol in the proportion of three volumes of ethanol to 1 volume of the solution. The obtained product was centrifuged and washed several times with ethanol.
2.7. Hemicellulose dosage

Hemicelluloses have been added to the fibrous suspension, at 0.2 % consistency (16 g pulp bleached eucalyptus kraft absolutely dry) and maintained under constant agitation. The entire contents were stirred for 10 minutes for adsorption to occur on the surfaces of the fibers. Then sheets were formed according to TAPPI test T205 (TAPPI, 2001). Hemicelluloses doses tested were 0 %, 1%, 2.5% and 5% based on the dry weight of the pulp, and differentiated in Hemicelluloses A (formed by the hemicelluloses fraction obtained after neutralizing the pH of the solution hemicelluloses alkaline) and Hemicelluloses B (obtained after the addition of ethanol to the resulting supernatant gives extraction of hemicelluloses A). To verify the effect of the hemicelluloses, the same procedure was performed without the addition of these carbohydrates.

2.8. Physical and mechanical tests

The formed handsheets were placed in an environment with a relative humidity of 50 ± 2% and a temperature of 23 ± 1 °C (TAPPI 402 SP).

Experimental tests were performed according to standard procedures and methodologies according TAPPI (TAPPI, 2001), as shown in the following table.

<table>
<thead>
<tr>
<th>Test</th>
<th>Methodologies</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drainage resistance</td>
<td>TAPPI 200 sp-01</td>
</tr>
<tr>
<td>Tensile resistance</td>
<td>TAPPI 494 om-96</td>
</tr>
<tr>
<td>Tear resistance</td>
<td>TAPPI T 414 om-98</td>
</tr>
<tr>
<td>Bulk</td>
<td>TAPPI 220 sp-01</td>
</tr>
</tbody>
</table>

3. Results and discussion

3.1 Quantitative Chemical characterization

The chemical composition of corn cob (percentage relative to the dry weight) is shown in Table 2. This raw material is defined by its content of glucose, xylose, arabinose, galactose, mannose, acetyl groups, lignin, ash, uronic acid. Due to the presence of sodium carbonate, the analysis of the acid insoluble lignin provided an overestimated value; however, the values obtained were corrected for ash content (Anglés et al., 1997).

<table>
<thead>
<tr>
<th>Component, %</th>
<th>Results</th>
<th>Van Dongen et al., 2011</th>
<th>Lili et al., 2011</th>
<th>Garrote et al., 2007</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glucose</td>
<td>47.1</td>
<td>34</td>
<td>34.6</td>
<td>34.3a</td>
</tr>
<tr>
<td>Xylose</td>
<td>28.0</td>
<td>28</td>
<td>27.0</td>
<td>31.1a</td>
</tr>
<tr>
<td>Arabinose</td>
<td>5.4</td>
<td>2.4</td>
<td>3.6</td>
<td>3.01a</td>
</tr>
<tr>
<td>Galactose</td>
<td>2.2</td>
<td>0.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mannose</td>
<td>0.2</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Acetyl groups</td>
<td>2.9</td>
<td>-</td>
<td>0.3</td>
<td>3.07</td>
</tr>
<tr>
<td>Uronic acids</td>
<td>2.2</td>
<td>1.8</td>
<td>-</td>
<td>3.45</td>
</tr>
<tr>
<td>Lignin</td>
<td>17.8</td>
<td>18.3</td>
<td>9.4b</td>
<td>18.8</td>
</tr>
<tr>
<td>Ash</td>
<td>1.2</td>
<td>-</td>
<td>2.5</td>
<td>1.3</td>
</tr>
</tbody>
</table>

a All sugars expressed as anhydro-units in polymers;
b Lignin values were measured as acid insoluble lignin contents;
c Lignin values were measured as acid insoluble lignin contents and acid soluble.
The chemical composition of corn cob showed that its total sugar constitution is very different from that found in Eucalyptus, presenting a total of 82.9 % while in Eucalyptus it was found 61 % (Batalha et al., 2012), where the differences are more significant in the amounts of xilose and arabinose. Total lignin was 17.8 %, while their uronic acid and ash contents were 2.2 % and 1.2%, respectively. In relation to the glucose content (47.1 %), the experimental result was higher than that reported by other authors (Van Dongen et al., 2011; Lili et al., 2011; Garrote et al., 2004), a fact that can be explained by the method used by each author for quantification of carbohydrates. Values of 28.0 % xilose; 5.4 % arabinose; 0.2 % mannose; and 2.9% acetyl groups, for samples determined in this study are closely comparable to those reported by them (Van Dongen et al., 2011; Lili et al., 2011; Garrote et al., 2004) for similar samples.

3.2. Physical and mechanical properties of the pulps and papers

The two hemicelluloses fractions, called Hemicelluloses A and Hemicelluloses B, were isolated from corn cobs, the first being obtained after neutralization of the pH of the alkaline solution and the second after the addition of ethanol to the supernatant of the same solution.

Silva et al. (1998) obtained differences in the values of the intrinsic viscosity of the fractions, being 56 ml / g for Hemicelluloses A and 75 ml / g for Hemicelluloses B. These authors indicate that the main difference between these two fractions are the largest hydrodynamic volume of Hemicelluloses B, driven by greater number of substituents (L-arabinose). The presence of substituents tending to increase the rigidity of the polymer chain and causing steric repulsions increase would be responsible for a greater hydrodynamic volume and intrinsic viscosity of hemicellulose B.

3.3. Drainage Resistance

Figure 1 shows that the pulps with lower levels of hemicelluloses had lower drainage resistance than those which contain a higher content of these carbohydrates.

The Reference pulp, without the addition of hemicelluloses, showed an 18 ° SR, while those that were added of hemicelluloses A and B showed a maximum value of 26 ° SR and 25, respectively, at a dosage of 5%.

The high content of hemicelluloses associated with a large population fibrous and low viscosity results in pulp with high water retention and very difficult to drain and dehydrated in the paper machine (Foelkel, 2007).

3.4. Tensile resistance
Figure 2 shows the effect of the addition of the hemicelluloses in the tensile strength of the paper. As it can be seen, by increasing doses of such carbohydrates, the tensile strength also increases. Hemicelluloses contribute greatly to intra and inter-linked fiber, resulting in handsheets with more tensile resistance (Milanez et al., 1982), which can also be clearly seen in this study.

Recently, it has been shown that the increase of the tensile strength of the sheet due to the addition of xylan can be completely explained by the higher content of xylan in the fiber surface, since the xylan located in the inner fiber presents no influence on the tensile strength and tear resistance (Schönberg et al., 2001).

In this study, the development of highest tensile index was achieved with a dose of 5% based on dry pulp in all situations. Was observed an increase of 62.3% in this property in the papers which were added 5% Hemicelluloses A, also with the same dosage, the pulp added Hemicelluloses B showed increased 53.4%.

3.5. Tear resistance

Figure 3 shows values to tear index for the papers produced in accordance with variations in the dosage of hemicelluloses. It is noted that values of tear strength were higher to the papers receiving higher doses of hemicelluloses.
It was observed in the same dosages, pulps which have received the Hemicelluloses B showed a greater tear resistance than those receiving Hemicelluloses A. It was observed that development was achieved at a maximum dose of 5%, with an increase of 12.8% for pulps added Hemicelluloses A and 20.7% for pulp added Hemicelluloses B.

Researchers noted the same trend in the Pinus and Eucalyptus refined pulps and said that hemicelluloses improved action of refining, but at the same time reduced the tensile index with respect to the tear index, due to the decrease in the proportion of content cellulose (Salomão, 2001). Other researchers found no change in the resistance of the fiber with different percentages hemicelluloses. They found no increase in tear index, although the tensile index of pulp has increased (Molin and Teder, 2002).

3.6. Bulk

Figure 4 shows the results of bulk for the papers produced by varying the dosage of hemicelluloses added. The highest values of bulk in papers were observed in papers with lower content of hemicelluloses, consequently generating more dense papers insofar as the dose is increased.

![Bulk as a function of dosage of hemicelluloses.](image)

In this study, the higher bulk was achieved in the papers that were not added hemicelluloses (3.14 cm³/g). It was observed that as you increase the content of hemicelluloses, results found showed the lower of bulk. In the dose of 5%, it was shown a reduction of 48.8% on papers added Hemicelluloses A and 59.9% on papers added Hemicelluloses B.

Pulps rich in Hemicelluloses tend to produce high density paper and reduced volume, which is not interesting for tissue products. Moreover, printing and writing papers need traction and can be benefited from pulps with high hemicellulose content (Schönberg et al., 2001; Anjos et al., 2005; Molina et al., 2008).

4. Conclusions

Based on the results, one can conclude that corn cobs are good sources of hemicelluloses, which is presented as an alternative to the use of these carbohydrate residues using these carbohydrates in the manufacture of papers. It is also concluded that the pulps with higher concentrations of hemicelluloses form paper with lower bulk, increased resistance to drainage and greater tensile strength. The two fractions of hemicelluloses found, when applied separately, results in handsheets with different physical and mechanical properties.
References


Foelkel, C. E. B., 2007. As fibras dos eucaliptos e as qualidades requeridas na celulose Kraft para a fabricação de papel. Eucalyptus Online Book & Newsletter.


