BIANCA MOREIRA BARBOSA

APLICAÇÕES DE XILANAS E LIGNINAS EXTRAÍDAS DE BIOMASSAS LIGNOCELULÓSICAS PARA OBTENÇÃO DE BIOPRODUTOS

Tese apresentada à Universidade Federal de Viçosa, como parte das exigências do Programa de Pós-Graduação em Agroquímica, para obtenção do título de *Doctor Scientiae*.

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Carla Priscilla T. Cabral
Carla Priscilla Távora Cabral

Efraim Lázaro Reis

Silvio Vaz Junior
(Coorientador)

Antônio Jacinto Demuner

Jorge Luiz Colodette
Jorge Luiz Colodette
(Orientador)

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SUMÁRIO

ABSTRACT

BARBOSA, Bianca Moreira, D.Sc., Universidade Federal de Viçosa, July, 2017. **Applications of xylans and lignins extracted from lignocellulosic materials for obtaining bioproducts**. Adviser: Jorge Luiz Colodette. Co-adviser: Sílvio Vaz Junior.

The search for better use of wood in the pulp and lignocellulosic biomass industry, such as the fibers of industrial processing corn, has fueled the interest in a more rational use of its components, particularly xylans and lignin. In this context, the objectives of this thesis, consisting of four chapters, were the application of xylans extracted from lignocellulosic materials and the use of Kraft lignin as a pellet additive. Initially, the impact of xylan removal and xylan redeposition on the properties of pulp for tissue paper and printing and writing paper (P&W). Removal of xylans decreased pulp beatability, water retention value and tensile index, but increased water absorption capacity, Klemm capillarity and bulk, presenting almost ideal properties for tissue paper grade pulps. In a second step of the research, cold caustic extraction (CCE) extracted xylans from bleached (BXL) and bleached (WXL) eucalyptus pulps (WXL) were added to a commercial brown pulp in the oxygen delignification (O-stage) step and then bleached. The bleachability of the pulp was not impaired by the deposition of WXL xylan, but slightly negatively affected by BXL xylans. Pulp beatability and the physical and mechanical properties were improved by deposition of xylan. Extraction of xylans by CCE with subsequent deposition in the pulp at the O-stage stage proved attractive for manufacturing high xylan P&W paper grades. Xylans extracted from corn fibers (16.9% xylans) by CCE were added to commercial brown pulp (eucalyptus and pinus) at O-stage and subsequently bleached. The deposition of hemicelluloses occurred in a variable degree (up to 7% in pulp weight). The bleachability of the pulp was not impaired by the deposition of xylans for eucalyptus and pinus. The deposition of hemicellulose in the fibers was more efficient in the eucalyptus pulp than in the pinus. Extraction of xylan from corn fibers by CCE with subsequent deposition in the pulp at O-stage increases the pulp beatability and quality for P&W paper grades. The chemical characterization of corn fibers, the isolation of hemicelluloses using NMR and FTIR-ATR was performed, in addition to a structural investigation of lignins, acid-soluble lignin (ASL) and acid insoluble lignin (AIL), formed by the Klason method by pyrolysis-gas chromatography/mass spectrometry (Py-GC-MS). Hemicellulose isolation can be considered efficient and more 45 primary pyrolysis products for ASL and 39 for AIL from corn fibers. Analytical pyrolysis of ASL from corn fibers showed prevalence of peaks related to products derived from extractive and proteins. Also, the Py-GC-MS technique allowed identifying the presence of derivatives lignin in ASL and AIL. The evaluation of the quality of the pellets produced from a mixture of eucalyptus and corn residue, with the addition of different percentages of Kraft lignin was carried out. For the production of pellets, wood with bark of a hybrid of *Eucalyptus grandis* x *Eucalyptus urophylla* and corn residue were used as raw material. The following proportions of corn residue in the mixture were 0, 20, 25 and 30% (w/w). Except for the control (0% w/w lignin), 2 and 5% (w/w) Kraft lignin were added to the raw material in the 4 different mixtures. Pellets were produced in a laboratory press pelletizer with horizontal circular array. The addition of Kraft lignin to eucalyptus and corn residue pellets improved bulk density, and mechanical durability. The mixing of eucalyptus with corn residue is an effective way to optimize properties of biomass solid fuel. Thus, similar amounts to that of the treatment with the proportion of 80% (w/w) eucalyptus and 20% (w/w) corn residue can be a viable alternative to the production of pellets.

RESUMO

BARBOSA, Bianca Moreira, D.Sc., Universidade Federal de Viçosa, julho de 2017. **Aplicações de xilanas e ligninas extraídas de biomassas lignocelulósicas para obtenção de bioprodutos**. Orientador: Jorge Luiz Colodette. Coorientador: Sílvio Vaz Junior.

A busca de uma melhor utilização da madeira na indústria de celulose e de biomassa lignocelulósica, como as fibras do milho de processamento industrial, alimentou o interesse em um uso mais racional de seus componentes, particularmente xilanas e lignina. Neste contexto, os objetivos desta tese, constituída por quatro capítulos, foram a aplicação de xilanas extraídas de materiais lignocelulósicos e a utilização de lignina Kraft como aditivo para pellets. Inicialmente foi discutido o impacto da remoção de xilanas e a redeposição de xilanas nas propriedades da polpa para papel *tissue* e de papel de imprimir e escrever (P&W). A remoção de xilanas diminuiu a resistência a drenagem, o valor de retenção de água e o índice de tração, mas aumentou a capacidade de absorção de água, capilaridade Klemm e o *bulk*, apresentando propriedades quase ideais para polpas de papel *tissue*. Em uma segunda etapa da pesquisa, foram adicionadas xilanas extraídas por extração caustica fria (CCE) de polpas de eucalipto não branqueadas (BXL) e branqueadas (WXL) a uma polpa marrom comercial na etapa deslignificação de oxigênio (O-estágio) e posteriormente foram branqueadas. A branqueabilidade da polpa não foi prejudicada pela deposição de xilana de WXL, mas ligeiramente afetada negativamente por xilanas BXL. A capacidade de refino da polpa e as propriedades físicas e mecânicas foram melhoradas pela deposição de xilana. A extração de xilanas por CCE com deposição subsequente na polpa na fase O-estágio mostrou ser atraente para a fabricação P&W. Xilanas extraídas de fibras de milho (16,9% de xilanas) por CCE foram adicionadas a polpa marrom comercial (eucalipto e pinus) no O-estágio e posteriormente branqueada. A deposição de hemiceluloses ocorreu em grau variável (até 7% no peso da polpa). A branqueabilidade da polpa não foi prejudicada pela deposição de xilanas para eucaliptos e pinus. A deposição de hemicelulose nas fibras foi mais eficiente na polpa de eucalipto do que no pinus. A extração de xilanas de fibras de milho por CCE com deposição subsequente na polpa na O-estágio aumenta a refinabilidade e a qualidade da polpa para o papel P&W. A caracterização química de fibras de milho, o isolamento das hemiceluloses utilizando RMN e FTIR-ATR foi realizado, além de, uma investigação estrutural das ligninas, solúvel em ácido (ASL) e lignina insolúvel em ácido (AIL), formada pelo método de Klason determinadas por pirólise acoplada à cromatografia gasosa e à espectrometria de massas (Pi-CG-EM). O isolamento de hemicelulose foi considerado eficiente e foram encontrados 45 produtos de pirólise primária para ASL e 39 para AIL a partir de fibras de milho. A pirólise analítica de ASL a partir de fibras de milho mostrou prevalência de picos relacionados a produtos derivados de extrativos e proteínas. Além disso, a técnica Pi-CG-EM permitiu identificar a presença de derivados de lignina em ASL e AIL. A avaliação da qualidade dos *pellets* produzidos a partir de uma mistura de eucalipto e resíduo de milho, com a adição de porcentagens diferentes de lignina Kraft foi realizada. Para a produção dos *pellets*, a madeira com a casca de um híbrido de *Eucalyptus grandis* x *Eucalyptus urophylla* e o resíduo de milho foram utilizados como matéria-prima. As seguintes proporções de resíduo de milho na mistura foram 0, 20, 25 e 30% (m/m). Com exceção do controle (0% m/m de lignina), 2 e 5% (m/m) de lignina Kraft foram adicionados à matéria-prima nas 4 misturas diferentes. Os pellets foram produzidos em uma prensa peletizadora laboratorial de matriz circular horizontal. A adição de lignina Kraft aos pellets de eucalipto e resíduos de milho melhorou a densidade aparente e a durabilidade mecânica. A mistura de eucalipto com resíduos de milho é uma forma eficaz de otimizar as propriedades do combustível sólido de biomassa. Assim, quantidades semelhantes às do tratamento com a proporção de 80% (m/m) de eucalipto e 20% (m/m) de resíduo de milho podem ser uma alternativa viável à produção de *pellets*.

GENERAL INTRODUCTION

The Biorefinery refers to a complex integration of processes, technology and equipment dedicated to the production of energy, fuels and chemicals from biomass. Lignocellulosic biomass is one of the most available and renewable resources which represent a promising low cost raw material for renewable energy production. The processes involved in the improvement of these renewable feedstocks should integrate the principles of green chemistry and green engineering, and low environmental impact technologies for the sustainable production of high value chemicals. Moreover, decreasing the dependency on fossil fuel reserves by developing a sustainable society and boosting rural development are important goals of modern society.

Lignocellulosic material consists of three structural components; cellulose, hemicellulose and lignin, as well as by some minor nonstructural components. Cellulose, which represents over 50% of biomass, is a linear polymer of cellobiose (D-glucopyranosyl-β-1,4-Dglucopyranose) units and presents a highly ordered structure. Hemicelluloses present an intermediate complexity degree, being formed by pentose and hexose units (often acetylated) in branched chains. They are polysaccharides that differ from cellulose for containing several types of sugar units in their composition (D-xylose, D-mannose, D-glucose, L-arabinose, etc). By contrast, lignin, the most recalcitrant plant constituent, forms a 3-D network including a variety of C-C and ether linked substructures.

Xylans are considered to be very important for production of printing and writing paper grades because they facilitate pulp refining and increase fiber bonding. In papermaking, some studies also reveal that the xylans retake can also improve paper properties such as tensile and other bonding strength of paper. Fibers rich in hemicelluloses tend to produce high density / low bulk paper sheets, which are not so interesting for tissue products. On the other hand, printing and writing (P&W) paper grades needs tensile strength and can benefit from high hemicelluloses contents in the fiber.

Corn fibers contain a considerable reservoir of xylan-type hemicelluloses which long ago were recognised as a good source of xylose. The fibers of the corn grain are agro-industrial waste generated in the production of starch or corn syrup. Because it is a food with a high content of lignocellulosic materials, it has a low commercial value, being applied only to animal feed. In previous papers, the xylan isolated from corn fibers has been shown to be applicable as an additive in papermaking, textile printing and the pharmaceutical industry. In the specific case of corn fibers, the xylans usually present a chemical structure formed by 4-O- methyl-D-glucuronic acid, L-arabinose and D-xylose in the ratio 2:7:19.

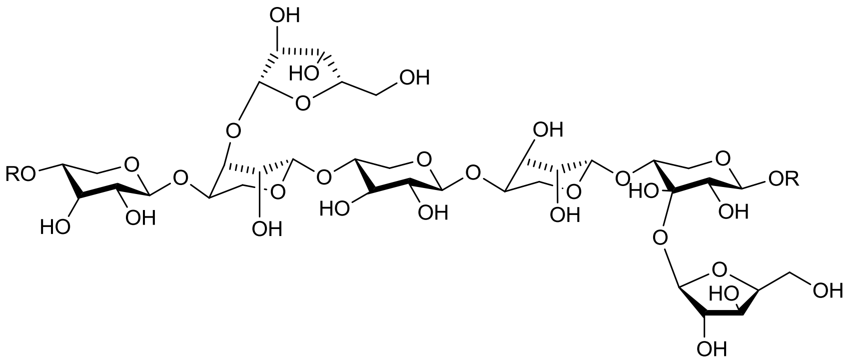

Figure 1. Typical xylan structure from corn fibers: 4-O-methyl-(glucurono)arabinoxylans.

Focus on development of added-value products derivatives from wood feedstock for advanced applications play an important role on the biorefinery perspective. Kraft lignin is obtained from black liquor generated by pulp mills by the Kraft process and can be extracted and used as other alternatives with more value-added, one example is the possibility of use as an additive for pellets. In this context, the goals of this thesis, comprised of four chapters, were to the application of xylans extracted from lignocellulosic materials and use the Kraft lignin as an additive for pellets.

On Chapter 1, the impact of xylans removal and of xylans redeposition on pulp properties for tissue and P&W paper grades, are discussed in this paper.

On the chapter 2, xylan-rich hemicelluloses were isolated from corn fibers and added in the eucalyptus and pinus pulp to produce paper. Then, the physical and mechanical properties were assessed.

Chapter 3, the chemical characterization of the corn fibers, hemicelluloses isolation and lignins structural investigation formed by the Klason method was carried out and assessed.

On Chapter 4, to evaluate the quality of the pellets produced from a mixture of eucalyptus and corn residue, with the addition of different percentages of Kraft lignin.

CHAPTER 1

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EFFECTS OF XYLAN IN EUCALYPTUS PULP PRODUCTION

ABSTRACT

The search for a better use of wood in the pulp industry has fuelled interest in a more rational use of its components, particularly xylans. The impact of xylans removal and of xylans redeposition on pulp properties for tissue and P&W paper grades, are discussed in this paper. Kraft pulp (15.6% xylans) treatment with 10-70 g/L NaOH resulted in pulps of 14.5-5.9% xylans. The treatments decreased pulp lignin and HexA contents and caused significant positive impact on subsequent oxygen delignification and ECF bleaching. Xylan removal decreased pulp beatability, water retention value and tensile index but increased water absorption capacity, capillarity Klemm and bulk. Overall, xylan depleted pulps showed almost ideal properties for tissue paper grade pulps. In a second step of the research, xylans extracted from unbleached (BXL) and bleached eucalyptus pulps (WXL) by cold caustic extraction (CCE) were added to a commercial brown pulp in the oxygen delignification (O-stage) and further bleached. Xylans deposition occurred at variable degree (up to 7% on pulp weight) depending upon the O-stage reaction pH. Pulp bleachability was not impaired by WXL xylan deposition but slightly negatively affected by BXL xylans. Pulp beatability was improved by xylan deposition. The deposited xylans were quite stable across bleaching and beating, with the WXL xylans being more stable than the BXL ones. At low energy consumption, the deposited xylans improved pulp physical and mechanical properties. Xylans extraction by CCE with subsequent deposition onto pulp in the O-stage proved attractive for manufacturing high xylan P&W paper grades.

Keywords: Redeposition of xylans, kraft pulping, pulp and paper.

1. INTRODUCTION

After kraft pulping, the only remaining hemicelluloses on eucalypt pulps are xylan backbones containing small amounts of uronic acids. For production of P&W paper grades, higher pulp xylan contents are desirable for their positive effect on pulp beatability and tensile strength (SCHONBERG et al., 2001). Tissue grade pulps require attributes such as softness, bulk and fast water absorption by capillarity that are purportedly negatively affected by pulp xylans (FOELKEL, 2007).

Furthermore, the xylans possess very high water retention values and tend to impair paper machine runability (FOELKEL, 2007). Thus, decreasing eucalypt pulp xylan content could be interesting for tissue grade applications. The control of xylan concentration may serve as instrument for eucalypt pulp differentiation aiming at manufacturing different products. The objective of this study was producing eucalyptus pulps of different xylan concentrations and evaluating their potential for application in different products. The control of pulp xylan was achieved through the techniques of cold caustic extraction and of xylan redeposition in the O-stage.

2. MATERIAL AND METHODS

Pulp xylan control *via* cold caustic extraction (CCE) was carried out using an industrial *Eucalyptus urograndis* unbleached kraft pulp (16.1 kappa number, 1226 $dm^3\ kg^{-1}$ viscosity, 15.6% xylans and 61.8 $mmol\ kg^{-1}$ HexA). Xylan removal was achieved by CCE (30 min, 30°C, 10% consistency) using four different alkali charges (10, 30, 50 e 70 $g\ L^{-1}$ NaOH). The xylan depleted pulps were bleached with the O-D-(EP)-D sequence and the pulps were beat and evaluated for hygroscopic and physical properties. Xylan redeposition onto an industrial eucalyptus kraft pulp was effected using xylans extracted from other kraft pulps *via* the CCE procedure. The xylans were removed from bleached and unbleached kraft pulps giving rise to the WXL (White Xylans Liquor) and BXL (Brown Xylans Liquor) extracts, respectively. Xylans were deposited onto pulp during the O-stage, according to Muguet et al. (2010). Pulp and spent liquor analyses followed Tappi standard procedures.

Xylans were isolated from CCE extracts according to Teleman et al. (1995) and their contents were measured by HPLC-PAD after acid hydrolysis, following the procedure described by Wallis et al. (1996). Pulp hexenuronic acid content and xylan molecular weights were determined according to Vuorinen et al. (1996) and Pinto et al. (2005), respectively. Scanning electron microscopy (SEM) images were acquired with a SEM microscopy LEO model 1430VP, operating at 11 kV. Pulp refining for physical testing was carried out in a PFI mill (1000-12000 revs) and the hand sheets tested for their properties in accordance to Tappi standard procedures, except for capillarity Klemm and water absorption capacity (Wa), which were carried out according to ISO 8787:86 and NBR 15004 standards, respectively.

3. RESULTS AND DISCUSSION

3.1 Pulp xylan control *via* CCE for tissue grade pulp production

The CCE at 70 $g\ L^{-1}$ NaOH removed 62% of the pulp xylan **(Table 1)**. This alkali charge represents 630 kg NaOH per ton of pulp at 10% consistency and therefore must be reused in order to make the process feasible. On the other hand, the concentration of the xylan removed (97 $kg\ ton^{-1}$of pulp) in the CCE extract reaches only 1.08 $g\ L^{-1}$ at 10% consistency. This concentration may be increased significantly by recycling the CCE extract in the process in order to be recovered for biorefinery uses. Eventually, part of the CCE extract must be purged and clean caustic make up is added in to avoid liquor saturation with xylans. The CCE treatment decreased yield as a result of lignin, HexA, xylans and other materials removal. For the 70 g L^{-1} NaOH treatment the yield loss was 14.3%, which was not totally explained by the xylan (9.7%), lignin (0.64%) and HexA (0.58%) losses. The remaining losses (3.4%) may be explained by low molecular weight degraded cellulose dissolution. Of the total kappa removed in the CCE treatment with 70 g L^{-1} NaOH (8.2 units), 3.9 and 4.3 units derived from HexA and lignin, respectively. Lignin and HexA are removed because they are linked to the xylan backbone. Pulp viscosity increased with the removal of low Mw xylans.

Table 1. Effect of NaOH concentration on CCE treatment performance.

Results	Ref.	NaOH, g L^{-1}			
		10	30	50	70
Xylans (%)	15.6	14.5	10.8	8.1	5.9
Yield (%)	-	98.5	96.7	89.2	85.7
Viscosity (dm^3 kg^{-1})	1226	1204	1245	1278	1308
HexA (mmol kg^{-1})	61.8	61.4	50.0	34.7	22.8
Total Kappa	16.1	15.2	13.3	10.5	7.9

No significant impact of the pulp xylan content (5.9-15.6%) on kappa drop (31.7-33.6%) across the O-stage was observed **(Table 2)**.Viscosity losses were significantly higher for the pulps containing less xylan, a result attributable to more significant exposure of cellulose microfibrils to oxygen. Bleaching was carried out according to Juste (2011), using a kappa factor of 0.16 in the first D stage and variable doses of ClO_2 in the second D stage in order to achieve the 90 ± 0.2% ISO brightness target for all pulps. A dose of 0.3% H_2O_2 was applied in the (EP) stage. The ClO_2 requirement to reach target brightness varied in the range of 0.52-1.23%, with the lower values obtained for the low xylan pulps because of their lower kappa number after the O-stage. The final viscosities varied in the range of 767-926 dm^3 kg^{-1} and were lower for the low xylan pulps.

Table 2. Effect of pulp xylan content on O-D-(EP)-D bleaching performance (JUSTE, 2011).

Results	**Pulp Xylan Content, %**				
	15.6	14.5	10.8	8.1	5.9
Kappa Number after O-stage	10.9	10.1	9.0	7.1	5.4
HexA after O-stage (mmol kg^{-1})	59.8	59.8	48.1	33.1	22.0
Viscosity after O-stage (dm^3 kg^{-1})	1101	1071	915	-	904
ClO_2 (%)	1.23	1.19	0.93	0.62	0.52
Final Brightness (% ISO)	89.8	89.8	89.9	89.8	90.1
Brightness Reversion (% ISO)	2.7	2.6	2.4	2.5	2.2
Final Viscosity (dm^3 kg^{-1})	926	911	813	-	767
Final HexA (mmol kg^{-1})	6.6	7.3	7.3	9.4	5.5

3.2 Pulp refinability, drainability and hygroscopic and strength properties

The xylan increase from 5.9 to 15.6% significantly decreased the energy consumption to achieve a given °SR **(Fig. 1)**, an effect likely caused by improved fiber hydration and flexibility. Since °SR measures pulp resistance to drainage, the higher the value the lower is the drainability. Thus, xylans impair pulp drainability significantly **(Fig. 1)**, a result attributable to xylans high water retention capacity. A poor drainability is undesirable particularly in low grammage tissue paper production where paper machines run at very high speed. Pulp water retention value (WRV) decreased and hornification increased with decreasing pulp xylan content **(Table 3)** in agreement with the increased pulp drainability. The pulp water retention capacity (Wa) increased with decreasing xylan content due to increased water penetration by capillarity (**Table 3**). This property is very favorable for tissue paper production which is refined to a very small degree. When refining is increased the pulp water absorption capacity decreases significantly (REINER, 1994), and the effect of xylan content becomes less significant. Capillarity Klemm (CK) was significantly increased by decreasing pulp xylan content **(Fig. 2).** Xylans are amorphous by nature with greater affinity to water than the crystalline cellulose microfibrils; thus, they decrease the velocity of the water flow by capillarity within the paper matrix. High values of CK are desirable for tissue grade papers that need to absorb water fast.

Table 3. Effect of pulp xylan content on WRV, hornification and Wa (unbeaten pulps).

Pulp Xylan Content, %	**15.6**	**14.5**	**10.8**	**8.1**	**5.9**
WRV, %	159	155	145	138	132
Hornification, %	37.8	38.2	40.8	41.6	42.3
Water retention Capacity (g H_2O/g pulp)	5.4	5.4	7.1	9.0	11.5

Decreasing pulp xylan content negatively affected tensile strength, regardless of refining energy (**Fig. 3**). No significant tensile difference were seen between the pulps containing 15.5 and 14.5% xylans but the values decreased sharply for xylan contents in the range of 10.8-5.9%. In tissue paper manufacture, pulp refining usually decreases fiber ability to absorb water by capillarity and therefore refining is used only to achieve the minimum tensile strength required for acceptable paper machine runability. Too high tensile values are undesirable due to decreased pulp softness/smoothness, which is very relevant for tissue paper grades. On the other hand, pulp of low xylan contents produce high bulk **(Fig. 4)** which is highly desirable for tissue paper production.

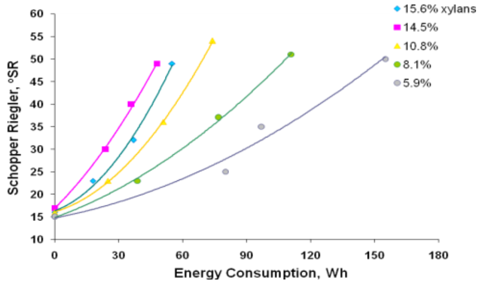

Figure 1. Effect of pulp xylan content on drainage resistance (°SR).

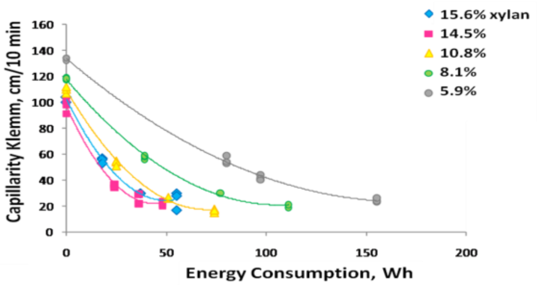

Figure 2. Effect of pulp xylan content on capillarity Klemm.

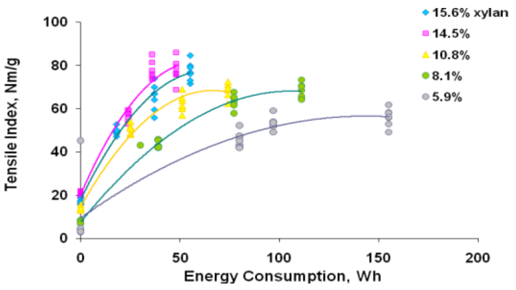

Figure 3. Effect of pulp xylan content on tensile index.

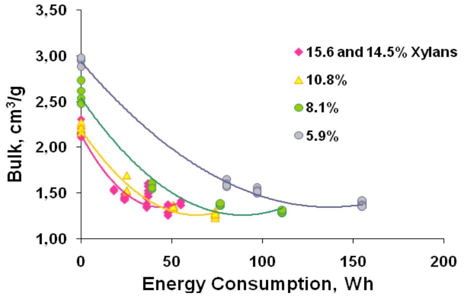

Figure 4. Effect of pulp xylan content on bulk.

3.3 Pulp xylan redeposition onto pulp for P&W paper grades

3.3.1. Xylans extraction and characterization

Table 4 shows that the (CCE) treatment was more effective in removing xylans from the bleached pulp (95.3%) than from the unbleached one (85.3%). This result is consistent with the higher xylan concentration in the liquor extracted from the bleached pulp (17.5 g L^{-1}) in comparison to that extracted from the unbleached pulp (15.8 g L^{-1}). This is likely explained by lignin-carbohydrate complexes (LCC) existing in the unbleached pulp. The CCE treatment removed significant amounts of lignin from the unbleached pulp. The xylans isolated from the bleached pulp showed lower M_w, bound lignin and uronic acids than the ones isolated from the brown pulp (**Table 4). The** lower

M_w of xylans extracted from bleached pulp is explained by oxidation effects occurring during bleaching, particularly in the O-stage. The lower uronic acids (UA) content was also expected, since some bleaching stages effectively remove them (DAHLMAN et al., 2003).

Table 4. Brown (BXL) and bleached (WXL) isolated xylans fraction composition.

Sample	**Carbohydrates**			**Bound Lignin**		**Properties**	
	Glucans (%)	Xylans (%)	UA (%)	Klason (%)	Soluble (%)	UA/ Xylans (%/%)	Mw (KDa)
BXL	1.00	78.4	14.2	2.25	4.10	0.181	19.1
WXL	1.76	92.2	5.68	0.00	0.33	0.062	15.1

3.3.2. Xylans deposition during oxygen delignification

Xylans deposition occurred in all cases, in minor or greater extent **(Fig. 5)** depending upon reaction pH value. Different patterns have occurred for BXL and the WXL xylan deposition. Hemicelluloses deposition onto fibers is more efficient at low pH values (DANIELSSON; LINDSTRÖM, 2005). At low electrolyte concentration the adsorption is favored if the chemical affinity of the polymer to the surface is high (ÖSTERBERG et al., 2001). This behavior was seen for the BXL deposition.

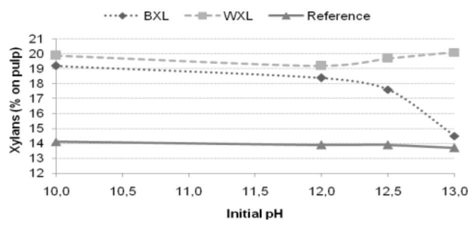

Figure 5. Effect of oxygen delignification starting pH value on xylan deposition onto base pulp for processes with addition of brown pulp xylans (BXL), white pulp xylans (WXL) and no xylans (Reference).

3.3.3. Impact of xylans deposition on O-stage performance

The presence of lignin in the xylan extract affected oxygen delignification efficiency, since the pulps treated with the BXL showed higher kappa numbers **(Fig. 6)** than those treated with WXL and the reference. The xylan deposition with both BXL and WXL extracts resulted in decreased pulp viscosity due to the low Mw of these hemicelluloses in relation to cellulose **(Fig. 7).** The increase in the O-stage initial reaction pH value had the expected effect of decreasing pulp kappa number and viscosity. SEM images of thin handsheets (50 g m^{-2}) prepared with reference pulp and pulps treated with WXL extracts at pH 12 are presented in **Figure 8.** The xylans appear aggregated to each other forming a web, thus helping interfiber bonding. This supports the theory that xylans can act as a stress transfer matrix (LIITIÄ et al., 2005).

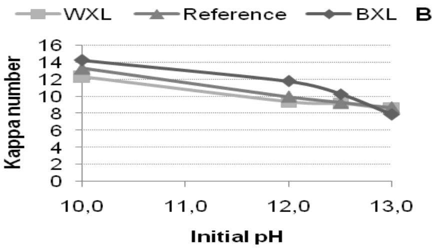

Figure 6. Effect of O-stage initial pH value on kappa number for processes with addition of BXL, WXL and no xylans (Reference).

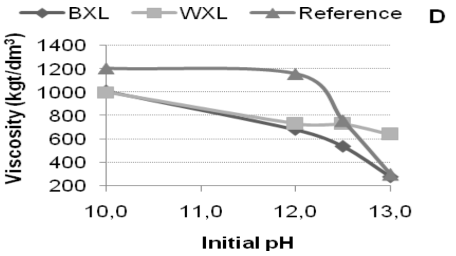

Figure 7. Effect of O-stage initial pH value on viscosity for processes with addition of BXL, WXL and no xylans (Reference).

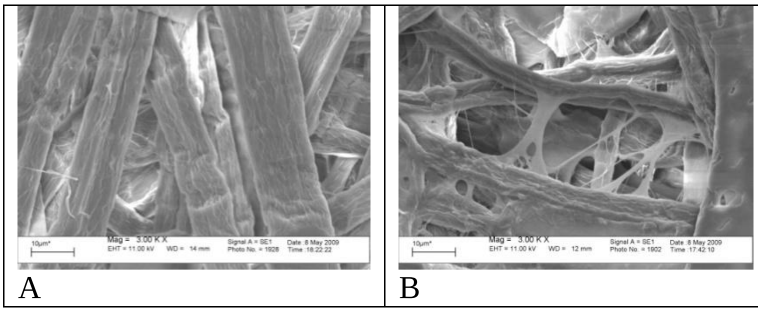
A
B

Figure 8. SEM images of the Reference at pH value 12 (A) and WXL addition at pH 12 (B).

The pulps treated with WXL and BXL at pH value 12.5 were bleached to a final brightness of 90 ± 0.2% ISO with the D-(EP)-D sequence (MUGUET et al., 2010). The amount of reagents needed to bleach the reference and WXL treated pulp samples were similar but the BXL treated pulp consumed larger amounts of ClO_2 to reach the brightness target than the other two samples. This result was anticipated since the BXL extract contained sizeable amounts of lignin, which contaminated the pulp during the O-stage to a point that the post-oxygen kappa number was one unit higher for this sample than for the other two.

3.3.4. Pulp physical and mechanical properties

High quality printing and writing paper grades require pulps of high tensile strength to withstand the forces the paper undergoes during manufacturing and use in high speed machines. The role of xylans during beating and in paper properties has been studied and they seem very important for P&W paper grades (BHADURI et al., 1995). The pulps containing higher xylan concentration required much less energy to reach the 60 N.m g^{-1} tensile index **(Fig. 9).** This leads to significant economical savings, taking into account that pulp beating is one of the most costly operations of the paper manufacturing process. Besides improving beatability, xylans redeposition onto fibers led to improved tear and tensile strengths at low beating energy levels **(Figs. 10-11).**

The deposited xylan stability was evaluated across bleaching and beating at 35 °SR, which is typical for eucalypt printing and writing paper grade pulp. The WXL low Mw and less substituted xylans seems to attach better to fibers, thus resisting more to bleaching and to the mechanical forces during beating than the BXL ones **(Fig. 12).**

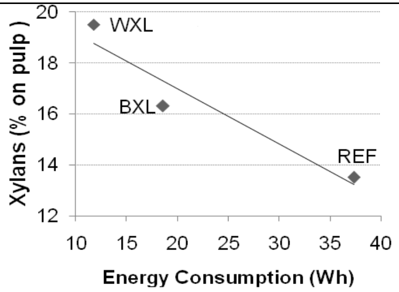

Figure 9. Energy consumption vs. xylans content at 60 N m g^{-1} tensile index for processes with addition of BXL, WXL and no xylans (REF).

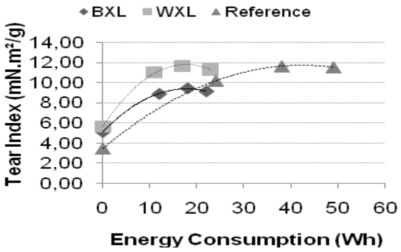

Figure 10: Tear index vs. energy consumption for processes with addition of BXL, WXL and no xylans (REF).

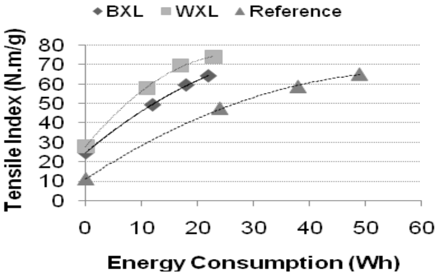

Figure 11: Tensile index vs. energy consumption for processes with addition of BXL, WXL and no xylans (REF).

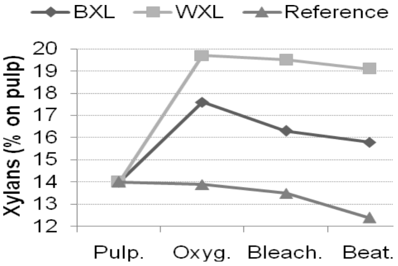

Figure 12. Deposited xylans stability after pulping, O-stage, bleaching and beating of pulps with addition of BXL, WXL and no xylans (Reference).

4. CONCLUSIONS

The treatments of removal xylans decreased pulp lignin and HexA contents and caused significant positive impact on subsequent oxygen delignification and ECF bleaching. Xylan removal decreased pulp beatability, water retention value and tensile index but increased water absorption capacity, capillarity Klemm and bulk.

Xylans deposition occurred at variable degree (up to 7% on pulp weight) depending upon the O-stage reaction pH. The deposited xylans were not impaired by WXL xylan deposition but slightly negatively affected by BXL xylans. Pulp beatability was improved by xylan deposition. At low energy consumption, the deposited xylans improved pulp physical and mechanical properties. Xylans extraction by CCE with subsequent deposition onto pulp in the O-stage proved attractive for manufacturing high xylan P&W paper grades.

REFERENCES

Associação de Normas Técnica de Celulose e Papel, ABCTP, Normas. Rio de Janeiro, ABNT, 2003.

BHADURI, S. K.; GHOSH, I.N.; DEB SARKAR, N. L. Ramie hemicelluloses as beater additive in paper making from jute-stick kraft pulp Industrial Crops and Product, 4, p.79-84, 1995.

DAHLMAN, O.; JACOBS, A.; SJÖBERG, J. Molecular properties of hemicelluloses located in the surface and inner layers of hardwood and softwood pulps, Cellulose, 10, p. 325-334, 2003.

DANIELSSON, S.; LINDSTRÖM, M. E. Influence of birch xylan adsorption during kraft cooking on softwood pulp strength, Nordic Pulp and Paper Researcher Journal, 20, p. 436-441, 2005.

FOELKEL, C. Eucalyptus Fibers and Kraft Pulp Requirements for Paper Manufacture, Eucalyptus Online Book & Newsletter, 2007.

JUSTE, V. Aperfeiçoamento de processos de produção de polpas para dissolução e para papel tissue a partir do eucalipto. 2011. MS thesis Universidade Federal de Viçosa.

LIITIÄ, T.; HORTLING, B.; HONKONEN, P.; SNECK, et al. Fiber morphology responsible for restricted solubility of softwood kraft pulp in LiCl/DMAc, In: International Symposium on wood, fiber and pulping chemistry, 3, p. 371-375, 2005.

MUGUET, M. C. S.; COLODETTE, J. L.; PEDRAZZI, C. Xylans deposition onto eucalyptus pulp fibers during oxygen delignification. Part 1: the influence of NaOH charge, reaction time and temperature, CIADICYP, Lisbon, 2010.

ÖSTERBERG, M.; LAINE, J.; STENIUS, P. et al. Forces between xylan-coated surfaces: effect of polymer charge density and background electrolyte, Journal of Colloid and Interface Science, 242, p. 59-66, 2001.

PINTO, P. C.; EVTUGUIN, C.; PASCOAL NETO, C. Structure of HWD glucuronoxylans: modific. and impact on pulp retention during wood kraft pulping. Carbohydrate polymers, 60, p. 489-497, 2005.

REINER, F. J. M. Mecanismo de ligação entre fibras e a importância do refino**.** O Papel, n. 1, p. 29-32,1994.

SCHONBERG, C.; OKSANEN, T.; SUURNAKKI, et al.The Importance of Xylan for the Strength Properties of Spruce Kraft Pulp Fibres, Holzforschung, *6*, p. 639, 2001.

Tappi Standard Methods, TAPPI - Techinical association of pulp and paper industry. atlanta: Tappi, 2001.

TELEMAN, A.; HARJUNPÄÄ, V.; TENKANEN, M.; BUCHERT, J. et al. Characterization of 4-deoxy-b-L-enopyranosyluronic acid attached to xylan in pine Kraft pulp and pulping liquor by ^{1}H and ^{13}C NMR spectroscopy. Carbohydrate research, 272, p. 55-71, 1995.

VUORINEN, T.; BUCHERT, J.; TELEMAN, A.; TENKANEN, M.; FAGERSTRÖM, P. Selective hydrolysis of hexenuronic acid groups and its application in ECF and TCF bleaching of kraft pulps, In: International Pulp Bleaching Conference, 43-51 (1996).

WALLIS, A.F.A.; WEARNE, R.H.; WRIGHT, P.J. Chemical analysis of polysaccharides in plantation eucalypt woods and pulps. Appita Journal, 49, p. 258-26, 1996.

CHAPTER 2

CORN FIBERS XYLANS ADDITION ON EUCALYPTUS AND PINUS PULP AND ITS EFFECT ON THE PULP PHYSICAL PROPERTIES

ABSTRACT

Corn fibers is a product found in significant amounts in the residues of agriculture and has fuelled interest in a more rational use of its components, particularly the hemicelluloses. The impact of hemicelluloses redeposition on pulp properties paper and writing (P&W) paper grades, are discussed in this paper. Xylans extracted from corn fibers (16.9% xylans) by cold caustic extraction (CCE) were added to a commercial brown pulp (Eucalyptus and Pinus) in the oxygen delignification (O-stage) and further bleached. Hemicelluloses deposition occurred at variable degree (up to 7% on pulp weight). Pulp bleachability was not impaired by xylan deposition for eucalyptus and pinus. Hemicelluloses deposition onto fibers was more efficient in eucalyptus pulp than pinus. Pulp beatability and physical and mechanical properties were improved by xylan deposition. Xylans extraction from corn fibers by CCE with subsequent deposition onto pulp in the O-stage increase pulp beatability and quality for P&W paper grades.

Keywords: hemicellulose; corn residues; properties of papers; bleaching.

1. INTRODUCTION

Hemicellulose is polysaccharide widely abundant in nature, representing about 20–35% of lignocellulosic biomass. The polysaccharide that differ from cellulose for containing several types of sugar units in their composition (D-xylose, D-mannose, D-glucose, L-arabinose, etc). They are branched polymers (amorphous) with shorter chains (degree of polymerization of up to 200 sugar units) compared with cellulose (FENGEL and WENEGER, 1989). The monosaccharides that form the structures of hemicelluloses are composed of hexose sugars (glucose, mannose and galactose) and pentose (arabinose and xylose), and can provide varying amounts of uronic acids and deoxy-hexose in some types of biomass.

Corn fibers contain a considerable reservoir of xylan-type hemicelluloses which long ago were recognised as a good source of xylose (KÁLMÁN *et al*., 2006). In previous papers, the xylan isolated from corn fibers has been shown to be applicable as an additive in papermaking (SILVA *et al*., 2015), textile printing (BARTOŠ *et al*., 1990) and the pharmaceutical industry (LICHNEROVÁ *et al*., 1991). In the specific case of corn fibers, the xylans usually present a chemical structure formed by 4-O-methyl-D-glucuronic acid, L-arabinose and D-xylose in the ratio 2:7:19 (SILVA *et al*., 1998).

In papermaking, some studies also reveal that the xylans retake can also improve paper properties such as tensile and other bonding strength of paper (SIHTOLA and BLOMBERG 1975, SJÖBERG 2002). Fibers rich in hemicelluloses tend to produce high density / low bulk paper sheets, which are not so interesting for tissue products. On the other hand, printing and writing (P&W) paper grades needs tensile strength and can benefit from high hemicelluloses contents in the fiber (SCHÖNBERG et al., 2001).

Commercial Kraft pulps from eucalyptus grown in Brazil usually contain 14-16% (w/w) xylans while pinus contains 5-10% (w/w), regardless of pulping technology utilized. Many attempts have been made to increase pulp xylan content for production the P&W paper grades, through optimization of pulping technology (SHIN and STROMBERG, 2007). However the degree of success in such approaches has been limited.

This study aimed at determination of proper conditions for xylan extracted from corn fibers by cold caustic extraction (CCE), added to a brown pulp (eucalyptus and pinus) in the oxygen delignification (O-stage) and its effect on pulp quality.

2. MATERIALS AND METHODS

2.1. Material

Pulps xylans redeposition during the O-stage was carried out using an industrial hybrid of *Eucalyptus urophylla* x *Eucalyptus grandis* unbleached kraft pulp (17.1 kappa number, 1020 dm^3 kg^{-1} viscosity, 15.5% (w/w) pentosan) and brown pulp of *Pinus* sp. (25.6 kappa number, 990 dm^3 kg^{-1} viscosity, 9.0% (w/w) pentosan). The corn fiber was obtained from an industrial processing. The materials were evaluated for their moisture content according to TAPPI T264 cm-97 standard procedure.

2.2. Xylans extracted from corn fibers and redeposition onto kraft pulp

Xylans were extracted from corn fibers following the methodology described by Barbosa, et al. (2016). Hemicellulose removal was achieved by CCE (30 min, 30 ^oC, 10% consistency) using alkali charge of 70 g L^{-1} NaOH and their contents were measured by high performance anion exchange chromatography with pulse amperometric detection (HPAEC-PAD) after acid hydrolysis, following the procedure described by Wallis et al. (1996). The solid content at the liquor was determined by means ABCP NF 10/75. The liquor rich in xylans were deposited onto pulp (eucalyptus and pinus) during the O-stage up to 7% (w/w) on pulp, according to Muguet et al. (2010) and was realized a reference treatment, for eucalyptus and pinus, without deposition of xylans. Pulp analyses followed Tappi standard procedures.

2.3. Elemental Chlorine Free (ECF) Bleaching

The pulps were fully bleached by the O/O-D*-(EP)-D_1 sequence for eucalyptus and O/O-D*-(EPO)-D_1-P for pinus. Table 1 describes the conditions used in each bleaching stage. The second chlorine dioxide stages (D) were carried out at 10% consistency, end pH value 5.5, 80 °C, 90 min, with variable amounts of chlorine dioxide to achieve the ISO brightness target of 90 ± 0.2% (LOMBARDI *et al.*, 2014). For eucalyptus with this sequence without the last P-stage, additional charges of chlorine dioxide were added to the D_1 stage. After each bleaching stage, the residual liquor was extracted for pertinent analysis and the pulp samples were washed with an equivalent of 9 m^3 of distilled warm water per ton of dry pulp. All experiments were run in duplicate.

Table 1. Conditions in each bleaching stage of eucalyptus and pinus pulps, for reference and pulps with deposition of xylans.

Parameters	**Eucalyptus**				**Pinus**				
	O/O	D*	(EP)	D_1	O/O	D*	(EPO)	D_1	P
Consistency (%)	11.5	11.0	11.0	11.0	11.5	11.0	11.0	11.0	11.0
Temperature (°C)	100	90	85	80	100	90	85	80	80
Time (min)	60	120	75	90	75	30	75	90	90
Pressure (kPa)	750	-	-	-	700	-	200	-	-
O_2 (kg odt^{-1})	15.0	-	-	-	22.2	-	4.0	-	-
ClO_2 (kg odt^{-1})	-	8.0	-		-	13.3	-		-
H_2O_2 (kg odt^{-1})	-	-	4.4	-	-	-	4.4	-	
NaOH (kg odt^{-1})	22.0	-	8.0		25.0	-	12.0		
H_2SO_4 (kg odt^{-1})	-	8.0	-		-	2.0	-	-	-
$MgSO_4$ (kg odt^{-1})	-	-	-	-	2.2	-	-	-	-

Where: O/O = double stage oxygen delignification; D* = hot chlorine dioxide stage; (EP) = alkaline extraction with hydrogen peroxide (EPO) = pressurized alkaline extraction with hydrogen peroxide; D_1 = chlorine dioxide bleaching stage, P = hydrogen peroxide stage. Odt = over dry ton.

2.4. Physical and mechanical tests

Pulps were beaten in a PFI mill at different energy inputs, made into hand sheets and tested for physical-mechanical properties according to TAPPI standards (Table 2), except for capillarity Klemm and water absorption capacity (Wa), which were carried out according to ISO 8787:86 and NBR 15004 standards, respectively.

Table 2. Analytical Procedures for analysis of pulps

Parameters	Methodologies
Tear Index	TAPPI T414 om-04
Tensile Index	TAPPI T494 om-06
PFI Beating	TAPPI T248 sp-08
Forming Handsheets for physical tests	TAPPI T205 sp-95
Drainage resistance - Schopper Riegler	TAPPI T423 cm-07

3. RESULTS AND DISCUSSION

3.1. Xylans extraction and characterization of liquor

The CCE treatment was effective in removing xylans from the corn fibers (56.3% w/w). Table 3 is showing the carbohydrates the corn fibers and at the liquor extracted. This result is consistent with the higher xylose and arabinose concentration in the liquor extracted from the corn fibers with 6% the solid content. This is likely explained through the chemical structure formed by 4-O-methyl-D-glucuronic acid, L-arabinose and D-xylose in the ratio 2:7:19 in corn fibers (SILVA *et al*., 1998).

Table 3. Carbohydrates analysis of corn fibers and liquor extracted.

	Glucose	Xylose	Arabinose	Galactose	Mannose
Corn fibers	32.9	16.9	11.3	3.1	0.7
Liquor extracted	2.8	28.8	16.4	4.7	nd

3.2. Xylans deposition during oxygen delignification and bleaching

Xylans deposition occurred in all cases, different patterns occurred for eucalyptus and the pinus. The O-stage yield of the reference eucalyptus pulp was 97.5%, while the pulp with xylan deposition showed a yield of 102.2% (w/w), that is, a yield gain of 4.7% (w/w). For pinus, this gain was less significant, from 96.9% in the reference pulp, to 99.4% (w/w), a gain of 2.5% (w/w) in yield. The pentosan content in eucalyptus pulp increased 1% (w/w) in relation reference, while in pinus pulp they were similar (Table 4).

Hemicelluloses deposition onto fibers is more efficient in eucalyptus pulp, because besides having chemical characteristics more favorable than the pinus. The reason might be the different dissolving mechanism of glucuronoxylan in hardwood from that of galactoglucomannan in softwood. During the O-stage, glucuronoxylan was dissolved mainly in polysaccharide form, while galactoglucomannan underwent degradation before being dissolved, which resulted in smaller molecules and lower polymerization in the galactoglucomannan, compared to the glucuronoxylan ones (WEIPING BAN *et al*., 2011). At polysaccharide form the adsorption is favored if the chemical affinity of the polymer to the surface is high and the shorter molecule chain usually shows poor adsorption ability (ÖSTERBERG *et al*., 2001).

The xylan deposition in both eucalyptus and pinus resulted in decreased pulp viscosity due to the low Mw of these hemicelluloses in relation to cellulose and the increased pulp kappa number. The pulps of eucalyptus and pinus reference and with deposition of xylan were bleached to a final brightness of 90 ± 0.2% ISO (Table 4).

Table 4. Effect of pulp xylan content on bleaching performance.

Results	**Pulps**			
	Euca Ref	Euca Xyl	Pinus Ref	Pinus Xyl
Kappa Number after O-stage	10.4	10.5	10.9	15.3
Viscosity after O-stage (dm^3kg^{-1})	839	703	765	645
ClO_2 (%)	1.1	1.3	0.9	1.3
Pentosan, %	13.1	14.4	8.4	8.5
Final Brightness (% ISO)	90.0	89.7	89.9	89.8
Brightness Reversion (% ISO)	2.9	3.7	3.5	3.5
Final Viscosity (dm^3 kg^{-1})	703	466	634	539

Where: Euca Ref: eucalyptus reference, Euca xyl: eucalyptus with deposition of xylan; Pinus Ref: pinus reference, Pinus xyl: pinus with deposition of xylan.

The amount of reagents needed to bleach the pulp reference and with deposition of xylan in pulp were similar but the pulp with deposition of xylan consumed larger amounts of ClO_2 to reach the brightness. This result was anticipated since the liquor extracted contained sizeable amounts of lignin, which contaminated the pulp during the O-stage to a point that the post-oxygen kappa number was one unit higher for this sample than for reference.

3.3. Physical, mechanical and hygroscopic properties of the pulps and papers

The pulp with xylan increase decreased the energy consumption to achieve a given °SR (Figure 1A) for the eucalyptus and pinus, an effect likely caused by improved fiber hydration and flexibility. Since °SR measures pulp resistance to drainage, the higher the value the higher is resistance to drainage. Thus, xylans impair pulp drainability significantly (Figure 1A), a result attributable to xylans high water retention capacity.

Pulp water retention value (WRV) increased and pulp water retention capacity (Wa) decreased with the deposition of xylan (Table 5) in agreement with the decreased pulp drainability. The pulp water retention capacity (Wa) increased with decreasing xylan content due to increased water penetration by capillarity (Table 5). When refining is increased the pulp water absorption capacity decreases significantly (SANG and ZHAO, 2014; REINER, 1994), and the effect of xylan content becomes less significant.

Table 5. Effect of pulp xylan content on WRV and Wa (unbeaten pulps)

Pulps Xylan Content, %	**Euca Ref**	**Euca Xyl**	**Pinus Ref**	**Pinus Xyl**
WRV, %	144	150	146	148
Water retention Capacity (g H_2O/g pulp)	4.7	3.9	3.0	2.6

Where: Euca Ref: eucalyptus reference, Euca xyl: eucalyptus with deposition of xylan; Pinus Ref: pinus reference, Pinus xyl: pinus with deposition of xylan.

Capillarity Klemm (CK) was significantly decreased with deposition of xylan in pulp (Figure 1B). Xylans are amorphous by nature with greater affinity to water than the crystalline cellulose microfibrils; thus, they decrease the velocity of the water flow by capillarity within the paper matrix. High values of CK are desirable for tissue grade papers that need to absorb water fast.

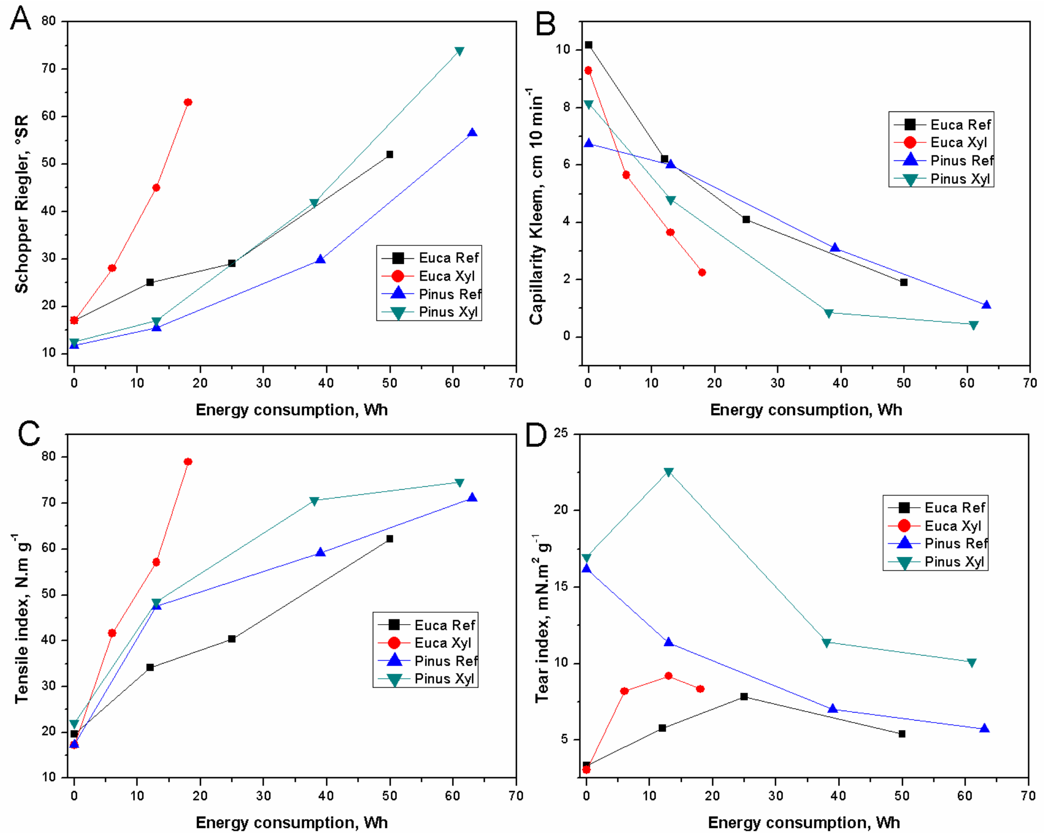

Figure 1. Effect of pulp xylan content on (A) drainage resistance (°SR), (B) capillarity Klemm, (C) tensile index, (D) tear index.

High quality printing and writing paper grades require pulps of high tensile strength to withstand the forces the paper undergoes during manufacturing and use in high speed machines (BHADURI *et al.*, 1995). The pulps containing higher xylan concentration required much less energy to reach the 60 N.m g^{-1} tensile index (Figure 1C). This leads to significant economical savings, taking into account that pulp beating is one of the most costly operations of the paper manufacturing process. Besides improving beatability, xylans redeposition onto fibers led to improved tear and tensile strengths at low beating energy levels (Figure 1C and 1D). The corn fibers xylans seems to attach better to fibers the eucalyptus, thus resisting more to bleaching and to the mechanical forces during beating than the pinus.

4. CONCLUSIONS

Corn fibers are good sources of hemicelluloses, which is an alternative for the use of these carbohydrate residues as an additive in papermaking. Hemicelluloses deposition onto fibers was more efficient in eucalyptus pulp than pinus, because the chemical characteristics more favorable in eucalyptus pulp. At low energy consumption, the pulps with deposition of xylan form paper with higher resistance to drainage and greater tensile and tear strengths. Pulp beatability was improved by xylan deposition. Xylans extraction by CCE with subsequent deposition onto pulp in the O-stage proved attractive for manufacturing high xylan P&W paper grades.

REFERENCES

ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS ABNT/ NBR 10664/Abr1989.

BARTOS', L.; PRCHAL, V.; RAJCOVA´, A.; EBRINGEROVA´, A.; GREGOROVA´, A. Rheological properties of hemicelluloses (in Slovak). Text. Chem. 20, 37–48, 1990.

BARBOSA, B. M.; COLODETTE, J. L.; MUGUET, M. C. S.; GOMES, V. J.; Oliveira, R. C. Effects of xylan in eucalyptus pulp production. Cerne, v. 22 n. 2 ,p. 207-214, 2016.

BHADURI, S. K.; GHOSH, I. N.; DEB SARKAR, N. L. Ramie hemicelluloses as beater additive in paper making from jute-stick kraft pulp. Ind Crops Prod., v. 4, p. 79-84, 1995.

FENGEL, D.; WENEGER, G., 1989. Wood chemistry, ultrastructure, reactions. Berlin: Walter de Gruyter.

DANIELSSON, S.; LINDSTRÖM, M. E., Influence of birch xylan adsorption during kraft cooking on softwood pulp strength, Nord. Pulp Pap. Res. J., 20, 436-441, 2005.

KÁLMÁN, G.; RECSEG, K.; GASPAR, M.; RÉCZEY, K. Novel approach of corn fiber utilization. In Twenty-Seventh Symposium on Biotechnology for Fuels and Chemicals. p. 738-750. Humana Press, 2006.

LICHNEROVA´, I.; EBRINGEROVA´, A.; HEINRICH, J. Xylans; perspective pharmaceutical auxiliary materials. Acta Fac. Pharm. (Bratislava) 45, 5–141, 1991.

LOMBARDI, L. R.; CARVALHO, A. M. M. L.; COLODETTE, J. L.; CARNEIRO, A. de C. O. Branqueamento ECF da polpa de *Acacia mangium* oriunda de plantio misto com eucalipto. O PAPEL, v. 75, n. 1, 2014.

MUGUET, M. C. S.; COLODETTE, J. L.; PEDRAZZI, C. Xylans deposition onto eucalyptus pulp fibers during oxygen delignification: part 1, the influence of NaOH charge, reaction time and temperature. Lisbon: CIADICYP, 2010.

ÖSTERBERG, M., LAINE, J., STENIUS, P. et al., Forces between xylan-coated surfaces: effect of polymer charge density and background electrolyte, J. Colloid. Interf. Sci., 242, 59-66, 2001.

REINER, F. J. M. Mecanismo de ligação entre fibras e a importância do refino. O Papel, n. 1, p. 29-32, 1994.

SANG, Y.; ZHAO, J. R. Reduction of water absorption capacity of cellulose fibres for its application in cementitious materials. J. Compos. Mater., v. 2, p. 2757-2763, Oct. 2014.

SCHÖNBERG, C.;OKSANEN, T.; SUURNÄKKI, A.; KETTUNEN, H.;BUCHERT, J. The Importance of Xylan for the strength properties of spruce kraft pulp fibres. Holzforschung, v. 6, p. 639-644, 2001.

SILVA, J. C.; OLIVEIRA R. C.; NETO, A. S.; PIMENTEL, V. C.; SANTOS, A. A. Extraction, Addition and Characterization of Hemicelluloses from Corn Cobs to Development of Paper Properties. Procedia Materials Science. 8: 793-801, 2015.

SILVA, S. S.; CARVALHO, R. R.; FONSECA J. L.; GARCIA, R. B., 1998. Extração e Caracterização de Xilanas de Sabugos de Milho. Polímeros: Ciência e Tecnologia. Abril/Junho.

SIHTOLA, H.; BLOMBERG, L. Hemicelluloses precipitated from steeping liqour in the viscose process as additives in papermaking. Cellul. Chem. and Technol.,v.9, n.5, p. 555-560, 1975.

SHIN, N. H.; STROMBERG, B. Xylan´s impact on eucalyptus pulp yield and strength – Myth or reality?. Proceedings of the 3rd International Colloquium on Eucalyptus Pulp. Belo Horizonte. Brazil, 2007.

SJÖBERG, J.; KLEEN, M.; DAHLMAN, O.; AGNEMO, R.; SUNDVALL, H. Analysis of carbohydrate and lignin in the surface and inner layers of softwood pulp fibers obtained employing various alkaline cooking process. Nord pulp pap res J., v. 17, p. 295-301, 2002.

TAPPI Standard Procedures. 2001. TAPPI Press, Atlanta, USA.

WALLIS, A.; WEARNE, R.; WRIGHT, P. Chemical Analysis of Polysaccharides in Plantation Eucalyptus wood and Pulps. Appita J., 49:258-262, 1996.

WEIPING BAN, XIAOWEN CHEN, GRASCON ANDREWS, ADRIAAN, V. H. Influence of hemicelluloses pre-extraction and re-adsorption on pulp physical strength II. Beatability and strength study. Cellul. Chem. and Technol., 45 (9-10), 633-641, 2011.

CHAPTER 3

CHEMICAL CHARACTERIZATION OF CORN FIBERS, HEMICELLULOSES ISOLATION AND LIGNINS STRUCTURAL INVESTIGATION FORMED BY THE KLASON METHOD USING PY-GC-MS

ABSTRACT

Currently, there has been increasing research interest in the lignocellulosic materials recovered from residual agricultural and agro-industrial activities such as corn fibers (CF). Therefore, studies for obtaining more information on the chemical structural composition are desirable. In this way, this study aimed to chemical characterization of corn fibers, isolation of hemicellulose using NMR and FTIR-ATR and structural investigation of the lignins, acid soluble (ASL) and acid insoluble lignin (AIL), formed by the Klason method using pyrolysis-gas chromatography/mass spectrometry (Py-GC-MS). The hemicelluloses were obtained, after neutralization and precipitation of the alkaline solution; the second, after the addition of ethanol in the supernatant of the same solution. Hemicellulose isolation was considered efficient and more 45 primary pyrolysis products for ASL and 39 for AIL from corn fibers. Analytical pyrolysis of ASL from corn fibers showed prevalence of peaks related to products derived from carbohydrates. Also, the Py-GC-MS technique allowed identifying the presence of derivatives lignin in ASL and AIL.

Keywords: lignocellulosic, wood chemistry, biorefineries, lignin derivatives and arabinoxylan.

1. INTRODUCTION

Corn is an important food for many people in Africa, Asia and Latin America and is used in animal feeding in North America and some parts of the world. Cobs, leaves, hull and stalks are important residues of corn processing and consumption. The corn fibers is biomass residues generated available from agricultural and forest processing constitute a potential because are mainly constituted by three structural components (lignin, cellulose and hemicellulose) and each compound has specific properties destined for different uses for chemical production.

Lignocellulosic residue can be reused as raw material in a different process from the original process, for instance, it can be used energetically for generation of heat or electricity in generator groups or thermoelectric plants (ZHANG *et al*., 2012). In this context, corn fibers is example of alternative source and contain a considerable reservoir of xylan-type hemicelluloses which long ago were recognized as a good source of xylose. In the specific case of corn fibers, the xylans usually present a chemical structure formed by 4-O-methyl-D-glucuronic acid, L-arabinose and D-xylose in the ratio 2:7:19 (SILVA *et al*., 1998). In previous papers, the xylan isolated from corn fibers has been shown to be applicable as an additive in papermaking (BARBOSA *et* *al*., 2016), textile printing (BARTOS *et al*., 1990) and the pharmaceutical industry (LICHNEROVÁ *et al*., 1991).

Lignins are complex aromatic heteropolymers produced by the oxidative combinatorial coupling of mainly three *p*-hydroxycinnamyl alcohol monomers differing in their degree of methoxylation, the *p*-coumaryl, coniferyl, and sinapyl alcohols and the method used to determine the total lignin is the method Klason (BOERJAN *et al*., 2003).

The Klason method is the most typical lignin determination procedure. The procedure separates lignin as an insoluble material by depolymerization of cellulose and hemicellulose in 72% (w/v) sulfuric acid (SA) followed by hydrolysis of the dissolved polysaccharides in boiling 3% (w/v) SA. However, part of the lignin is dissolved in the filtrate as so-called acid-soluble lignin (ASL) and the part acid insoluble lignin (AIL). For quantification of ASL is necessary to use UV technique (GOLDSCHMID, 1971). So, for quantitative determination of lignin content the Klason method is considered good, but it does not apply for the study of structural composition of lignin (BERAMENDI-OROSCO *et al*., 2004).

An alternative and valuable analysis used for the structural characterization of lignin is pyrolysis coupled with gas chromatography/mass spectrometry (Py-GC-MS) (SILVÉRIO *et al*., 2008). This analysis requires very small samples, without any preparation, over short periods of time and based on thermal degradation of lignin, producing components that can be analyzed by gas chromatography/mass spectrometry.

Nevertheless, a significant portion of the produced corn residues is underexplored in terms of alternative application. Due to the amount of this biomass as an industrial waste, there is great interest in developing methods for the production chemicals from this important raw material in a sustainable way. Therefore, the aim of this study was the chemical characterization of corn fibers, the isolation of hemicelluloses by NMR and FTIR-ATR and the characterization lignin structures formed for the Klason method (ASL and AIL) by Py-GC-MS.

2. MATERIALS AND METHODS

2.1. Raw material

Corn fibers (CF) were obtained from an industrial plantation. The raw material was dried at room temperature and grinded in a laboratory mill, then sieved and classified according to TAPPI T257 cm-12 standard procedure (TAPPI, 2000) .All samples were extracted with acetone and subjected to moisture determination in accordance with TAPPI T204 cm-07 standard procedure (TAPPI, 2000).

2.2. Quantitative chemical characterization

The carbohydrate composition of CF was evaluated by high performance anion exchange chromatography with pulse amperometric detection (HPAEC-PAD). It was performed after pre-treatment (30 °C, 1 h) with aqueous 72% (w/v) H_2SO_4 followed by hydrolysis with 3% (w/v) H_2SO_4 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 4 mm) analytical column. The monosaccharides were separated isocratically with 0.001 mol L^{-1} NaOH (45 min, flowrate 1 mL min^{-1}) (WALLIS *et al.*, 1998).

The solid residue after hydrolysis was considered as AIL, according to T222 cm-11 standard procedure (TAPPI, 2000). Acid soluble lignin (ASL) was determined by measuring the UV-absorbance of the filtrate and analyzed by UV technique and was determined according to equation 1, where 215 nm is the absorbance values of the lignin filtrate and the 280 nm is used for as correction for the potential interference from furfural and hydroxymethylfurfural formation from carbohydrates during the acid hydrolysis (GOLDSCHMID, 1971).

$$\text{ASL\%} = \frac{4.53(A215-A280)}{300}\ x\ 100 \qquad (1)$$

The structural composition of lignin, particularly syringyl/guaiacyl (S/G ratio) was obtained by nitrobenzene oxidation were analyzed according to Lin and Dence (1992). Ashes were determined by calcination according to TAPPI standard T211 om-12 (TAPPI, 2000). Extractives in acetone were analyzed according to TAPPI T204 cm-07 standard procedure. Total uronic acids in raw material hydrolysates were measured by the colorimetric method, involving 3,5-dimethylphenol (SCOTT, 1979). The content of acetyl groups was also determined by SOLÁR *et al.* (1987). The protein content was determined by Kjeldahl method (IDF, 1993). All results were calculated from two replicate determinations.

2.3. Hemicelluloses isolation and characterization

Hemicelluloses were obtained following the methodology described in (SILVA *et al.*, 1998), with adaptations. The CF sawdust was subjected to aqueous extraction at a ratio of 30 g of CF to 1,000 mL of distilled water with constant stirring for 12 hours. The mixture was centrifuged and the solid phase was dried in climatic room at 23 °C and 50% humidity for 24 hours. After drying, the material obtained was subjected to the delignification process at 1:10 ratio (w/v) using hydrogen peroxide 2% (w/v) at pH value of 11 and 70 °C for 2 h. The delignified raw material was washed with distilled water with three times the volume of suspention.

Solubilization of hemicelluloses was performed by alkaline treatment, when the material was then subjected to 10% NaOH (w/w) at 25 °C for 24 h, in low agitation, with a ratio of 1:10 (w/v). Then, the solution was neutralized by adding glacial acetic acid (pH value of 7.0). The hemicelluloses were precipitated by the addition of ethanol in the proportion of three volumes of ethanol to 1 volume of the solution. The obtained product was centrifuged for 10 minutes, at 4000 rpm, resulting in a consistency of 20%.

Acetylation process was used to increase the hydrofilicity and characterization by NMR analysis. The esterification of arabinoxylan was carried out using experimental conditions, as described by Stepan et al. (2011).

2.3.1. Nuclear magnetic resonance analysis

Nuclear magnetic resonance analysis (NMR) measurements were carried out on the isolated hemicelluloses. The acetylated hemicelluloses (~10 mg) were dissolved in 0.4 mL $CDCl_3$. One dimensional ^1H NMR spectra was acquired with an MERCURY-300/Varian spectrometer at 300.069 MHz (32 k data points, 30 excitation pulse duration of 2.2 ls, spectral width of 6 kHz, acquisition time of 3.3 s and relaxation delay of 10 ms) in 5 mm probes with direct detection, using TMS as internal standard ($\delta = 0.00$).

2.3.2. Fourier transform infrared spectroscopy - attenuated total reflectance (FTIR-ATR)

A Varian 660-IR spectrometer equipped with a liquid nitrogen-cooled mercury cadmium telluride detector and an attenuated total reflectance (ATR) probe was used in this work. The sample was put on the ATR probe to collect FTIR spectrum. During the experiment, 60 scans were coadded to achieve an acceptable signal-to-noise ratio, with wave number ranging from 4000 cm^{-1} to 500 cm^{-1}. All the spectra were recorded at a resolution of 4 cm^{-1}.

2.4. Lignins structural investigation (Klason method) by PY-GC-MS

For the investigation of structural lignin formed by Klason method, it was performed the pre-treatment of CF (30 °C, 1 h) with aqueous 72% (w/v) H_2SO_4 followed by hydrolysis with 3% (w/v) H_2SO_4 in an autoclave (100 °C, 3 h). The AIL lignin and ASL were prepared, as shown in Figure 1 for further analysis of pyrolysis.

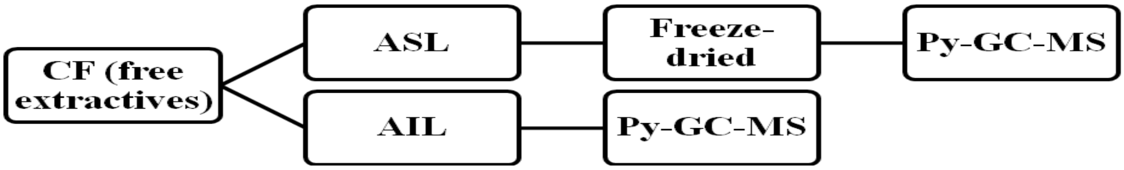

Figure 1. The lignin preparation scheme for pyrolysis

2.4.1. Pyrolysis-gas chromatography/mass spectrometry (PY- GC-MS)

The pyrolysis of the samples was performed in duplicate with a micro furnace pyrolyser Pyr A-4 model (Shimadzu) coupled to a GC–MS apparatus (Shimadzu, model PQ5050A), using a fused silica capillary column (DB-5, 30 m x 0.25 mm ID, 0.25 μm film thickness). A finely divided sawdust sample (100 μg) was deposited in a small platinum cup that was then inserted into a quartz tube (2 x 40 mm) placed in the pyrolysis chamber. The pyrolysis was carried out at 550 °C for 10s, as previously described (DEL RÍO *et al.*, 2005; BARBOSA *et al.*, 2008). The pyrolysis chamber was kept at 250 °C and purged with helium to transfer the pyrolysis products as quickly as possible to the GC column. The chromatograph oven was ramped from 40 °C (4 min) to 300 °C at a rate of 4 °C min^{-1}. The final temperature was held for 40 min. The injector and GC–MS interface were kept at 200 °C. Mass spectrometer was operated by the electron impact ionization mode at 70 eV and mass scan range was 40–600 Da. The temperatures of the detector and the GC–MS interface were 250 and 290 °C, respectively. Compounds were identified by comparing their mass spectra with the GC–MS spectral library (Willey 333,000), with data from the literature and when necessary by mass fragmentography (RALPH and HATFIELD, 1991; DEL RÍO *et al.*, 2005; BARBOSA *et al.*, 2008; OUDIA *et al.*, 2007).

3. RESULTS AND DISCUSSION

3.1. Chemical characterization of CF

The chemical compositions of CF (percentage on oven-dry weight basis) are shown in Table 1, as well as the data based on two replicate determinations. The raw material are defined by their content of sugar composition (glucose, xylose, arabinose, galactose, mannose, acetyl groups, uronic acids), lignin (ASL, AIL, S/G ratio and total lignin), extractives, ash, and protein.

Table 1. Chemical composition of CF.

Sugar composition, % (w/w)							**Lignin, %(w/w)**		**Extractives, % (w/w)**	**Ash, %(w/w)**	**Proteins, %(w/w)**
Gluc	Xyl	Ara	Gal	Man	AG	Ur	ASL	AIL	14.0	0.9	11.5
32.9	16.9	11.3	3.1	0.7	1.9	1.0	8.0	4.0			
^{a}Abbreviations. Ara: arabinose; Xyl: xylose; Man: mannose; Gal: galactose; glc: glucose; AG: acetyl groups; UR: uronic acids							**Total lignin**: 12.0 % S/G: 0.09				

The chemical composition of CF showed that total lignin was 14.0%, while the uronic acids and ash contents were 1.0% and 0.9%, respectively. In relation to glucose content (32.9%), the experimental result was similar reported by other authors (KÁLMÁN *et al*, 2006; VAN DONGEN *et al*, 2011; LILI *et al.*, 2011). Values of xylose (16.9%), arabinose (11.3%), mannose (0.7%), and acetyl groups (1.9%) for samples determined in this study are closely comparable to those reported by them (VAN DONGEN *et al*, 2011; BARBOSA *et al.*, 2014) for similar samples of corn fibers.

The lignin content for ASL and AIL were 8.0 and 4.0%, respectively. These values are acceptable for chemical production. However, its low S/G ratio that is, low number of syringyl units, will condense more during the acid hydrolysis procedure and produce low ASL in the filtrate (GOMES *et al*, 2015). The S/G ratio of CF reflects in the content of lignin ASL and AIL.

Because of the current importance of corn fibers for the production of bioproducts and biofuels, were analyzed lignins structural investigation of AIL and ASL. The chemical composition is important factor in developing methods for the production chemicals from this raw material in a sustainable way (BURUNOV and MAZZA, 2008).

3.2. Hemicelluloses isolation and characterization

The hemicelluloses were evaluated through FTIR-ATR and NMR. An FTIR-ATR spectrum from isolation hemicellulose was shown in Figure 2. The bands found at 3340 and 2979–2899 cm^{-1} indicates the OH stretching and CH bond deformation of CH_2 and CH_3 groups, respectively (EGÜÉS *et al.*, 2014). The prominent band around 3340 cm^{-1} represents the hydroxyl stretching vibrations of the hemicelluloses and water involved in hydrogen bonding (SUN *et al.*, 2004).

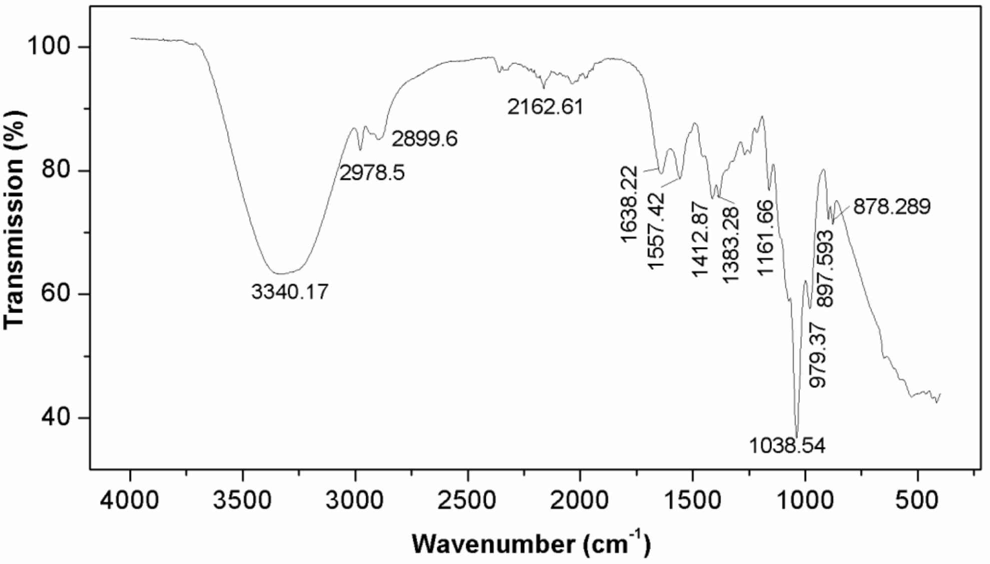

Figure 2. FT-IR spectra unmodified hemicelluloses.

The typical signal pattern for hemicellulosic moiety, had a specific band maximum in the 1200–1000 cm^{-1} region (SUN *et al.*, 2004). At 1038 cm^{-1}, was possible to see stretching and bending vibrations of C–O, C–C, C–OH, and C–O–C (Figure 2). According to Sun et al. (2004), bands between 1175 and 1000 cm^{-1} are typical of xylans. It was possible to see two low-intensity shoulders at 1038 cm^{-1} peak (at 1162 and 979 cm^{-1}), which have been reported to be attached only at positions of the xylopyranosyl constituents (SUN and TOMKINSON, 2002). The intensity changes of these two bands indicate the contribution of arabinosyl substituent. Therefore, it was used for the identification of arabinoxylan structures.

The efficiency of acetylation reaction was also verified by ^1H NMR, as shown in the Figure 3. Important peaks appeared in the spectrum at 1.9-2.0, 4.5 and 5.0 ppm, indicating methyl protons of ester chains, anomeric proton of xylan and anomeric proton of *D*-arabinofuranosyl, respectively (EGÜÉS *et al.*, 2014; SUN *et al.*, 2004).

The degree of arabinose substitution of xylan is the key factor that positively affects the maximum degree of substitution and the ratio obtained among xylose and arabinose was to each 9 units of xylose there is 1 unit of arabinose, aproximely, as exemplify in the Figure 3. So, the maximum degree of substitution of this material is obtained through the sum of available OH groups per sugares multiplied by the sugares concentraction. Other authors found different values to DS of different raw material by NMR spectrum e.g. Ren et al. (2007) obtained degree of substitution of acetylated hemicelluloses between 0.49 and 1.53 by variation of the conditions of reaction, such as reaction temperature, reaction time, dosage of catalyst and amount of acetic anhydride.

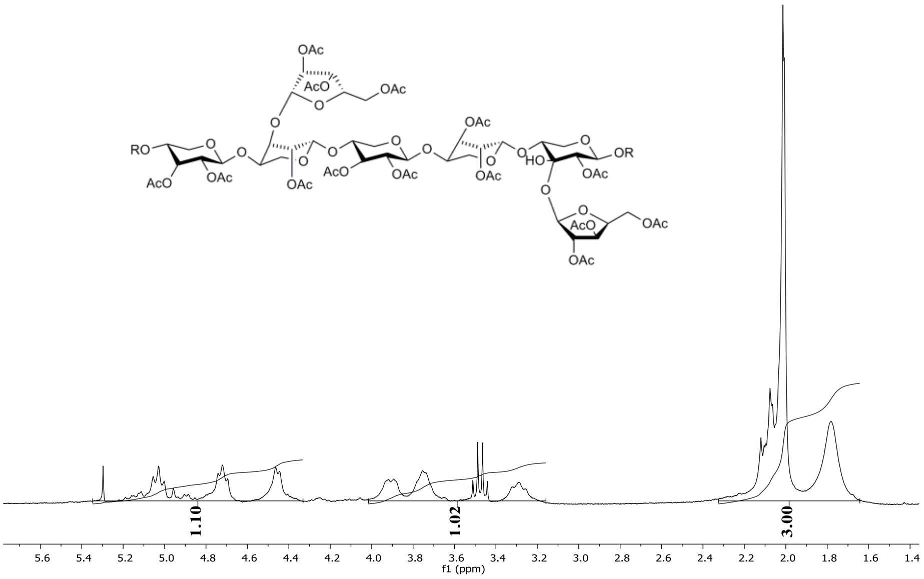

Figure 3. ^{1}H NMR spectrum acetylated hemicellulose (dissolved in $CDCl_3$) and structure of acetylated 4-O-methyl-(glucurono)arabinoxylans.

3.3. Identification of fragments of ASL pyrolysis by Py-GC-MS

The analytical pyrolysis method is based on the degradation of lignin into monomeric fragments induced by thermal energy under inert atmosphere, producing a mixture of relatively simple aromatic compounds. These compounds can be directly separated by gas chromatography and identified by mass spectrometry (RALPH and HATFIELD, 1991; ZIER *et al*., 1997; BARBOSA *et al*., 2008). So, the lignin can be characterized on the basis of the products from pyrolysis.

The samples from corn fibers were pyrolized and the pyrolysis products were separated and characterized by Py-GC-MS. A typical pyrogram of CF is shown in Figure 4. It was possible to identify a total of 47 compounds for CF (Table 2). These compounds were classified broadly as carbohydrates derivatives products, lignin derivatives and other (extractives and proteins derived).

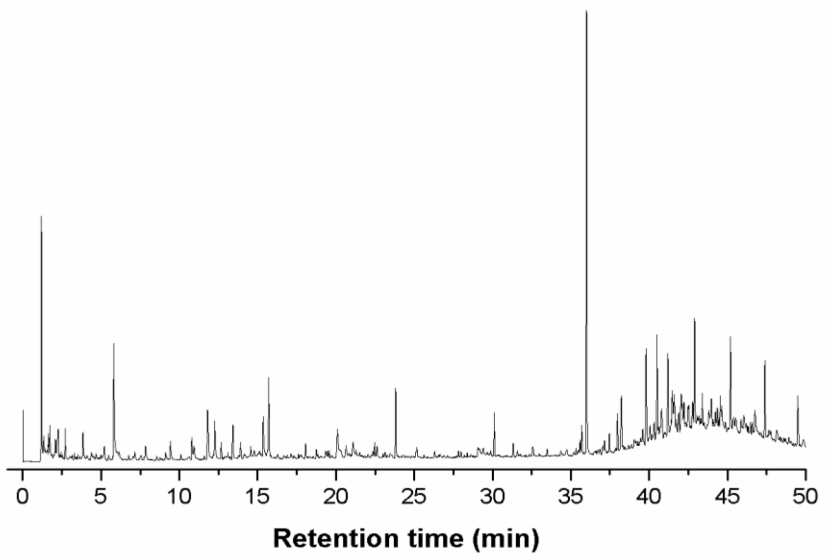

Figure 4. Pyrograms of acid-soluble lignin of corn fibers. Peak identities for compounds are shown in Table 2.

Table 2. Main compounds identified by Py-GC-MS in acid-soluble lignin of CF.

Retention	**Compound**	**% Relative area**	**Origin**
1.195	Chloroacetic acid	8.58	C,L
1.340	NI	0.56	-
1.653	Ethylene glycol	0.73	O
1.734	5-Methylfuran	0.64	C
2.257	Acetic acid	1.95	C,L
2.737	Dimethylnitrosamine	-	O
3.834	Methylbenzene	0.75	O
5.811	Furfural	4.96	C
6.740	Furfuryl alcohol	-	C
9.435	1,2-Cyclopentanedione	0.67	C
10.791	5-Methylfurfural	0.95	C
11.803	Phenol	3.65	L
12.258	NI	1.28	-
12.673	1-Chloro-2-ethylhexane	0.7	O
13.420	2,4-Dimethyl-1-decene	2.02	O
13.914	Phenylacetaldehyde	0.64	O
14.561	2-Cresol	0.38	L
15.359	4-Cresol	1.81	L
15.713	Guaiacol	3.4	L
18.067	NI	0.76	-
18.753	4-Ethylphenol	0.31	L
19.582	5-Methylguaiacol	0.25	L
20.094	Catechol	1.48	L
20.651	2,3-Dihydrobenzofuran	0.54	C
21.074	5-Hydroxymethylfurfural	0.63	C
22.472	2-tert-Butylphenol	0.61	L

22.616	4-Ethylguaiacol	0.55	L
23.137	2-Methyl-5-isopropylphenol	0.2	L
23.810	4-Vinylguaiacol	3.55	L
25.104	Syringol	0.11	L
25.165	2-Methyl-6-tert-butylphenol	0.17	L
27.822	2,6-Di-tert-butylphenol	0.28	L
27.992	Acetone anil	0.31	O
28.381	Dimethyl phthalate	0.13	O
29.076	NI	0.32	-
30.109	4-Methyl-2,6-di-tert-butylphenol	2.23	O
31.323	2-Butyl-5-isobutylthiophene	0.7	O
31.601	Lauric acid diethanolamide	0.21	O
35.700	Ethylhexyl benzoate	1.37	O
36.013	Ethylphenoxy benzene	26.34	O
37.162	3,5-di-tert-Butyl-4-hydroxybenzaldehyde	0.48	O
37.465	1,3-Diphenyl-1-butene	0.98	O
37.986	Octadecane	1.89	O
38.239	Nonadecane	4.01	O
39.806	Diisobutyl phthalate	5.72	O
40.503	Henicosane	5.34	O
41.189	Methyl palmitate	4.46	O

C: carbohydrates; L: lignin; O: other, NI: unidentified

Around 20% of total compounds identify for the CF is constituted by products derived from carbohydrate pyrolysis. Acetic acid, 5-methylfuran, furfural, furfuryl alcohol, 3-furaldehyde, cyclopentanone, 5-methylfuran, 5-hydroxymethylfurfural, 2,3-dihydrobenzofuran were some carbohydrates derivatives found.

The main products derived from lignin are phenol, 2-cresol, 4-cresol, guaiacol, 4-ethylphenol, 5-methylguaiacol, catechol, 2-tert-butylphenol, 4-ethylguaiacol, 2-methyl-5-isopropylphenol, 4-vinylguaiacol, syringol, 2-methyl-6-tert-butylphenol, 2,6-di-tert-butylphenol. These substances were identified in previous works involving lignin degradation by analytical pyrolysis (DEL RÍO *et al.*, 2007).

Other compounds also detected included dimethylnitrosamine, ethylene glycol, methylbenzene, 1-chloro-2-ethylhexane, 2,4-dimethyl-1-decene, phenylacetaldehyde, acetone anil, dimethyl phthalate, 4-methyl-2,6-di-tert-butylphenol, 2-butyl-5-isobutylthiophene, lauric acid diethanolamide, ethylhexyl benzoate, ethylphenoxy benzene, 3,5-di-tert-butyl-4-hydroxybenzaldehyde, 1,3-diphenyl-1-butene, octadecane, nonadecane, diisobutyl phthalate, henicosane, methyl palmitate. These may be generated by degradation of extractives and proteins.

It was observed that the content of other components compound CF is greater than carbohydrate and lignin. Although not commonly investigated, the amount of acid soluble lignin seems to be related to the lignin S/G ratio. Amounts of syringyl monomers will condense less during the strong acid hydrolysis treatment, since the C5 position in the aromatic ring is blocked in the syringyl units. These blocked C5 positions prevent C5 condensation. Therefore, lignin containing high S/G ratio, that is, high number of syringyl units, will condense less during the acid hydrolysis procedure and produce more soluble lignin in the filtrate (GOMES *et al*, 2015). However, when we observe the S/G ratio (0.09) in Table 1, the CF does have the low value and high ASL (8%). This demonstrates that the quantification of acid soluble lignin by UV method is not consistent (GOLDSCHMID, 1971). Despite the existing correction for compounds derived from carbohydrates by method it is evident that there are other components that affect the result of the acid soluble lignin content (GOLDSCHMID, 1971).

3.4. Identification of fragments of AIL pyrolysis

The principle of the pyrolysis technique is the fragmentation of lignin into monomeric compounds (LIMA *et al*., 2008). The pyrograms (Figure 5) for the AIL samples of CF showed the prevalence the lignin derivatives. It was identified 39 compounds for CF (Table 3).

Grass lignins are composed of monomeric phenylpropanoid units known as *p*-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) in different ratios, with H-units still comparatively minor. Moreover, grass are by presence of considerable amounts of typified the *p*-hydroxycinnamates (*p*-coumarates and ferulates) ferulic linked to lignin or/and polysaccharide (DEL RIO *et al*., 2015). The pyrogram analysis showed the presence of lignin and *p*-hydroxycinnamate derivatives. The 4-vinylphenol were coming from *p*-hydroxycinnamate. The main pyrolysis products derived from lignin were phenol, 4-cresol, 2-methyl-3-buten-1-ol, guaicol, syringol, 4-vinyl-2-methoxy-phenol, syringylaldehyde.

By pyrogram analysis, it is possible to realize than the AIL for CF is composed main for derivates from guaiacyl lignin (guaicol, 5-methylguaiacol, 4-ethylguaiacol, 4-propylguaiacol, acetoguaiacone, vanillylacetone, isoeugenol, eugenol for example) and syringyl lignin (syringol, methylsyringol, syringylaldehyde, acetosyringone). This has expected since the acid insoluble lignin, therefore the lignin more condensed.

Among the carbohydrate derivatives, the only compounds identified were furfural and acetic acid, indicated the lignin derived by hydrolysis acid from method Klason lignin is effective for isolation of lignin. The other compounds identified are showing relative areas above 50% of total peaks.

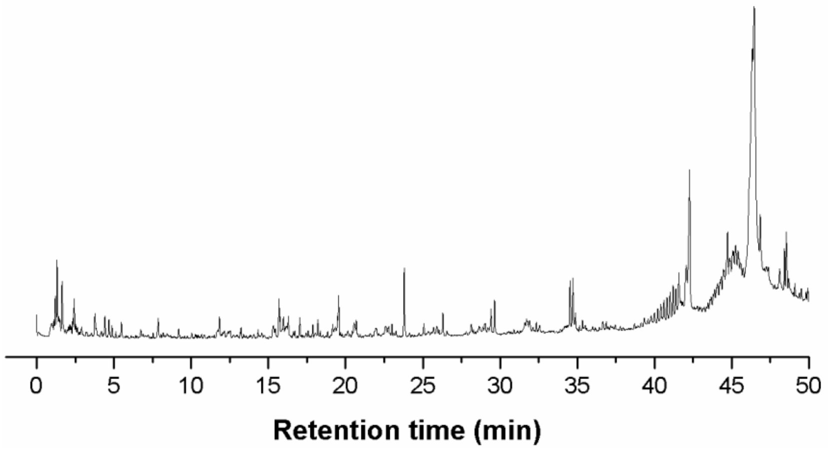

Figure 5. Pyrograms of AIL from corn fibers. Peak identities for compounds are shown in Table 3.

Table 3. Main compounds identified by Py-GC-MS in AIL of corn fibers.

Retention	Compound	% Relative area	Origin
1.231	Chloracetic acid	2.85	C,L
1.378	2-Methyl-3-buten-1-ol	6.07	L
1.584	Ethylene glycol diformate	5.15	O
1.785	Acetic acid	2.56	C,L
3.865	Methylbenzene	1.60	O
4.725	Pyrrolidinoethanamine	1.05	O
5.828	Furfural	1.11	C
11.767	Phenol	1.32	L
14.550	2-Cresol	0.60	L
15.366	4-Cresol	1.85	L
15.741	Guaiacol	2.50	L
16.369	2,5-Dimethylphenol	1.12	L
17.693	2-Ethylphenol	0.97	L
18.033	3,6-Dimethylphenol	2.07	L
18.742	4-Ethylphenol	0.49	L
19.055	3-Methylguaiacol	0.84	L
19.607	5-Methylguaiacol	3.12	L
20.651	4-vinylphenol	0.75	L
21.262	4-Ethylanisole	1.21	O
22.634	4-Ethylguaiacol	0.68	L
23.106	2-Allylphenol	0.28	L
23.214	Homocatechol	0.32	L
23.842	4-vinyl-2-methoxy-phenol	6.40	L

24.164	3-Methoxy-5-methylphenol	0.16	L
25.137	Syringol	0.98	L
25.228	Eugenol	0.60	L
25.584	4-Propylguaiacol	0.81	L
26.902	Isoeugenol	1.84	L
28.200	Methylsyringol	1.17	L
29.387	Acetoguaiacone	1.58	L
31.944	NI	1.08	-
32.249	Methyl p-hydroxyhydrocinnamate	0.80	O
34.520	Syringylaldehyde	4.15	L
34.996	Vanillylacetone	1.00	L
36.523	Acetosyringone	0.73	L
36.907	Methyl p-coumarate	0.80	O
38.880	NI	0.69	-
39.138	4-hydroxy-3-methoxy-Cinnamic acid	1.19	L
42.081	Palmitinic acid	7.71	O
46.461	Linoleic acid	40.15	O

C: carbohydrates; L: lignin; O: other; NI: unidentified

4. CONCLUSION

The results obtained in this study showed that the hemicelluloses extraction process was efficient. The isolated hemicelluloses from corn fibers allowed the confirmation of the presence of arabinoxylan and their importance as a source of xylose for the production of chemicals or additives in printing and writing paper.

The present work constitutes, to our knowledge, the structural characterization of lignins formed for Klason method of corn fibers. Forty five primary pyrolysis products of ASL from CF were identified. Analytical pyrolysis of ASL from CF showed prevalence of peaks related to products derived from extractives and proteins.

Thirty-nine primary pyrolysis products of AIL from CF were identified. Only furfural and acetic acid were identified as derivatives compounds of carbohydrate during pyrolysis of AIL. The peaks of lignin derivatives prevalence, indicated the lignin derived by hydrolysis acid from method Klason lignin is effective for isolation of lignin. The Py-GC-MS technique allowed identifying the presence of residual lignin in AIL and ASL from corn fibers.

REFERENCES

BARBOSA, L.C.A., SILVÉRIO, F.O., MALTHA, C.R.A., FIDÊNCIO, P.H., CRUZ, M.P., PILÓ-VELOSO, D., MILANEZ, A.F.. Effect of storage time on the composition and content of wood extractives in eucalyptus cultivated in Brazil. Bioresour. Technol. 99, 4878 – 4886, 2008.

BARBOSA, B. M.; COLODETTE, J. L.; LONGUE JUNIOR , D., GOMES, F. J. B., MARTINO, D. C. Preliminary studies on furfural production from lignocellulosics. J Wood Chem Tech., 34:178–190, 2014.

BARBOSA, B. M.; COLODETTE, J. L.; MUGUET, M. C. dos S.; GOMES, V. J.; Oliveira, R. C. Effects of xylan in eucalyptus pulp production. Cerne, v. 22 n. 2 ,p. 207-214, 2016.

BARTOS, L.; PRCHAL, V.; RAJCOVA, A.; EBRINGEROVA, A.; GREGOROVA, A. Rheological properties of hemicelluloses (in Slovak). Text. Chem. 20, 37–48, 1990.

BERAMENDI-OROSCO, L. E., CASTRO-DIAZ, M., SNAPE, C. E, VANE, C. H., LARGE, D. J. Application of catalytic hydropyrolysis for the rapid preparation of lignin concentrates from wood. Org. Geochem. 35, 61-72, 2004.

BOERJAN, W.; RALPH, J.; BAUCHER, M. Lignin biosynthesis. Annu Rev Plant Biol, 54: 519–546, 2003.

BURANOV, A.U.; MAZZA, G. Lignin in straw of herbaceous crops. Ind Crops Prod., 28(3), 237–259, 2008.

DEL RÍO, J. C.; GUTIÉRREZ, A.; HERNANDO, M.; LANDÍN, P.; ROMERO, J.; MARTÍNEZ, A. T. Determining the influence of eucalypt lignin composition in paper pulp yield using Py-GC/MS. J. Anal. Appl. Pyrol., 74, 110–115, 2005.

DEL RÍO, J. C.; GUTIÉRREZ, A.; RODRÍGUEZ, I. M.; IBARRA D.; MARTINEZ, A. T. Composition of non-woody plant lignins and cinnamic acids by Py-GC/MS, Py/TMAH and FT-IR. J. Anal. Appl. Pyrolysis, 79, 39–46, 2007.

DEL RÍO, J. C.; LINO, A. G.; COLODETTE, J. L.; LIMA, C. F.; GUTIÉRREZ, A.; MARTINEZ, A. T. FACHUANG, Lu; RALPH, J.; RENCORET, J. Differences in the chemical structure of the lignins from sugarcane bagasse and straw. Biomass Bioenergy, 81, 322-338, 2015.

EGÜÉS, I.; STEPAN, A. M.; ECEIZA, A.; TORIZ, G.; GATENHOLM, P.; LABIDI, J. Corncob arabinoxylan for new materials. Carbohydr Polym., 102, 12– 20, 2014.

GOLDSCHMID, O. Ultraviolet spectra, In: Lignins: occurrence, formation, structure and reactions, Sarkanen, K. V. and Ludwig, C. H. (eds), Wiley-Interscience, New York, 241-266, 1971.

GOMES, F. J. B., COLODETTE, J. L., BURNET, A., BATALHA, L. A. B., SANTOS, F. A.; DEMUNER, I. F. Thorough Characterization of Brazilian New Generation of Eucalypt Clones and Grass for Pulp Production. IJFR, 10p, 2015.

INTERNATIONAL DAIRY FEDERATION. Standards 20 B. Milk. Determination of nitrogen content. Brussels: IDF, 1993.

KÁLMÁN, G., RECSEG, K., GASPAR, M.; RÉCZEY, K.. Novel approach of corn fiber utilization. In Twenty-Seventh Symposium on Biotechnology for Fuels and Chemicals. p. 738-750. Humana Press. 2006.

LICHNEROVA´, I.; EBRINGEROVA´, A.; HEINRICH, J. Xylans; perspective pharmaceutical auxiliary materials. Acta Fac. Pharm. (Bratislava) 45, 5–141, 1991.

LILI,W.; YIJUN, J.; CHUNHU, L., et al.Microwave-Assisted Hydrolysis of Corn Cob for Xylose Production in Formic Acid. Materials for Renewable Energy & Environment (ICMREE), Shanghai, China, May 20-22, 2011.

LIMA, C. F.; BARBOSA, L. C. A.; RIBEIRO, M. C., SILVERIO, F. O., COLODETTE, J. L. Comparison between analytical pyrolysis and nitrobenzene oxidation for determination of syringyl/guaiacyl ratio in *Eucalyptus* spp. lignin. Bioresources 3(3), 701-712, 2008.

OUDIA, A., MÉSZÁROS, E., SIMÕES, R., QUEIROZ, J. and JAKAB, E. Pyrolysis-GC/MS and TG/MS study of mediated laccase biodelignification of *Eucalyptus globulus* kraft pulp, J Anal Appl Pyrolysis, 78, 233-242, 2007.

RALPH, J.; HATFIELD, R. D. Pyrolysis-GC-MS characterization of forage materials. J. Agric. Food Chem. 39, 1426-1437, 1991.

SCOTT, R. W. Colometric determination of hexuronic acids in plant materials. Anal. Chem., n. 7, p. 936-941, 1979.

SILVÉRIO, F. O., BARBOSA, L. C. A., and VELOSO, D. P. The pyrolysis as analytic Technique, Quim. Nova, v.31, n.6, p. 1553-1561, 2008.

SILVA, S. S.; CARVALHO, R. R.; FONSECA, J. L.; GARCIA, R. B. Extração e Caracterização de Xilanas de Sabugos de Milho. Polímeros: Ciência e Tecnologia. Abril/Junho, 1998.

SOLÁR, R.; KACIK, F.; MELCER, I. Simple method for determination of O-acetyl groups in wood and related materials. Nord. Pulp Pap. Res. J., 4:139-141, 1987.

STEPAN, A. M.; HÖIJE, A., SCHOLS, H. A.; WAARD, P.; GATENHOLM, P. J. Appl. Polym. Sci, v. 125, n. 3, p. 2348–2355, 2012.

SUN, X. F., SUN, R. C., SUN, J. X. Oleoylation of sugarcane bagasse hemicelluloses using N-bromosuccinimide as a catalyst. J Sci Food Agric., 84(8), 800–810, 2004.

TECHNICAL ASSOCIATION OF THE PULP AND PAPER INDUSTRY. Tappi Standard Methods. Atlanta: TAPPI, 2000.

VAN DONGEN, F.E.M.; VAN EYLEN, D.; KABEL,M.A. Characterization of substituents in xylans from corncobs and stover. Carbohydr Polym., 86(2), 722–731, 2011,

WALLIS, A.; WEARNE, R.; WRIGHT, P. Chemical Analysis of Polysaccharides in Plantation Eucalyptus wood and Pulps. Appita J., 49:258-262, 1996.

ZHANG, Y.; GHALY, A. E.; LI, B. Physical properties of corn residues. Am J Biochem Biotechnol., 8(2), 44-53, 2012.

CHAPTER 4

KRAFT LIGNIN AND CORN RESIDUE ADDITION IN THE PRODUCTION OF EUCALYPTUS PELLETS

ABSTRACT

Pellets have become an important renewable energy source for industrial and domestic use. The market has become more demanding in terms of the quality of the product, which can be improved by using different additives, such as Kraft lignin. Thus, the objective of this work was to evaluate the quality of the pellets produced from a mixture of eucalyptus and corn residue, with the addition of different percentages of Kraft lignin. For the production of pellets, wood with bark of a hybrid of Eucalyptus grandis x Eucalyptus urophylla, with 6 years of age, from an experimental planting, together with corn residue from industrial processing were used as raw material. The following proportions of corn residue in the mixture were 0, 20, 25 and 30% (w/w). Except for the control (0% lignin), 2 and 5% (w/w) Kraft lignin were added to the raw material in the 4 different mixtures. Pellets were produced in a laboratory press pelletizer with horizontal circular array. The following properties of the pellets were evaluated: moisture content, high heating value, C, H, O, N, immediate chemical analysis, energy density, bulk density, ash content, length and diameter, hardness, mechanical durability and fines content. The addition of Kraft lignin to eucalyptus and corn residue pellets improved bulk density, and mechanical durability. The mixing of eucalyptus with corn residue is an effective way to optimize properties of biomass solid fuel. Thus, similar amounts to that of the treatment with the proportion of 80% eucalyptus and 20% corn residue can be a viable alternative to the production of pellets.

Keywords: additive; solid fuel; mechanical strength, agricultural waste.

1. INTRODUCTION

In the search for new energy sources to compete with the fuels currently available in the market, lignocellulosic wastes have become one of the most promising options as alternative forms of energy. Agricultural residues such as rice husk, straw and corn cob are alternative source of lignocellulosic as well as forest residues, such as wood residue from harvest and processing can be directly used as fuels.

Wood is the most-used raw material for energy production. Brazil has great forest potential, totaling 7.8 million hectares in 2015 (IBÁ, 2016), of which 5.6 million are dedicated to *Eucalyptus* plantations. Although, just 14% is destined for charcoal-fired steelworks (IBÁ, 2016). The use of *Eucalyptus* for energy purposes is mainly due to low ash generation and less corrosion of the combustion equipment, when compared with agricultural biomass (STELTE *et al*., 2012).

However, when it comes to waste, the pretreatment of lignocellulosic materials is required, which is performed by the densification of the material, by using temperature and pressure, resulting in a material with granulometric homogeneity, higher density and resistance to the generation of fines. This procedure is known as pelletization. The increase in temperature, according to Chen et al. (2009), makes lignin "plasticized" and acts as a natural binder of the particles after compaction of particles. The quality of the pellets can be improved by using binding additives in raw material, as Kraft lignin (AHN *et al.*, 2014).

Kraft lignin is obtained from black liquor generated by pulp mills by the Kraft process, where they produce surplus energy that is obtained by burning the black liquor. To exploit black liquor, besides the generation of electric and steam energy, Kraft lignin can be extracted and used as other alternatives with more value-added, one example is the possibility of use as an additive for pellets. Therefore, the concept of biorefinery in the forestry industry is applied. Since separation and purification can be carried out by several industrial processes, this would be a promising alternative as an additive to pellet production. Lignin is a macromolecule that makes part of the chemical constitution of wood, and acts on the adhesion of the particles to form the pellets. The properties of Kraft lignin are specific to the extraction process, and will positively or negatively affect pellet properties (BERGHEL *et al.*, 2013).

In this context, pellets can be an important alternative to transform biomass into higher value-added product used for energy purposes. Pellets are a new type of compressed fuel that enables the use of more modern firing equipment and facilitates long-distance biomass transportation.

It’s very important to diversify the Brazilian energy matrix with the introduction of renewable energy sources and potentiate the use of forest and agricultural residues to reduce costs. Therefore, the objective of this work was evaluate the quality of the pellets of a mixture of lignocellulosic residues (Eucalyptus and corn) produced with the addition of different percentages of Kraft lignin.

2. MATERIALS AND METHODS

2.1. Materials and properties of *in natura* particles

Wood with bark of a 6-years-old *Eucalyptus grandis* x *Eucalyptus urophylla* clone, from an experimental planting and corn residue from industrial processing were used as raw materials for the production of the pellets. Kraft lignin was separated from the black liquor by the LignoBoost process. This process, according to Berghel et al. (2013), is based on lignin precipitation by gradually lowering the black liquor pH value, followed by filtration, washing and dewatering. Drying and make sawdust is sometimes necessary, though ideally a woody feedstock should have a moisture content of 8–15% (w/w) (Paula *et al*., 2011) before entering the pellet mill.

Eucalyptus and corn residues from industrial processing were collected. The residues were reduced to smaller fractions, using the Willey mill, according to TAPPI standard T257 cm-85 (1996), and later, the particles were selected in a set of sieves of 40 and 60 mesh for analysis structural chemical composition, immediate chemistry, ultimate chemical analysis, and higher calorific value.

Characterization of the residues and the Kraft lignin followed the procedures described in Table 1. The bulk density was performed from the mass determination in a volume of 1000 cm^3.

Table 1. Characterization of residues, Kraft lignin and their respective methodologies

	Parameter	Procedure
Residues	Moisture content	ABNT NBR 11941 (2003)
	Extracts	TAPPI T264 cn-97 (1997)
	Insoluble lignin	Gomide e Demuner (1986)
	Soluble lignin	Goldschmid (1971)
	Immediate Chemical Analysis	ABNT NBR 8112 (1983)
	Higher Heating Value	ASTM D-2015-66 (1982)
	Ultimate Chemical Analysis	Equipment CHNS- module O
Lignin	Immediate Chemical Analysis	ABNT NBR 8112 (1983)
	High Calorific Power	ASTM D-2015-66 (1982)
	Ultimate Chemical Analysis	Equipment CHNS- module O

The data obtained from the characterization of the residues and Kraft lignin were analyzed statistically by analysis of variance. According to the result, means were compared by the Tukey test at 5% probability.

2.2. Pellet production

Pellets were produced in a laboratory press pelletizer with horizontal circular array (AmandusKahl, model 14-175), with capacity for 50 kg h^{-1} production. The compression channels of the array had 6.0 mm internal diameter and 20.0 mm length.

About 1.5 kg of pellets was produced per batch, being three batches per treatment. To feed the pelletizer, a system consisting of an electric motor, a 38-speed controller, and an endless screw was used. The pelletizing temperature ranged from 95 to 100 °C, and the rollers rotation speed was 1500 rpm.

From this, pellets were produced with 4 different proportions of mixture of the two biomasses, eucalyptus and corn residue, and 3 proportions of the kraft lignin added, being 12 treatments with 3 replications, totaling 36 pellet batches. Table 2 shows the experimental plan.

Table 2. Experimental Plan.

Treatments	Corn residue (%)	Eucalyptus (%)	Kraft lignin (%)
T1	0	100	0
T2			2
T3			5
T4	20	80	0
T5			2
T6			5
T7	25	75	0
T8			2
T9			5
T10	30	70	0
T11			2
T12			5

2.3. Classification of Pellets according to Quality Standards

The mixture of eucalyptus and corn residue pellets were classified as non-woody pellets, whose quality specifications are in accordance with DIN EN 14961-6 (Deutsches Institut Für Normung, 2012) (Table 3). This standard refers to the quality of non-woody pellets for non-industrial use, and was used for classification of pellets in class A or B.

Table 3. Specifications for non-woody pellets

Properties (Unit)	Origin	
	A	B
	Herbaceous biomass; Fruit biomass; Biomass mixture	Herbaceous biomass; Fruit biomass; Biomass mixture
Diameter (mm)	6 ± 1	6 ± 1
Length (mm)	3.15 ≤ length ≤ 40	3.15 ≤ length ≤ 40
Moisture content (%)	≤ 12	≤ 15
Ash content (%)	≤ 5	≤ 10
Mechanical durability (%)	≥ 97.5	≥ 96.0
Fines (%)	≤ 2	≤ 3
Net Heating Value - NHV (MJ Kg^{-1})	≥ 14.1	≥ 13.2
Bulk density (kg m^{-3})	≥ 600	≥ 600
Nitrogene (%)	≤ 1.5	≤ 2.0
Sulfur (%)	≤ 0.20	≤ 0.20
Chlorine (%)	< 0.20	< 0.30

Source: Adapted from DIN EN 14961-6 (Deutsches Institut Für Normung, 2012a).

2.4. Evaluation of pellet properties

Pellets were reduced to smaller fractions, using the Willey mill, according to TAPPI standard T257 cm-85 (1996), and later, the particles were selected in a set of sieves of 40 and 60 mesh for immediate chemical analysis (fixed carbon content and volatile content), ash content, ultimate chemical analysis (C, H, O) and higher calorific value.

Ash content analysis was determined according to the procedure established in the ASTM - D1762-84 standard (American Society for Testing Materials, 2001) and immediate chemical analysis according to ABNT NBR 8112 (1983). The high heating value (HHV) and ultimate chemical analysis was obtained according to the DIN EN 14918 standard (Deutsches Institut Für Normung, 2010b), using an adiabatic calorimeter pump IKA® model 300.

Moisture content of the pellets, after being stored for seven days, was determined according to the methodology described in the DIN EN 14774-1 standard (Deutsches Institut Für Normung, 2010a), in a kiln at 105 ± 2 ºC.

Mechanical durability and fine content (particles smaller than 3.15 mm) were determined by using the Ligno-Tester, Holmen® according to the DIN EN 15210-1 standard (Deutsches Institut Für Normung, 2010d) and the equipment’s instructions. Pellet samples were blown by means of an air jet that simulates the natural destruction of pellets during transportation and handling in an inverted quadrangular pyramidal chamber. To determine the fines content, airflow had a pressure of 30 mbar for 30 seconds, and a sample of 0.300 kg of pellets was used. Subsequently, untreated samples were subjected to another controlled airflow (70 mbar) for 60 seconds to determine the mechanical durability, using 0.100 kg of pellets.

Bulk density of pellets was determined according to the DIN EN 15103 standard (Deutsches Institut Für Normung, 2010c).

Hardness (kg) was determined by the diametral compression test of the pellet in an Amandus Kahl manual durometer, with a scale of 0 to 100 kg. One pellet at a time was inserted in the durometer, and increasing load was applied until sample breakage. Afterwards, the maximum load (kg) the pellet withstands before breaking was read. The hardness of 30 pellets per batch was evaluated.

Diameter (mm) and length (mm) of the pellets were obtained according to the DIN EN 16127 standard (Deutsches Institut Für Normung, 2012), measured in a digital caliper.

2.5. Data analysis

The experiment was carried out in a completely randomized design with 12 treatments and three replications (pellet batches).

Results were subjected to analysis of variance (ANOVA), to verify the differences between the treatments. When significant differences were observed, the Scott test was applied at 95% significance.

3. RESULTS AND DISCUSSION

3.1. Biomass Properties

Water has a crucial role in the pelletizing process and, along with lignin content, the moisture content of the feed is one of the most important parameters determining pellet durability (SAMUELSSON *et al.*, 2009). The moisture content for the corn residue and eucalyptus particles was on average 8.82% (wb) and 14.0% (wb), respectively. Thus, the corn residue moisture content is in accordance to that suggested by other authors for pellet production, which varies between 8-15% (wb) (Paula *et al.*, 2011).

Table 4 shows the mean values of the physical and chemical properties of the residues and the Kraft lignin. The HHV of wood (18.9 MJ kg^{-1}) and corn (19.2 MJ kg^{-1}), were significantly lower than that Kraft lignin (26.3 MJ kg^{-1}). It is noted that Kraft lignin has a great energetic potential to be used as an additive in pellets, or to be used in other by-products, adding value. The improvements concern properties such as higher heating values and lower ash contents. As well as lower slagging tendencies, and lower emissions of fine particles during combustion as compared to wood (stem) pellets.

Table 4. Mean values of the physical and chemical properties of the particles of lignocellulosic residues and Kraft lignin.

Characterization	Residues		Kraft Lignin
	Eucalyptus	**Corn**	**Industrial**
Bulk density (kg m^{-3})	137 (b)	-	492 (a)*
Higher Heating Value (MJ kg^{-1})	18.9 (b)	19.2 (b)	26.3 (a)
Lower Heating Value (MJ kg^{-1})	17.5 (b)	18.0 (b)	25.1 (a)
Energy Density (10^4 MJ m^{-3})	1.5 (b)	1.9 (a)	-
Ultimate chemical analysis (%)	C = 49.2; N = 0.2; H = 5.9; O = 44.3; S = 0.1	C = 50.1; N = 1.3; H = 5.1; O = 41.2; S = 1.4	C = 66.2; N = 0.2; H = 5.6; O = 23.4; S = 2.4
Volatile Content (%)	89.13 (a)	84.33 (a)	
Ash (%)	0.3 (c)	0.8 (c)	1.1 (c)
Fixed Carbon Content (%)	10.60 (b)	14.86 (b)	
Extractives soluble in alcohol / toluene (%)	5.2 (a)	5.8 (a)	-
Soluble Lignin (%)	2.6 (d)	8.0 (c)	12.7 (c)
Insoluble Lignin (%)	33.2 (b)	4.0 (d)	85.4 (a)
Total Lignin (%)	35.8 (b)	12.0 (c)	98.1 (a)
Holocellulose (%)	59.0 (b)	64.8 (a)	0.2 (c)

*Means followed by the same letter in parentheses for wood residues (within the same row), and for Kraft lignin (within the same row), do not differ from each other by the Tukey test at 5% probability.

Pellet quality is largely a function of the type of feedstock and process parameters. Some feedstock parameters have a greater effect on pellet durability than other. The lignin content is possibly the most important parameter, followed by moisture content, as these two factors directly interact to affect the temperature at which lignin softens. There are some conflicting results found in the effect of extractives on pellet durability: some studies suggest they lubricate the passage of material through the mill, whereas a few other studies suggest they have a role in binding (WHITTAKER and SHIELD, 2017).

Lignin, extractive and holocellulose content for the biomass they showed evidence some different components in between the feedstocks. The effect of extractive content may be dependent on the particle size distribution and the lignin content. Changes in moisture content may also have positive or negative effects on durability, though it appears that there is some interaction with the extractive content.

3.2. Pellet properties

Table 5 shows the ultimate chemical analysis, immediate chemical analysis, energy density, HHV and hardness of pellets.

Table 5. Ultimate chemical analysis, immediate chemical analysis, energy density, HHV and hardness of pellets.

Corn residue (%)	Kraft Lignin (%)	C (%)	H (%)	O (%)	Fixed Carbon Content (%)	Volatile Content (%)	Energy Density (10^4 MJ m^3)	Hardness (Kg cm^2)	HHV (MJ kg^{-1})
0	0	50.4 a	6.1 a	42.8 c	14.9 b	84.8 a	5.4 b	65.2 a	20.0 a
0	2	50.8 a	6.0 a	42.6 c	13.9 b	85.3 a	5.5 a	65.8 a	20.1 a
0	5	49.8 b	5.9 a	43.7 a	16.9 a	82.8 b	5.5 a	58.0 b	20.1 a
20	0	49.6 c	6.2 a	43.2 b	15.1 b	84.7 a	4.9 c	49.4 c	19.3 c
20	2	50.4 a	6.2 a	42.2 d	14.5 b	85.2 a	4.5 d	50.2 c	19.8 b
20	5	49.6 c	6.1 a	43.3 b	16.9 a	82.7 b	4.4 e	56.0 b	19.4 c
25	0	49.5 c	6.1 a	43.2 b	15.3 b	84.4 a	4.0 g	47.5 c	19.4 c
25	2	50.1 b	6.2 a	42.6 c	14.0 b	85.8 a	4.4 e	51.8 c	19.6 c
25	5	50.5 a	6.1 a	42.1 d	17.3 a	82.3 b	4.3 f	54.4 c	19.8 b
30	0	49.6 c	6.1 a	43.1 b	13.9 b	85.7 a	3.7 h	40.4 d	19.3 c
30	2	50.3 a	5.4 b	43.1 b	14.6 b	85.0 a	4.0 g	48.0 c	19.5 c
30	5	50.0 b	6.1 a	42.4 d	16.1 a	83.5 b	3.6 i	47.4 c	19.5 c

*Means followed by the same letter in parentheses for wood residues (within the same row), and for Kraft lignin (within the same row), do not differ from each other by the Scott test at 5% probability.

Biomass is composed of elements C, H, O, N, S, and Cl, where the former three are the major, representing up to 97–99% (w/w) of the biomass organic mass. Ultimate analysis gives the weight percent of the elements. In Table 4, the ultimate chemical analysis (C, H and O %) of the three main elements indicate of addition of the Kraft lignin affected the treatments for pellets production. Kraft lignin is an organic compound extracting by pulping black liquor, producing a material with high energy density and low ash content. Already the fixed carbon content increased with the addition of 5% (w/w) of Kraft lignin and the volatile content decreased. It should be noted that fuel materials with high fixed carbon content present slower burning, implying a longer residence time inside the burners compared to other that have lower fixed carbon content (BRITO and BARRICHELLO, 1982; SANTOS *et al.*, 2013).

Biomass has not been widely utilized due to its relatively low energy density when compared with fossil fuels. This low energy density results in inhibitive transportation costs and inconvenient storage and handling. In Table 5, it can be observed that with the increase of the corn residue addition, there was a decrease in energy density, which may be related to the lower lignin content of corn residue (12.0% w/w) in relation to eucalyptus (35.8% w/w).

In relation to the hardness (Table 5), a high value was observed without corn residue. According to Zamorano et al. (2011), the compressive strength of the pellets is related to the adhesion forces between particles. Thus, since eucalyptus has the greatest amount of lignin, it consequently has more points of contact between the particles of the pellets, leading to greater adhesion and therefore greater the hardness.

HHV of the pellets (Table 5) was observed higher value with 0% of corn residue. For all treatments was similar, with no effect the addition of Kraft lignin, except the treatment with 25% (w/w) of corn residue that presented an addition of HHV with the addition of 5% (w/w) of Kraft lignin. According to Demirbas (2002), higher lignin contents contribute to the increase in the higher calorific value of the fuel, since lignin's HHV of 26.3 MJ kg^{-1} is higher than the other primary components of the wood. Higher HHV means a smaller mass and hence smaller volume of pellets will be needed to provide the desired energy. Therefore, the HHV of Kraft lignin was not high enough to contribute to the increase of HHV of the pellets, for most treatments, since the maximum percentage of lignin added was of 5% (w/w).

3.2.1 Properties of the pellets in accordance with DIN EN 14961-1

The common standard (EN-14961-2) will form the platform for a certification system with the European Standard Committee, identifying the specifications for different categories of pellets (KARKANIA *et al.*, 2012). Generally, the highest grades have the strictest standards and offer the best combustion properties. The specifications for heating pellets are stricter than for industrial pellets, requiring lower contents of ash, fines, nitrogen, sulphur and chlorine (Table 3). The DIN EN 14961-1 standard also introduces some sustainability criteria to regulate the environmental impacts of sourcing and trading of non-woody pellets. In Figures 1 and 2, the properties of the pellets that are in accordance European quality standards.

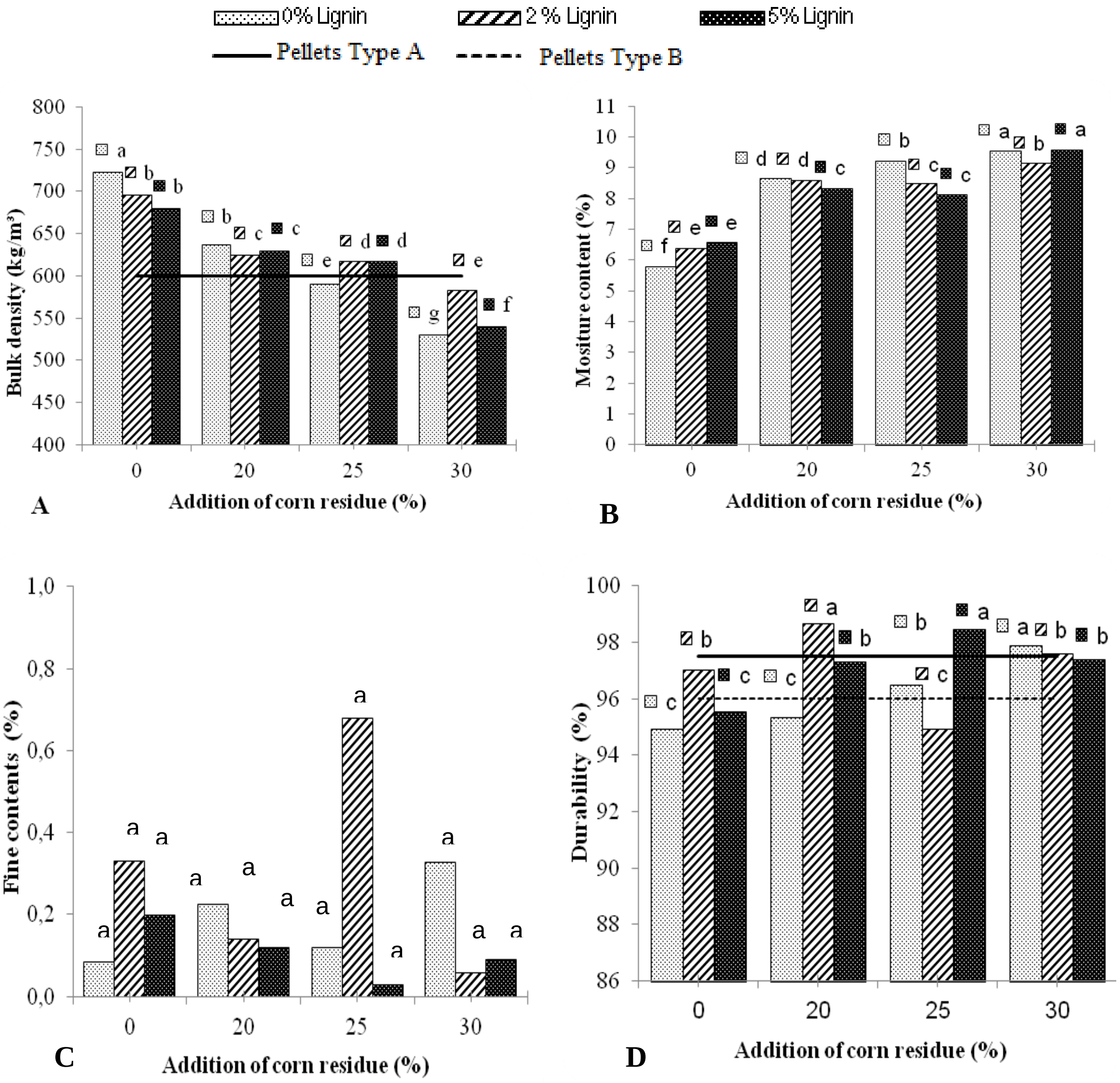

Figure 1. Properties of pellets for the treatments: A - Bulk density (kg m^{-3}); B – Moisture content (%); C - Fine content (%); D - Durability (%). Bars followed by the same small letter don't differ among themselves at 5% probability (Scott, $p > 0.05$).

Densification of biomass could result in a significant increase in the bulk density of biomass. Bulk density is defined as the mass per unit volume of biomass. Figure 1A shows the results of bulk density of all the evaluated treatments. The observed higher the bulk density was with 0% (w/w) of corn residue. Therefore, greater the mass that can be transported or stored in a fixed volume container, thus minimizing transport and storage costs. Reduction of the bulk density is observed as the proportion of the corn residue increases. Conversely, the addition of Kraft lignin there is a significant difference, but, as the difference is present at 0% (w/w) of added Kraft lignin, it is likely that it is due to process variables rather than to a difference between the treatments.

Pellets with 30% (w/w) addition of corn residue did not meet the DIN EN 14961-1(2012) standard, which should be greater than 600 kg m^{-3}.

Biomass, by its nature is hygroscopic. Stable pellets can be formed with a range of moistures between 8 and 12% (wb) depending on the biomass in question. For the moisture content of the pellets (Figure 1B) tended to increase due to the higher proportions of corn residues in the mixture and addition of lignin varied according to the different treatments. Higher moisture content increase the extent at which pellets ‘relax’ after formation, which can decrease durability and reduces the temperature at which lignin plasticises (Tg), which increases bonding between particles (STELTE *et al,*. 2011). All treatments met the requirements of DIN EN 14961-6 (2012), which indicates a maximum moisture value of 12% (wb) for Type A pellets.

For fine content, no statistical difference was observed between the evaluated treatments, which evidences that the addition of both corn residues and Kraft lignin did not influence this property of the pellets (Figure 1C). Regardless of the treatment, percentage of fines was below the maximum allowed by the European standard, which stipulates values lower than 2%. Therefore, they were classified (all treatments) as pellets type A, in accordance with DIN EN 14961-1 (2012), because they are below the 2% limit.

Mechanical durability is the most important physical quality of a pellet (TABIL and SOKHANSANJ, 1996), which simulates the resistance of the pellets to mechanical impacts during storage and transportation, must be greater than or equal to 97.5%, according to the DIN EN 14961-2 standard (2012). Figure 1D, with 0% (w/w) of corn residue, only the pellets produced with 2% (w/w) lignin were in accordance with the standard, being classified as type B pellets. By adding 20% (w/w) of corn residue, pellets with 2% (w/w) of lignin were classified as type A, and with the proportion of 5% (w/w) of lignin classified as type B pellets; however, 0% (w/w) of lignin for this proportion did not meet the standard. The addition 25% (w/w) of corn residues, 5% (w/w) of lignin had the best results for the production of pellets. Pellets produced with 0% (w/w) lignin were classified as type B, and those produced with 2% (w/w) lignin did not meet the standard. The percentage of 30% (w/w) of corn residue pellets produced with 0% (w/w) and 2% (w/w) of lignin classified as type A pellets, and those produced with 5% (w/w) lignin classified as type B pellets.

Figure 2 shows the results of the ash contents, nitrogen content and size of the pellets. Ash content as can be seen in Figure 2A varied greatly among treatments and were classified as pellets type A, in accordance with DIN EN 14961-1 (2012), because they are below the 5% limit. Higher ash content is undesirable for pellets, since they are inversely proportional to HHV, besides being the combustion residue and depending on the constitution chemistry of the ashes, it is possible to form incrustations in the combustion equipment (OBERNBERGER and THEK, 2010).

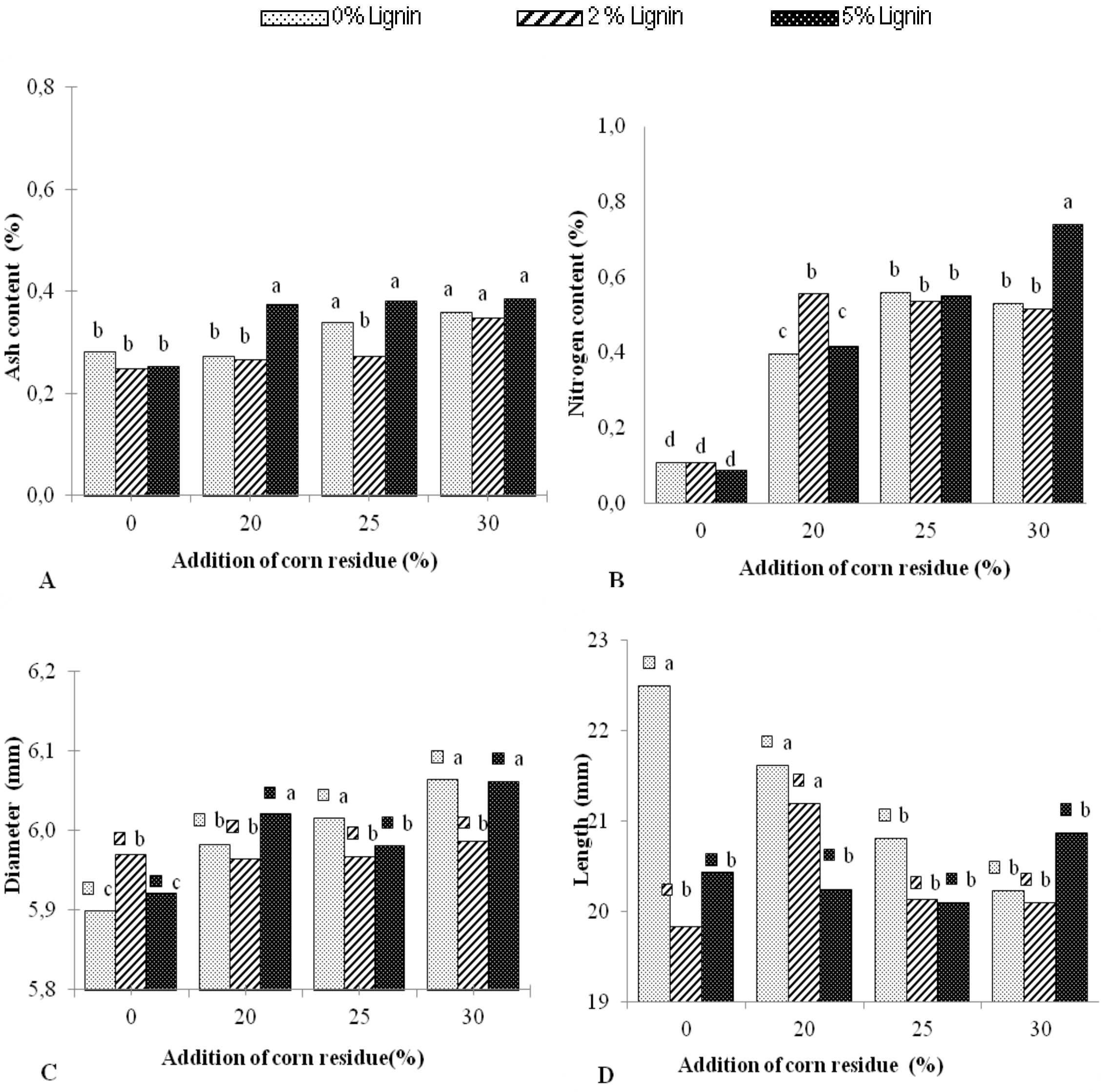

Figure 2. Properties of pellets for the treatments: A - Ash content (%); B – Nitrogen content (%); C - Diameter (mm); D - Mean length of the pellets (mm). Bars followed by the same small letter don't differ among themselves at 5% probability (Scott, $p > 0.05$).

In theory, a nitrogen content of agricultural residues is higher than those of woody biomass due to the large amounts of N fertilizer applied during crop growth (LIU et al., 2014). The Figure 2B the higher nitrogen content is the pellets with the addition 30% (w/w) of corn residue and 5% (w/w) of lignin. This is also shown in the EN classes all treatments of pellets are classified as type A, in accordance with DIN EN

14961-1 (2012), because they are below the 1.5% limit. Higher nitrogen content can lead to elevated NOx emissions which, along with SO_2 has great environmental relevance in terms of acid rain (WHITTAKER and SHIELD, 2017).

The strong, uniformed-size of biomass pellets with high bulk density makes them easier handle, transport, and store. The values of diameter (5 - 7 mm) and length (3.15 - 40 mm) are in accordance with the requirements of the DIN EN 14961-2 standard (Deutsches Institut Für Normung, 2011), as observed in Figures 2D, for all the treatments. According to Narra et al. (2010), the dimensions and shape of the pellets should be homogeneous for the best functioning of small scale furnaces and automatic heating equipment.

4. CONCLUSIONS

Besides the technical and operational advantages of pellets, when compared with other fuel sources, the association with residual biomass during the production process makes the product with potential to compete in the pellet market. The mixing of eucalyptus with corn residue is an effective way to optimize properties of biomass solid fuel. Therefore, the addition of up to 20% (w/w) of corn residue has the potential to improve pellet quality, with or without the additive Kraft lignin.

The addition of Kraft lignin to the production of pellets improved the properties of mechanical durability in some treatments, allowing the transportation of a greater amount of mass and energy, besides maintaining the integrity of the biofuels during handling and use.

REFERENCES

AMERICAN SOCIETY FOR TESTING MATERIALS - ASTM. D1762-84: Standard Test Method for Chemical Analysis of Wood Charcoal. Philadelphia: ASTM International, 2p. (2001).

AHN, B. J.; CHANG, H. S.; LEE, S. M.; CHOI, D. H.; CHO, S. T.; HAN, G. S.; YANG, I. Effect of binders on the durability of wood pellets fabricated from Larix kaemferi C. and Liriodendron tulipifera L. sawdust. Renewable Energy, v. 62, p. 18-23, 2014.

BERGHEL, J.; FRODESON, S.; GRANSTROM, K.; RENSTROM, R.; STAHL, M.; NORDGREN, D.; TOMANI, P. The effects of kraft lignin additives on wood fuel pellet quality, energy use and shelf life. Fuel process technol., v. 112, p. 64-69, 2013.

BRITO, J. O.; BARRICHELO, L. E. G. Aspectos técnicos da utilização o da madeira e carvão vegetal como combustíveis. In: Seminário de abastecimento energético industrial com recursos florestais, 2, São Paulo, p. 101-137,1982.

CHEN, L. J.; XING, L.; HANA, L.; Renewable energy from agro-residues in China: solid biofuels and biomass briqueting technology. Renew Sust Energ Rev., Oxford, U.K., v.13, n. 9, p. 2689-2695, 2009.

DEMIRBAS, A. Relationships between heating value and lignin, moisture, ash and extractive contents of biomass fuels. Energ explor exploit, v. 20, n. 1, p. 105-111. 2002.

DEUTSCHES INSTITUT FÜR NORMUNG, D. I. N. DIN EN 14775: Determination of ash . Berlim: CEN, 2009. 12 p.
______DIN EN 14918: Determination of calorific value. Belim: CEN, 2010b. 63 p.
______DIN EN 15103: Determination of bulk density. Berlim: CEN, 2010c. 14 p.
______DIN EN 15210-1: Solid biofuels – Determination of mechanical durability of pellets and briquettes – Part 1: Pellets. Berlim: CEN, 2010d. 12 p.
______DIN EN 15104: Determination of total content of carbon, hydrogen and nitrogen – Instrumental methods. Berlim: CEN, 2011a. 15 p.
______DIN EN 15296: Conversion of analytical results from one basis to another. Berlim: CEN, 2011b. 15 p.
______DIN EN 14961-6: Solid biofuels – Fuel specifications and classes – Part 6: Non-woody pellets for non-industrial use. Berlim: CEN, 2012a. 16 p.
______DIN EN 16127: Determination of length and diameter of pellets. Berlim: CEN, 2012b. 11 p.

INDÚSTRIA BRASILEIRA DE ÁRVORES – IBÁ. Relatório anual da Indústria Brasileira de Árvores, ano base 2015. Brasília: IBÁ, 100 p. 2016.

KARKANIA, V.; FANARA, E.; ZABANIOTOU, A. Review of sustainable biomass pellets production – A study for agricultural residues pellets' market in Greece. Renew Sust Energ Rev, 2012;16(3):1426–36.

LIU, C.W., SUNG, Y., CHEN, B. C., LAI, H.Y. Effects of nitrogen fertilizers on the growth and nitrate content of lettuce *(Lactuca sativa* L.). Int J Environ Res Public Health. 11(4):4427-4440, 2014.

NARRA, S.; TAO, Y.; GLASER, C.; GUSOVIUS, H. J.; AY, P. Increasing the Calorific Value of Rye Straw Pellets with Biogenous and Fossil Fuel Additives. Energy & Fuels, v. 24, p. 5228-5234, 2010.

PAULA, L. E. R.; TRUGILHO, P. F.; REZENDE, R. N.; ASSIS, C. O.; BALIZA, A. E. R. Produção e avaliação de pellets de resíduos lignocelulósicos. Pesquisa Florestal Brasileira, v. 31, n. 66, p. 103-112, 2011.

REN, J.L., SUN, R.C., LIU, C.F., COA, Z.N., LUO, W. Acetylation of wheat straw hemicelluloses in ionic liquid using iodine as a catalyst. Carbohydr. Polym. 70 (4), 406–414, 2007.

SAMUELSSON, R.; THYREL, M.; SJÖSTRÖM, M.; LESTANDER, T. A. Effect of biomaterial characteristics on pelletizing properties and biofuel pellet quality. Fuel Process Technol 90(9):1129–34, 2009.

SANTOS, R. C.; CARNEIRO, A. C. O.; PIMENTA, A. S.; CASTRO, R. V. O.; MARINHO, I. V.; TRUGILHO, P. F.; ALVES, I. C.N.; CASTRO, A. F. N. M.

Potencial energético da madeira de espécies oriundas de plano de manejo florestal no estado do Rio Grande do Norte. Ciência Florestal, Santa Maria, v.23, n.2, p.491-502, 2013.

STATISTICA. (2010). StatSoft, Inc. version 10.0 (data analysis software system), http://www.statsoft.com.

STELTE, W.; SANADI, A. R.; SHANG, L.; HOLM, J. K.; AHRENFELDT, J.; HENRIKSEN, U. B. Recent developments in biomass pelletization - a review. Bioresources, v. 7, n. 3, p. 4451-4490, 2012.

STELTE, W.; HOLM JK, SANADI, A. R; BARSBERG, S.; AHRENFELDT, J.; HENRIKSEN, U.B. Fuel pellets from biomass: the importance of the pelletizing pressure and its dependency on the processing conditions. Fuel; 90(11):3285–90, 2011.

TABIL, L.; SOKHANSANJ, S. Process conditions affecting the physical quality of alfalfa pellets. Appl. Eng. Agric. 12 (3), 345–350, 1996.

TECHNICAL ASSOCIATION OF THE PULP AND PAPER INDUSTRY, T. A. P. P. I. T 257 cm-85: Sampling and preparing wood for analysis. Atlanta: TAPPI, 1985. 5 p.

OBERNBERGER, I.; THEK, G. The pellet handbook: The production and thermal utilisation of pellets. London: Earthscan, 593 p. 2010.

WHITTAKER, C.; SHIELD, I. Factors affecting wood, energy grass and straw pellet durability – A review. Renew sust energ rev, 71, p. 1–11, 2017.

ZAMORANO, M.; POPOV, V.; RODRÍGUEZ, M. L.; GARCÍA-MARAVER, A. A comparative study of quality properties of pelletized agricultural and forestry lopping residues. Renewable Energy, v. 36, n. 11, p. 3133-3140, 2011.

OVERALL CONCLUSIONS

Biomass components (cellulose, hemicelluloses and lignin) were successfully studied and exploited for obtaining bioproducts. The main focuses of this work was the utilization of xylans extracted from lignocellulosic materials and use the Kraft lignin as an additive for pellets.

In the Chapter 1, the treatments of removal xylans decreased pulp lignin and HexA contents and caused significant positive impact on subsequent oxygen delignification and ECF bleaching. The deposited xylans were not impaired by WXL xylan deposition but slightly negatively affected by BXL xylans. Pulp beatability was improved by xylan deposition. At low energy consumption, the deposited xylans improved pulp physical and mechanical properties. Xylans extraction by CCE with subsequent deposition onto pulp in the O-stage proved attractive for manufacturing high xylan P&W paper grades.

In the Chapter 2, corn fibers are good source of hemicelluloses, which is an alternative for the use of these carbohydrate residues as an additive in papermaking. Hemicelluloses deposition onto fibers was more efficient in eucalyptus pulp than pinus. At low energy consumption, the pulps with deposition of xylan form paper with higher resistance to drainage and greater tensile and tear strengths. Pulp beatability was improved by xylan deposition. Xylans extraction by CCE with subsequent deposition onto pulp in the O-stage proved attractive for manufacturing high xylan P&W paper grades.

In the Chapter 3, the isolated hemicelluloses from corn fibers allowed the confirmation of the presence of arabinoxylan and their importance as a source of xylose for the production of chemicals or additives in printing and writing paper. The present work constitutes, to our knowledge, the structural characterization of lignins formed for Klason method of corn fibers. Forty five primary pyrolysis products of ASL from CF were identified. Analytical pyrolysis of ASL from CF showed prevalence of peaks related to products derived from extractives and proteins. Thirty-nine primary pyrolysis products of AIL from CF were identified. The Py-GC-MS technique allowed identifying the presence of residual lignin in AIL and ASL from corn fibers.

In the Chapter 4, the mixing of eucalyptus with corn residue is an effective way to optimize properties of biomass solid fuel. Therefore, the addition of up to 20% (w/w) of corn residue has the potential to improve pellet quality, with or without the additive Kraft lignin. The addition of Kraft lignin to the production of pellets improved the properties of mechanical durability in some treatments, allowing the transportation of a greater amount of mass and energy, besides maintaining the integrity of the biofuels during handling and use.