MARCELO COELHO DOS SANTOS MUGUET SOARES

MÉTODOS ALTERNATIVOS PARA DEPOSIÇÃO DE XILANAS EM POLPAS DE EUCALIPTO

Dissertação apresentada à Universidade Federal de Viçosa, como parte das exigências do Programa de Pós-Graduação do Mestrado Profissional em Tecnologia de Celulose e Papel, para obtenção do título de *Magister Scientiae*.

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APROVADA: 18 de Dezembro de 2009.

_____
Prof. José Lívio Gomide
(Co-Orientador)

_____
Prof. Rubens Chaves de Oliveira
(Co-Orientador)

_____
Prof. Jorge Luiz Colodette
(Orientador)

À Minha mãe Elizabete, que por muito tempo, mesmo sozinha, conseguiu me dar a melhor educação possível, tanto dentro de casa, mostrando valores, como em instituições de ensino. Meu muito obrigado!!!!!! Sem você isso nunca seria possível, tanto minhas conquistas até hoje, quanto aquelas que tenho certeza estão por vir nessa minha nova jornada na Finlândia e no mundo. Tenho certeza que entende a minha vontade de poder estudar no exterior, para poder retribuir ao máximo tudo que fez por mim. Te amo incondicionalmente !!!

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A todos vocês....

Dedico

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BIOGRAFIA

Marcelo Coelho dos Santos Muguet Soares nasceu em 14 de setembro de 1986, em Nilópolis, Rio de Janeiro.

Em Dezembro de 2003, concluiu o 2º grau no Alternativa Colégio, em Rio das Ostras, Rio de Janeiro.

Em Março de 2004, iniciou o curso de Engenharia Florestal, na Universidade Federal de Viçosa, sendo o mesmo concluído em julho de 2008.

Em Agosto de 2008, iniciou o curso de pós-graduação no nível de Mestrado Profissionalizante em Tecnologia de Celulose e Papel, na Universidade Federal de Viçosa, sendo o mesmo concluído em Dezembro de 2009.

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RESUMO

SOARES, Marcelo Coelho dos Santos Muguet, M.Sc., Universidade Federal de Viçosa, dezembro de 2009. **Métodos alternativos para deposição de xilanas em polpas de eucalipto.** Orientador: Jorge Luiz Colodette. Co-orientadores: Rubens Chaves de Oliveira e José Lívio Gomide.

Polpas kraft de eucalipto são amplamente utilizadas para papéis de imprimir e escrever (P&W). Papéis P&W necessitam de resistência para suportar o processo de produção e também de uso final. Não só a qualidade do produto final é importante, mas também se busca constantemente aumento na produção. O objetivo deste estudo foi avaliar uma nova técnica que alia ganhos de rendimento com ganhos em propriedades da polpa. Foi estudada a deposição de xilanas em polpas de eucalipto durante a deslignificação com oxigênio. Foram utilizadas três polpas industriais de eucalipto (duas polpas marrons e uma branqueada). As xilanas foram extraídas de polpa marrom ou branqueadas pelo processo CCE (*Cold Caustic Extraction* = Extração Cáustica a Frio). Os extratos contendo xilanas foram aplicados a uma amostra de polpa marrom na etapa de deslignificação com oxigênio. Estudaram-se os mais importantes parâmetros da deslignificação com oxigênio (tempo, temperatura e carga de álcali) e suas influências na deposição de xilanas. Foram realizados estudos estruturais das xilanas isoladas e seus efeitos na refinabilidade da polpa. Obtiveram-se altos níveis de deposição das xilanas extraídas de polpas branqueadas (WXL – White Xylans Liquor), independentemente das condições operacionais utilizadas na deslignificação com oxigênio. O nível de deposição das xilanas extraídas de polpa marrom (BXL – Brown Xylans Liquor) foi influenciado negativamente pelo aumento do pH da deslignificação com oxigênio. As polpas que receberam as xilanas WXL apresentaram melhores desempenhos nas operações de branqueamento e refino e melhores propriedades físicas em relação às extraídas de BXL. As xilanas WXL apresentam menos grupos laterais, o que influenciou positivamente as suas deposições e estabilidade durante o branqueamento e refino, resultando menores perdas em relação às xilanas BXL. Foi concluído que a deposição de xilanas na deslignificação com oxigênio apresenta viabilidade técnica, pois é efetiva e não requer grandes instalações/mudanças na linha de fibras. Porém a viabilização econômica depende da disponibilidade de xilanas de baixo custo,

extraídas, por exemplo, de resíduos agrícolas ou rejeitos fibrosos da indústria de polpa.

ABSTRACT

SOARES, Marcelo Coelho dos Santos Muguet, M.Sc., Universidade Federal de Viçosa, december, 2009. **Alternative methods of xylans deposition onto eucalyptus pulps.** Advisor: Jorge Luiz Colodette. Co-Advisors: Rubens Chaves de Oliveira and José Lívio Gomide.

Eucalyptus kraft pulps are widely used for printing and writing (P & W). P & W papers need strength to support the production process and also end-use. Not only the quality of the final product is important, but also the constantly search to increase the production. The aim of this study was to evaluate a novel technique that combines yield gains with paper properties gains. Xylans deposition onto eucalyptus pulp fibers during oxygen delignification was studied. Three industrial eucalyptus pulps (two Brown and one bleached). The xylans were extracted from brown and bleached pulps by the CCE process (Cold Caustic Extraction). The liquor containing large amounts of xylan was used instead of water in the oxygen delignification. The most important parameters of oxygen delignification (time, temperature and alkali) and their influence on deposition of xylans were studied. Structural studies of isolated xylans and its influence on the deposition levels and pulp refinability were carried out. High deposition levels of the xylans extracted from bleached pulp (WXL – White Xylans Liquor), regardless of the operational conditions used in the oxygen delignification. The deposition levels of the xylans extracted from brown pulp (BXL – Brown Xylans Liquor) was negatively influenced by increasing pH of oxygen delignification. The pulps treated with WXL showed better performance on bleaching and refining operations, as well as in paper properties. WXL xylans had less side groups, which positively influenced deposition levels and stability across bleaching and refining operations, resulting in lower losses comparing to the BXL xylans. It was concluded that xylans deposition during oxygen delignification shows technical feasibility, because it is effective and there is no need of big changes/additions to the fiberline. However, the economic viability depends on low-cost xylans availability, for example, from agricultural wastes or mill fibrous rejects.

INTRODUÇÃO GERAL

Polpas celulósicas branqueadas de eucalipto são utilizadas principalmente para a fabricação de papéis sanitários (*tissue*) e de impressão e escrita (*P&W* = *Printing and Writing*). As demandas de qualidade desses dois tipos de papéis são diferentes, sendo a natureza das polpas que lhes dão origem um fator determinante. As polpas destinadas aos papéis de P&W, de maior interesse para esse estudo, são refinadas antes de serem convertidas em papel e o custo desta operação tem impacto significativo no custo total de fabricação. O consumo de energia durante a refinação é muito influenciado pela qualidade da polpa, especialmente no que tange a sua morfologia e constituição química. Por exemplo, polpas de menor coarseness (morfologia) e maior teor de hemiceluloses (química) consomem menos energia durante a operação de refino.

A influência das hemiceluloses no processo de produção de polpa e nas propriedades do papel dela proveniente tem sido muito estudada (MOLIN e TEDER, 2002; ANNERGREN et al., 1962; SIHTOLA e BLOMBERG, 1975; SCHÖNBERG et al., 2001; SJÖBERG et al., 2002; ERIKSSON e SJÖSTRÖM, 1968; LAINE, 1996; LIITI et al, 2005; KERSAVAGE, 1973; KIM et al., 1975, BHADURI et al., 1995, PEDRAZZI et al., 2009). Além de aumentar o rendimento da linha de fibras, as hemiceluloses facilitam o refino da polpa e aumentam a quantidade de ligações entre fibras, resultando em ganhos de propriedades físicas e mecânicas do papel.

Muito se tem feito visando aumentar o conteúdo de hemiceluloses, principalmente de xilanas, das polpas de eucalipto (AURELL, 1965; HANSSON e HARTLER, 1969; YLLNER e ENSTRÖM, 1956, 1957; DANIELSSON, 2007). Estudos mostram que as xilanas dissolvidas no licor negro podem reprecipitar e serem readsorvidas durante a fase final do cozimento, porém isto já é conhecido há

muitas décadas (YLLNER e ENSTRÖM, 1956, 1957). Estudos também promovem a readsorção de xilanas em polpas já branqueadas (HANNUKSELA et al., 2002; HANNUKSELA et al., 2003; KHONKE et al, 2008), porém nenhum estudo relata a deposição de xilanas na linha de fibras, especialmente na deslignificação com oxigênio.

Novas técnicas para aumentar o teor de xilanas de polpas celulósicas, sem prejuízos das suas qualidades são desejáveis. O objetivo deste estudo foi desenvolver um novo conceito para a deposição de xilanas à polpa Kraft de eucalipto, na etapa de deslignificação com oxigênio. Nesta etapa, é possível controlar as principais variáveis que influenciam a adsorção de xilanas em polpas, que são pH, temperatura, tempo de reação e teor de xilanas. A técnica proposta é de fácil implementação em escala industrial, pois a maioria da infra-estrutura necessária à sua implementação já existe na maioria das fábricas de polpa kraft. A técnica tem potencial para aumentar o teor de hemiceluloses da polpa e o rendimento da linha de fibras, sem prejuízos das propriedades óticas, já que a deposição das xilanas ocorre previamente ao branqueamento da polpa.

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CAPÍTULO I

Xylans deposition onto eucalyptus pulp fibers during oxygen delignification. Part 1: the influence of NaOH charge, reaction time and temperature

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Key words: xylans, oxygen delignification, xylans deposition, fiberline yield gains

Abstract

Xylans deposition onto pulp fibers may improve fiberline yield and improve pulp quality for printing and writing paper grades. In this study a novel technique was proposed for xylan deposition onto eucalyptus kraft pulp by removing xylans from an external source and using the xylan rich extract in the oxygen delignification stage. Firstly, xylans were extracted from a bleached pulp, using a CCE (Cold Caustic Extraction) stage. Secondly, the xylans were precipitated by reducing the pH extract pH to 5 and then added into the oxygen delignification reactor, replacing water. The impact of reaction time (30-60min), temperature (85 - 105^{o}C) and alkali charge (10-30 kg/odt NaOH) on xylan deposition was investigated. It was concluded that xylan deposition was highly efficient regardless of the reactor operational conditions. Within the range studied there were no visible effects of time, temperature and alkali charge on the amounts of xylan deposited. Oxygen delignification yield gains of 5.6-8.5 % were achieved and they were solely derived from the xylan added weight.

Introduction

Xylans deposition seems to be an interesting technique aimed at improving fiberline yield and producing printing and writing (P&W) paper grade pulps of higher quality. The concept of xylans deposition involves a loss of solubility. Linder et al. (2003) proposed a mechanism of assembly of xylan onto cellulose surfaces. Xylans exist in solution both as dissolved single molecules and as aggregated structures. It seems that xylans tend to exist more in the aggregated form than in single molecules. The xylans molecules tend to associate through interactions between the unsubstituted part of the chain. Furthermore, xylans have aromatic substituents, which are covalently bound to lignin residues, favoring hydrophobic interactions that favor aggregation. On the other hand, 4-O-Me-Glucuronic acids negatively charged tend to increase repulsion, favoring dissolution. The higher the number and size of the aggregates the lower seems the xylan solubility, favoring the diffusion to the surface. Henriksson and Gatenholm (2001) stated that the assembly process can be driven by other factors. One important factor is the strong affinity between xylan and cellulose, where the two polysaccharides have suitable hydrogen bonding sites so that hydrogen bonding between them is likely to occur. Many attempts have been made to increase xylan content in pulp fibers, especially during the cooking process (AURELL, 1965; HANSSON and HARTLER, 1969; YLLNER and ENSTRÖM, 1956, 1957; DANIELSSON, 2007). Hemicelluloses deposition takes place in higher extent at low hydroxide ion concentration (AURELL, 1963, 1965; HANSSON and HARTLER, 1969; YLLNER and ENSTRÖM, 1957). At low electrolyte concentration the adsorption is favored if the chemical affinity of the polymer to the surface is high (ÖSTERBERG et al., 2001). Danielsson (2007) also studied the effect of hydroxide ion concentration and reached the same results. One explanation is that the partly deprotonized hydroxyl groups on xylans, with a pK_a close do 14 at room temperature, become protonized when the hydroxyl ion concentration drops, decreasing their solubility, thus favoring the deposition. Ribe et al. (2009) ensure that at low media pH, hemicelluloses deposition occurs in greater extent. In addition, temperature seems to play an important role regarding xylans deposition. Both pK_a and pH can be affected by temperature variations. When temperature is increased, pH and pKa is decreased, leading to a slight increase in adsorption. This was confirmed by Danielsson (2007), using same conditions, only varying the temperature. Many studies (RIBE et al., 2009; KÖHNKE et al., 2008, KÖHNKE and GATENHOLM, 2007, DANIELSSON, 2007) also show that xylans deposition increases with reaction time, but the highest rate occurs at the beginning of the reaction.

In this study, a novel approach to xylans deposition is offered. The xylans are deposited during the oxygen delignification stage. The xylans were extracted from an external source and the influence

of the main oxygen delignification reaction parameters such as NaOH charge, reaction time and temperature was investigated.

Materials

In this study, one brown and one bleached *Eucalyptus spp.* kraft pulps were used. The bleached pulp was used for the xylans extraction and the brown pulp was used for the deposition experiments. Both pulps came from an industrial source and are characterized in Table 1.

Table 1*:* Characteristics of the original pulps.

Characteristics	Brown Pulp	Bleached Pulp
Kappa number	13.9	0.9
Viscosity (kg/dm^3)	1318.4	858.5
Brightness (%ISO)	42.9	90.0
Xylans Content (% on pulp)	14.0	16.5
HexA's (mmol/kg)	51.9	9.3

Methods

Pulp characterization

The original pulps and the ones after the xylan deposition experiments were evaluated for their kappa number, viscosity and brightness according to T236 om-06, T230 om–08, and T452 om-08 in Tappi standard procedures, respectively. Pulp xylan contents were measured by HPLC-PAD after acid hydrolysis, following the procedure described by WALLIS et al, 1996. Pulp HexA's content was measured according to Vuorinen et al., 1996. All analyses were made with two repetitions.

Xylans extraction from pulps

The xylans were extracted from the bleached eucalyptus pulp sample, using a CCE (Cold Caustic Extraction) stage. A charge of 240 g of sodium hydroxide was applied to 300 g o.d. (oven dried) pulp, at a 10% consistency. The experiment was run during 30 minutes, at 25 ºC. Following, the liquor was separated from pulp fibers using a centrifuge and the liquid phase was collected in a proper recipient. This liquor from now on referred as "white xylan liquor - WXL" was then stored in a freezer for further use. The fibrous residues were discarded. Many extractions were made in order to collect enough extract for further use in the oxygen delignification experiments.

Liquor Characterization

The liquors were evaluated for their sugar concentrations. A 10 ml liquor sample was hydrolyzed with 3 ml of H_2SO_4 72% during 60 minutes at 30^{o}C. After, this solution was diluted to 84 ml with deionized water and autoclaved during 60 minutes. After autoclaving, the liquors were filtrated off. The filtrate was diluted to 250 ml and stored. A sample of 2,5 ml of the filtrate was diluted 20 times and injected in an HPLC according to Wallis et al (1996), using fucose as internal standard. All analyses were made with two repetitions.

Xylans Deposition

Xylans deposition was carried out during the oxygen delignification. 1500 ml of WXL were neutralized with concentrated sulfuric acid until pH 5 ± 0.1 that is near distilled water pH, in order to precipitate the xylans inside the liquor. The extract with the precipitated xylans were added to 250 g o.d. of the brown pulp in a mixer/reactor Mark V (Quantum technologies), reaching 10% of consistency. The following fixed conditions were used in the oxygen delignification stage: 408 kPa pressure, 20 kg O_2/odt (oven dried ton of pulp).The reaction time (30 and 60 min), temperature (85, 95 and 105^{o}C) and alkali dose (10, 20 and 30 kg/odt) were varied within the range usually applied in the oxygen delignification stage. The experiments were carried out with two repetitions. After the

deposition experiments, the pulps were thoroughly washed and evaluated for their kappa number, viscosity, brightness and xylan content, according to methods aforementioned.

Results and discussion

Xylan Extraction Studies

The cold caustic extraction (CCE) extraction treatment was highly effective in removing xylans from the bleached kraft pulp. About 95,3% of the xylans were extracted under industrially used conditions (800kg NaOH/odt, 30 minutes, and 25 ^{o}C). The xylan concentration in the extract was 17.5 g/L and the final pH 13.7. The fully bleached pulp used to obtain the xylans contained no detectable amounts of lignin and therefore no lignin was present in the extracts. The c.a. 0.5 kappa number measured in the pulp was likely comprised of hexenuronic acids. Due to the low temperature used in the CCE stage, no cellulose was removed from the pulp as seen by the non-detectable level of glucans in the extract. The high selectivity of the CCE treatment for xylans warrants a pure material for deposition, which is desirable.

Effect of oxygen delignification reaction conditions on xylans deposition

The main oxygen delignification variables are alkali and oxygen charges, and reaction time, temperature, pressure and consistency. Only the variables alkali charge (10, 20 and 30 kg/odt), and reaction time (30 and 60 min) and temperature (85, 95 and 105^{o}C) were evaluated in the xylan deposition experiments. These variables were chosen for their higher likelihood of affecting xylan deposition in relation to others. However, further studies on the effects of oxygen dose, and reaction pressure and consistency are recommended.

Alkali charge

The results presented in Figure 1 indicate that WXL charge within the range of 10-30 kg NaOH/odt has no significant effect on xylan deposition. The original brown pulp contained 14% xylans and after the deposition procedures across oxygen delignification the pulp xylan contents increased to a range of 19.2-20.9%. Thus, the deposition process was highly efficient since 5.2-6.9% xylans were deposited over the fibers under the various conditions of time, temperature and alkali dose. However, the alkali dose, in the range of 10-30 kg/odt, which is typical of oxygen delignification, had negligible effect on the amount of xylan deposited. The slope of the curves shown in Figure 1 is small and presents no clear trend in this range of alkali doses. These results were somewhat expected considering the old concept that xylans start to precipitate at a pH around 13.2. Since all alkali doses used were not sufficiently high to reach the threshold pH in which xylans become soluble, the no effect of alkali is justified. Figure 2 show that final reaction pH varied in the range from 8.5 to 12.5 depending upon oxygen delignification operational conditions. This result is quite significant for it warrants a quite flexible operation of the oxygen delignification in regard to alkalinity.

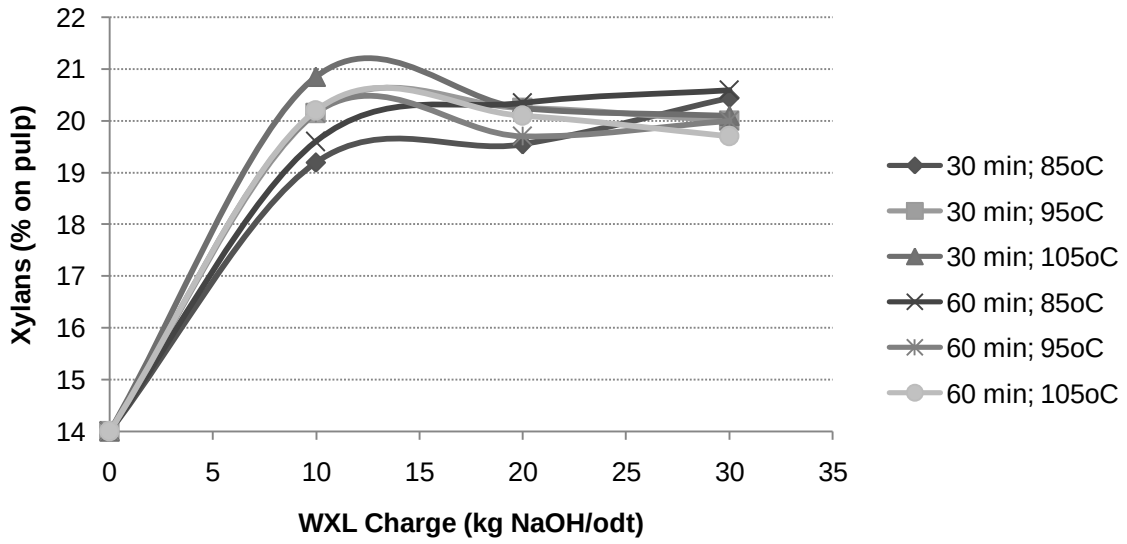

Figure 1: The effect of WXL assisted oxygen delignification alkali charge on final pulp xylan content. WXL is a solution 80g/L NaOH, containing 17,5 g/L xylans.

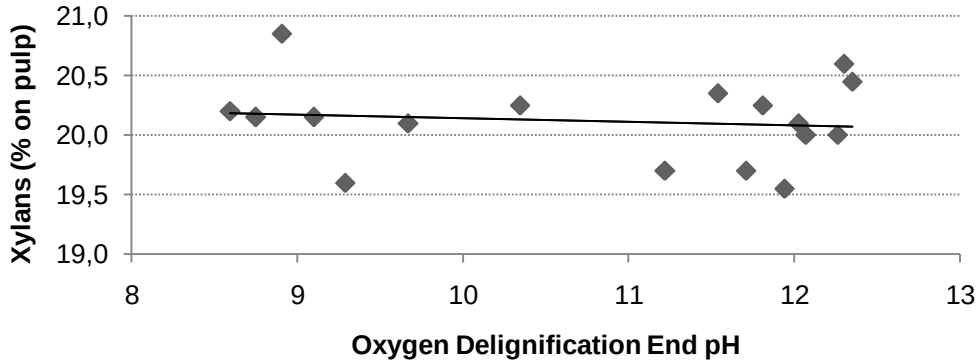

Figure 2: The influence of WXL assisted oxygen delignification end pH on final pulp xylan content. WXL is a solution 80g/L NaOH, containing 17,5 g/L xylans.

Effect of reaction time and temperature

Figure 3 shows the effect of reaction time and temperature on xylan deposition during WXL assisted oxygen delignification. It is seen that deposition increases with increasing reaction time from 30 to 60 min but this is true only for the 85^{o}C temperature. For the 95 and 105 ^{o}C temperatures, increasing reaction time had either no effect or a negative effect on xylan deposition. The positive and negative effects are quite small, however. Reaction temperature also had some effect on xylan deposition. The largest xylan deposition value (6.9%) was achieved at 105 ^{o}C, 10kg NaOH/odt during 30 min reaction and the lowest at 85 ^{o}C, 10kg NaOH/odt during 30 min (5.2%). However, the temperature effect was somewhat erratic and dependent upon the other variables. For example, for the alkali dose of 30 kg NaOH/odt, the lowest xylan deposition was achieved at 105^{o}C whereas the highest occurred at 85^{o}C.

It is worth noting that the observed effects of time and temperature on xylan deposition were generally small within the range of values investigated. It is possible that more significant effects of these variables could have been seen if higher/lower values have been tested, but those would not be of interest for this work given the narrow range of time and temperature that can actually be used in the oxygen delignification stage.

Other workers (DANIELSSON, 2007, studying xylans deposition during cooking in the temperature range of 140 to 160^{o}C and RIBE et al, 2009 studying xylans deposition onto unbleached

pulps in the temperature range of 86 to 127°C) have shown a positive effect of temperature on xylans deposition.

The possible interactions among alkali charge and reaction temperature and time were statistically investigated through the F-test. At the 5% significance level, no significant interactions among the three variables were observed, considering the levels studied. In other words, the xylan deposition values were statistically equal for the factorial combinations of alkali charge, temperature and time (Table 2).

Table 2: Statistical results for the factorial experiment

	SS	Degr.	MS	F	p
Intercept	14496,16	1	14496,16	266256,0	0,000000
Time	0,02	1	0,02	0,3	0,574776
Temperature	0,36	2	0,18	3,3	0,059188
Alkali	0,10	2	0,05	0,9	0,411333
Time*Temperature	1,17	2	0,59	10,7	0,000847*
Time*Alkali	0,03	2	0,01	0,2	0,781460
Temperature*Alkali	3,29	4	0,82	15,1	0,000014*
Time*Temperature*Alkali	0,51	4	0,13	2,4	0,091897
Error	0,98	18	0,05		

The interactions time vs. temperature and temperature vs. alkali showed significance, but it was due to the low result obtained by the following condition: 30 minutes, 85 °C and 30 kg NaOH/odt, dislocating the mean, but when mean Tukey test was carried among them, all means were statistically the same, corroborating the result obtained to the parameters evaluated alone, and the interaction among the three of them.

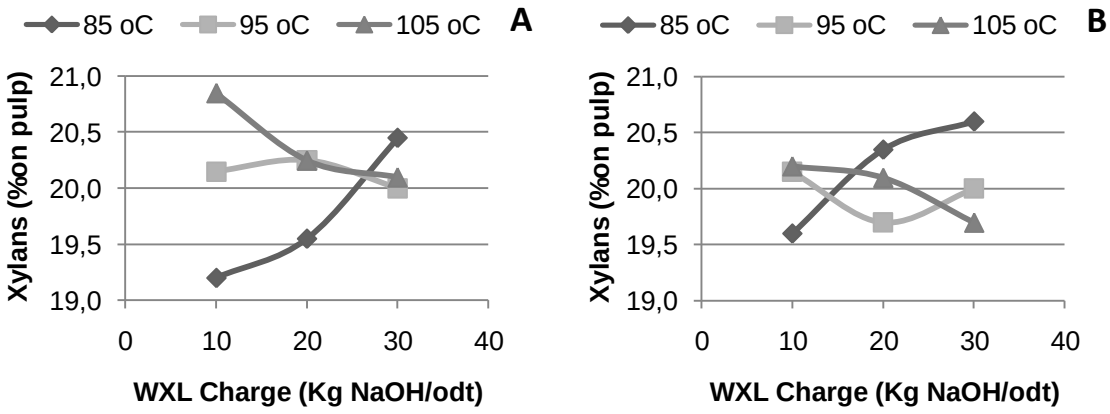

Figure 3: Effect of WXL assisted oxygen delignification reaction time (A – 30 minutes and B – 60 minutes) and temperature on final pulp xylan content. WXL is a solution 80g/L NaOH, containing 17.5 g/L xylans.

Oxygen delignification performance

The fact that xylans were deposited during the oxygen delignification reaction had no impairment on process performance (Table 3). Table 3 shows a comparison between oxygen delignification experiments carried out with pure NaOH and with the WXL liquor containing dissolved xylans. Overall, the oxygen delignification efficiencies measured by kappa drop and brightness gain were similar in the two cases, suggesting that xylans do not affect the oxygen reactions, at least at the level investigated (6.1%). On the other hand, viscosity drop was quite significant in the experiment with WXL, a result that can be explained by the low molecular weight of the xylans that were deposited in comparison with those of the cellulose chains. The viscosity drop was totally related to the xylans deposited. The difference in final pH can be related to the high ionic strength created when dropping the pH for the preparation of the WXL used for the oxygen delignification experiments.

The results of Figure 4 show that alkali charge, time and temperature affect significantly the oxygen delignification process as anticipated. When the condition of lowest time, temperature and alkali was used, the kappa removal across the O-stage was about 10% only, with the opposite being observed when the highest range of conditions was used (30% of kappa removal).

Table 3: Comparison between the oxygen delignification carried with pure NaOH and with WXL (solution 80g/L NaOH, containing 17.5 g/L xylans)

	O_2 Delignification with Pure NaOH	**O_2 Delignification with WXL**
Kappa In	13.9	13.9
Viscosity In, kg/dm^3	1318.4	1318.4
Brightness In, % ISO	42.9	42.9
Alkali charge, % NaOH	2.0	2.0
Oxygen charge, % O_2	2.0	2.0
Temperature, ^{o}C	105	105
Time, min	60	60
Consistency, %	10	10
Pressure, kPa	408	408
Kappa Out	9.7	9.9
Viscosity Out, kg/dm^3	1193.9	1015.2
Brightness Out, %ISO	53.3	52.9
Final pH	11.4	9.7
Xylans Deposited, %	0.0	6.1
Yield Gain, %	0.0	6.1
Kappa Drop, %	30.2	28.6
Viscosity Drop, %	9.4	23.0
Brightness Gain, % ISO	10.4	10.0
Selectivity, K drop/Visc. Drop	3.20	1.25

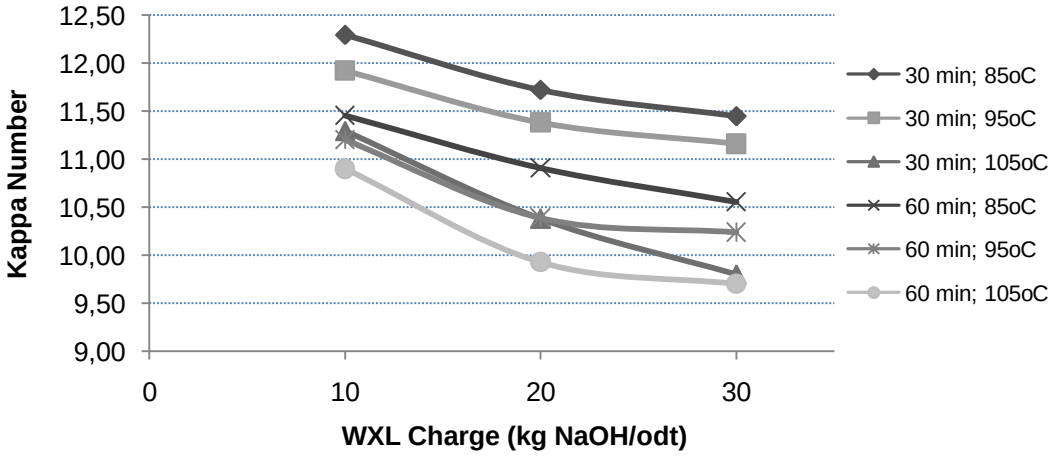

Figure 4: The effect of alkali charge and reaction time and temperature on pulp kappa number measured after the WLX assisted oxygen delignification stage. WXL is a solution 80g/L NaOH, containing 17,5 g/L xylans.

The same trend aforementioned for kappa number was also encountered for pulp viscosity (Figure 5). In other words, pulp viscosity tended to decrease with increasing oxygen delignification conditions severity. It is known that xylan content affects pulp viscosity substantially because xylans are short chain carbohydrates compared to cellulose. However, the variation in pulp xylan content (19.2-20.9%) in this case was not sufficiently high to cause significant changes in pulp viscosity.

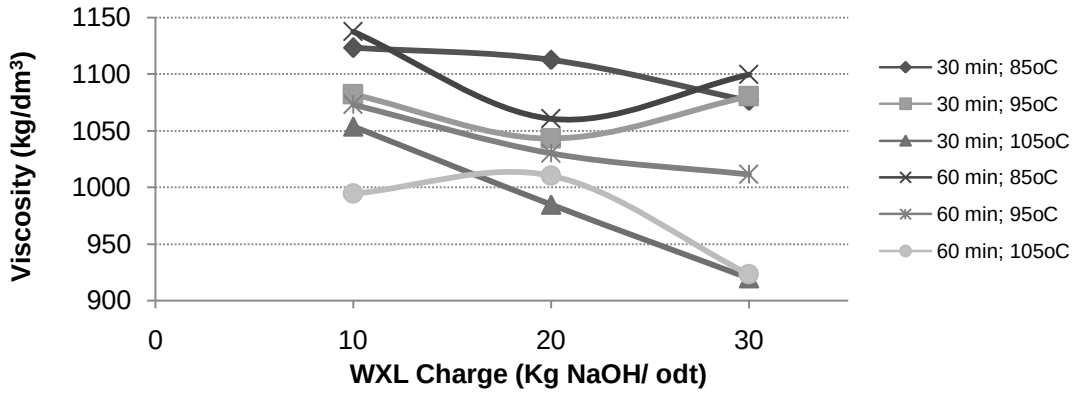

Figure 5: The effect of alkali charge and reaction time and temperature on pulp viscosity measured after the WXL assisted oxygen delignification stage. WXL is a solution 80g/L NaOH, containing 17.5 g/L xylans

There were significant effects of alkali charge and reaction time and temperature on brightness, with the largest benefits being achieved at the highest range of the conditions evaluated (Fig. 6). Pulp brightness gain across oxygen delignification tends to correlate inversely with kappa number drop. This trend was observed in this study (Fig. 4 *vs* Fig. 6) and indicates that the excess xylan present in the system does not change the oxygen delignification reaction pathways.

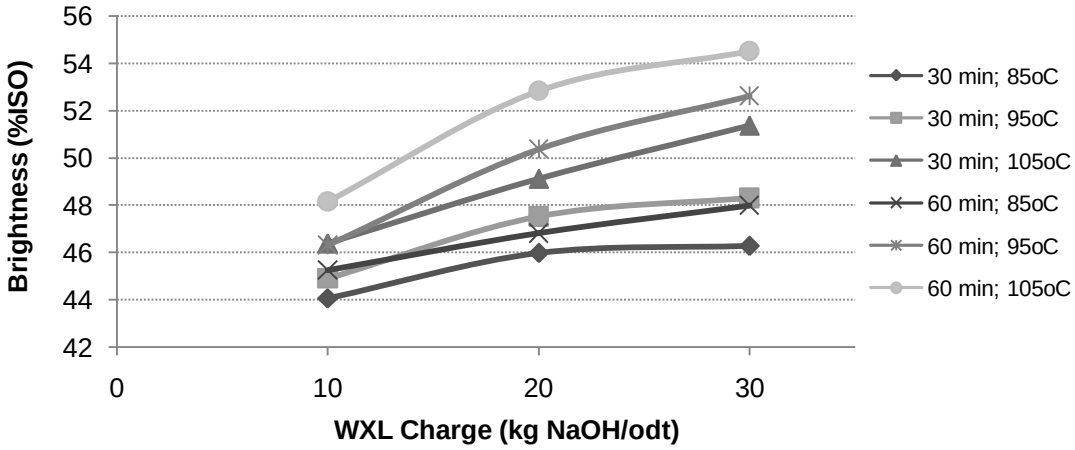

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Figure 6: The effect of alkali charge and reaction time and temperature on pulp brightness measured after the WXL assisted oxygen delignification stage. WXL is a solution 80g/L NaOH, containing 17.5 g/L xylans.

Figure 7 shows the effect of O-stage operation conditions on final pH. As expected, the highest final pH was achieved at the 30 kg/odt alkali charge, 30 min reaction and 85^{o}C. At the lower time and temperature, less alkali is consumed during the O-stage.

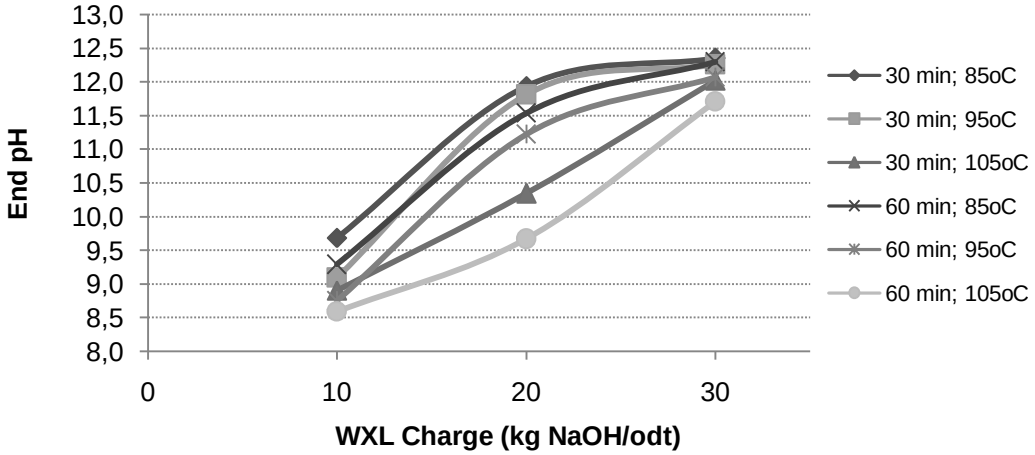

Figure 7: The effect of alkali charge and reaction time and temperature on pulp end pH, measured after the WXL assisted oxygen delignification stage. WXL is a solution 80g/L NaOH, containing 17.5 g/L xylans.

Potential Fiberline Yield Gains

The oxygen delignification stage of eucalyptus pulps usually causes yield drops in the range of 1.5-2.0%. This drop derives from lignin removal (~1%) and the remaining comes from low molecular weight carbohydrate dissolution, particularly xylans. However, when xylans were deposited from the WXL during oxygen delignification, significant yield gains were attained. Gains in the range of 5.2-6.9%. were achieved for the various conditions of alkali charge, time and temperature investigated. These gains were much in line with the xylan deposition values reported in Figure 3. By discounting the typical O-stage yield losses from the amount of xylan deposited onto the fibers one can determine approximately derive the yield gains.

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Conclusions

Xylans deposition onto pulp fibers was affected only slightly by alkali dose, reaction time and temperature in the range of 10-30 kg NaOH/odt, 30-60 min, 85 - 105^{o}C, respectively. Under these conditions xylan deposition in the range of 5.2-6.9% were achieved. These levels of xylan deposition represented the same oxygen delignification yield increasing. These gains in xylan content and yield shows the feasibility of the process, which can be carried in oxygen delignification stages existing in pulp mills. Other advantages include the production of pulp containing high xylan content for certain special applications. This subject will be discussed in more details in the next chapters.

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CAPÍTULO II

Xylans deposition onto eucalyptus pulp fibers during oxygen delignification. Part 2: novel approach and the influence of xylans' structure

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Key words: xylans, oxygen delignification, xylans deposition, fiberline yield gains

Abstract

Eucalyptus fibers are largely used for printing & writing (P&W) paper grades. Pulps for P&W papers require significant refining and can benefit from a high content of xylans, which purportedly facilitate this operation. Pulps derived from eucalyptus grown in Brazil contain low xylan content in relation to other hardwoods. This study investigated a novel alternative to improve eucalyptus pulp xylan content through deposition of this polymer across the oxygen delignification stage. Reaction pH was the only variable evaluated in the oxygen stage, with the remaining kept constant and similar to industrial practice. Firstly, xylans were extracted from commercial brown and bleached pulps by means of the so-called CCE (cold caustic extraction) process. Secondly, the extracted xylans were added to a commercial brown pulp while still in the caustic solution. Xylans deposition occurred in the same extent, regardless of pH in the range of 10-13 using the liquor extracted from the bleached pulp (WXL – White Xylans Liquor), whereas pH affected significantly the deposition of xylans extracted from brown pulp (BXL – Brown Xylans Liquor). Xylans deposition increased as the BXL pH decreased. For all conditions tested, the xylans from the WXL deposited in greater extent than the ones from BXL. The deposition process, resulted pulps containing 6.1 % more xylans than the reference, with an equivalent yield increase. Scanning Electron Microscopy images showed the presence of aggregates and webs formed by the deposited xylans. Xylans extraction by CCE with subsequent deposition in the oxygen delignification is an interesting technique to manufacture eucalyptus pulps of high xylan content. The process show potential for it needs no additions/modifications of current pulp mill installations.

Introduction

Eucalyptus fibers are largely used for printing & writing (P&W) paper grades. Pulps for P&W papers require significant refining and can benefit from a high content of xylans, which purportedly facilitate this operation. 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. It is well known that hemicelluloses contribute significantly to pulp fiber bonding strength (LEOPOLD and MCINTOSH, 1961; PETTERSSON and RYDHOLM, 1961; SPIEGELBERG, 1966; KETTUNEM et al., 1982). These hemicelluloses are present in the whole extension of the fiber wall, both on the fiber surface, and in the innermost layers (BACHNER et al, 1993; MOBARAK et al, 1973; SCHÖNBERG et al, 2001).

Many attempts have been made to increase xylan content in pulp fibers, especially during the cooking process (AURELL, 1965; HANSSON and HARTLER, 1969; YLLNER and ENSTRÖM, 1956, 1957; DANIELSSON, 2007). Xylans are soluble and easily removed in the kraft process due to their significant amounts of acetyl groups and amorphous structure. The partial degradation and dissolution of hardwood xylans during alkaline pulping consumes reagents and decreases pulp yield (CLARK, 1985). These xylans that are dissolved in the black liquor are thought to be precipitated onto the fibers (YLLNER e ENSTRÖM, 1956). The xylans deposition during the cooking process increase both yield and tensile strength (DAHLMAN et al., 2003; DANIELSSON and LINDSTRÖM, 2005, CLARK, 1985). Danielsson (2005) studied xylans deposition during kraft pulping and observed that pulps containing precipitated xylans of low and high Mw were stronger than the reference, which did not receive the black liquor enriched with xylans.

Other workers have tried to increase pulp xylan contents in lab scale through their addition on bleached pulp (KÖHNKE and GATENHOLM, 2007). Xylans deposition onto bleached pulps has been shown to occur in both external surface and inner layers of the fiber (MITIKKA-EKLUND, 1996; SCHÖNBERG et al., 2001; LINDER and GATENHOLM, 2004). So, it is reasonable to assume that xylans deposited on never dried bleached pulp would act as "native xylan" upon drying and function as stabilizers of the cellulose fibrils, thus preventing aggregation/hornification (KÖHNKE and

GATENHOLM, 2007). This method is cumbersome since it would require highly purified xylans of very high production costs. Furthermore, xylan addition to bleached pulp reduces its brightness, thus requiring an extra bleaching stage with low reagents charges to restore it and reach the commercial values.

This study offers a novel approach to xylans deposition onto eucalyptus pulp fibers. The xylans are deposited during the oxygen delignification stage, with no purification requirements after they are extracted from an external source. Both the xylan extraction from an external source and their deposition onto kraft pulp during the O-stage are discussed in this paper.

Materials

Two brown (A and B) and one bleached (C) by the sequence O/O-D(EP)DP *Eucalyptus spp.* kraft pulps were used. Samples A and C were used as source of xylans for the extraction studies. Sample B was used as base material for the xylan deposition studies. All pulps samples originated from an industrial source. The characteristics of the pulps are shown in Table 1.

Table 1*:* Initial characteristics of the pulps samples

Characteristics	A	B	C
Kappa number	14.0	13.9	0.9
Viscosity (kg/dm^3)	1105.7	1318.4	858.5
Brightness (%ISO)	39.5	42.86	90.0
Xylans Content (% on pulp)	16.5	14.0	16.5
HexA's (mmol/kg)	52.2	51.9	9.3

Methods

Pulp characterization

The original pulps and the ones after the xylan deposition experiments were evaluated for their kappa number, viscosity and brightness according to T236 om-06, T230 om–08, and T452 om-08 in Tappi standard procedures, respectively. Pulp xylan contents were measured by HPLC-PAD after acid hydrolysis, following the procedure described by WALLIS et al 1996. Pulp HexA's content was measured according to Vuorinen et al., 1996. All analyses were made with two repetitions.

Xylans extraction from pulps

The xylans were extracted from the bleached and brown eucalyptus pulp sample, using a CCE (Cold Caustic Extraction) stage. A charge of 240 g of sodium hydroxide was applied to 300 g o.d. (oven dried) pulp, at a 10% consistency. The experiment was run during 30 minutes, at 25 ºC. Following, the liquor was separated from pulp fibers using a centrifuge and the liquid phase was collected in a proper recipient. The liquor extracted from the bleached pulp (C), from now on referred as "white xylan liquor - WXL" and the liquor extracted from the brown pulp (A) from now on referred as "brown xylan liquor - BXL" were then stored in a freezer for further use. The fibrous residues were discarded. Many extractions were made in order to collect enough extract for further use in the oxygen delignification experiments.

Liquor Characterization

The WXL and BXL liquors were evaluated for their sugar concentrations. A 10 ml liquor sample was hydrolyzed with 3 ml of H_2SO_4 72% during 60 minutes at 30^{o}C. After, this solution was diluted to 84 ml with deionized water and autoclaved during 60 minutes. After autoclaving, the liquors were filtrated off. The filtrate was diluted to 250 ml and stored. A sample of 2,5 ml of the filtrate was diluted 20 times and injected in an HPLC according to Wallis et al (1996), using fucose as internal standard. All analyses were made with two repetitions.

Xylans Characterization

The xylans were isolated according to Teleman (1995) with slight modifications. 100 ml of each liquor were mixed with 200 ml of 1,4-dioxane and glacial acetic acid under mixing. The solution was covered and allowed to stand for two days under refrigeration. The clear solution was decanted and the precipitated was transferred to a centrifuge tube. After centrifugation (15 min at 2500 rpm), the precipitated was successively washed with 20 ml portions of 1,4-dioxane-water (2:1), 1,4-dioxane, methanol and acetone. The precipitated was dried inside a dissecator with silica gel blue, under vacuum with portions of diphosphorus pentoxide, until constant weight. The isolated xylans were characterized for their sugar composition exactly as described above for the liquors, but instead of using 10 ml of liquor, 300 mg of the xylans were used. The isolated xylans were characterized for their M_w distribution using size exclusion chromatography (SEC) according to PINTO et al (2005). All analyses were made with two repetitions.

Xylans Deposition

The oxygen delignification time and temperature conditions (60 min. at 105 ^oC) were chosen on the basis of the experiments discussed in chapter 1, which took into account O-stage efficiency (kappa drop), selectivity (viscosity drop), brightness gain and yield. The alkali charges were varied in this study so that pH values in the range of 10-13 were reached. The difference among the experiments discussed in chapter I and the ones discussed here were that in this case the alkaline xylan extracts were not neutralized to pH 5, with the alkalinity existing in the extracts serving as the alkali source for the oxygen delignification stage. 1500 ml of each xylans liquors (WXL and BXL) were neutralized with concentrated sulfuric acid until different pH: 10.0 ± 0.1, 12.0 ± 0.1, 12.5 ± 0.1 and 13.0 ± 0.1, totalizing 8 samples. The initial NaOH charges measured by titration were: pH 10 = 0.15 kg/odt; pH 12 = 25 kg/odt; pH 12,5 = 70 kg/odt; pH 13 = 150 kg/odt. The xylans liquors were added to 250 g o.d. (oven dried) of sample B in a mixer/reactor Mark V (Quantum technologies), reaching a consistency of 10%. The following fixed conditions were used in the oxygen delignification stage: 500 kPa pressure, 20 kg O_2/odt (oven dried ton of pulp). The reference followed the same conditions, except that sodium hydroxide solutions at the same initial pHs were used instead of xylan extraction liquors. After xylan deposition experiments, the pulps were evaluated for their kappa number, viscosity, brightness and xylans content according to methods aforementioned.

Scanning Electron Microscopy (SEM) images

Fine paper hand sheets (Grammage of 50 g/m^2) were prepared from reference and xylan treated pulp samples. They were pressed and dried according to Tappi standard method T205 sp-95. The samples were coated with gold using SEM Electron Microscopy Sciences model 550X. The samples images were acquired with A SEM microscopy LEO model 1430VP, operating at 11 kV. None of the images were modified with photo manager softwares.

Results and discussion

Xylans Extraction and Characterization

Table 2 shows that the CCE treatment was more effective in removing xylans from the bleached pulp (sample C) than from the brown pulp (Sample A). It can be seen that 95,3% of the xylans were removed from the bleached pulp (C), while only 85,3% of the xylans were removed from the brown pulp (A). This result is corroborated by the presence of higher xylan concentration (Table 3) in the liquor extracted from the bleached pulp (WXL) in comparison to that extracted from the brown pulp (BXL). This is likely explained by complexes lignin-carbohydrate (LCC) existing in the brown pulp. While xylans and lignin are very alkali soluble, LCC's are less soluble. Thus, removal of xylans linked to lignin is more challengeable than pure xylan. The CCE treatment removed significant amounts of lignin from the brown pulp. The value of 0.75 % on pulp lignin found in the BXL is equivalent to a kappa removal of 5 units (Table 3). The pulp sample A lost 10 kappa units across CCE, from 14 to 4,5. Since only 5 units came from lignin, the remaining is attributable to HexA and LCC removal. Approximately four units derived from HexA that dropped from 52.2 mmol/kg (5.2 kappa units) to 10.3 (1 kappa unit). Thus, the remaining one unit likely derived from LCC's.

Table 2: Characteristics of pulp A and C after the CCE stage

Characteristics	A	C
Kappa number	4,5	0.1
Xylans Content (% on pulp)	2.7	0.9
HexA's (mmol/kg)	10.3	0.9
Xylans Extraction yield (%)	85.3	95.3

Table 3: BXL and WXL liquor composition and Characterization

	Glucans (g/L)	Xylans* (g/L)	Lignin (g/L)	pH
WXL	ND**	17,47	0.00	13.7
BXL	ND**	15,82	0.92	13.6

*considering only the xylose backbone
**Not Detected

The xylans isolated from the WXL showed lower M_w, bound lignin and uronic acids than the ones isolated from the BXL (Table 4). The lower Mw of xylans extracted from bleached pulp is explained by oxidation effects occurring during bleaching, particularly in the oxygen delignification stage. The lower lignin content of the WXL was obvious since the original pulp from which the xylans were extracted was previously bleached. The lower uronic acids (UA) content was also expected, since some bleaching stages effectively remove them. On the other hand, xylans isolated from the BXL were only modified by the pulping process. The decrease in uronic acids (UA) across bleaching was also found by Dahlman et al. (2003) in hardwoods pulps.

Table 4: BXL and WXL isolated xylans fraction composition and characterization

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	19.085
WXL	1.76	92.2	5.68	0.00	0.33	0.062	15.127

*considering only the xylose backbone

Xylans deposition

Xylans deposition occurred in all cases, in minor or greater extent (Fig. 1). Different patterns have occurred between the BXL and the WXL xylan deposition. Many studies suggest that hemicelluloses deposition onto fibers is more efficient at low pH values (AURELL, 1963, 1965; HANSSON and HARTLER, 1969; YLLNER and ENSTRÖM, 1957; RIBE et al, 2009, DANIELSSON, 2007). 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. On the other hand, the media pH did not affect WXL xylans deposition. The presence of lignin in the BXL liquor seemingly disturbed xylans deposition at the higher pH range (>12). This theory is supported by Westbye et al. (2007) who claim that xylans can interact with soluble lignin by phenolic groups bound on its backbone. The fact that lignin was found in the extracted xylan preparation (Table 3) corroborates this claim. With decreasing pH the xylans and soluble lignin tend to assemble forming aggregates, which then start to precipitate onto the fibers. On the other hand, there is no lignin bound to the xylans present in the WXL; thus, xylans tend to self-assemble, regardless of pH value in the range from 10 to 13.

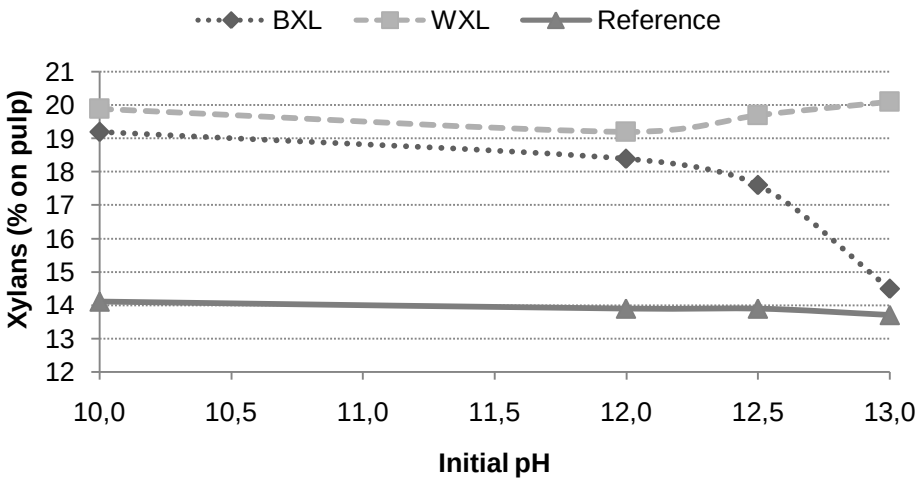

Figure 1: Effect of oxygen delignification starting pH on xylan deposition onto base pulp (sample B) for processes with addition of brown pulp xylans (BXL), white pulp xylans (WXL) and no xylans (REF).

The UA/xylan ratio seemingly affects xylans deposition. Linder et al. (2003) proposed a mechanism where uronic acids, that are negatively charged, seem to repulse one xylan chain from another, preventing formation of aggregates. It can be seen that xylans with lower uronic acids (WXL) deposited in greater extent. These results are in accordance with Danielsson (2007) who found that eucalyptus xylans with lower uronic acids substitution tend to form bigger aggregates and deposit onto fibers in larger quantities.

When referring to M_w, molecules with lower M_w tend to deposit more efficiently onto fibers due to high entropy. Smaller molecules tend to have better conformation, thus attaching better to each other, forming bigger aggregates and then depositing in greater extent. The xylans isolated from the WXL had lower M_w, and deposited more effectively. Pinto et al., 2005 showed that during pulping M_w decreases with decreasing uronic acids content, corroborating the results found for BXL and WXL isolated xylans.

The quantitative deposition values are shown in Figure 2. The WXL deposition occurred in higher extent regardless of pH value. The higher xylans concentration and chemical structure of WXL extract when comparing with BXL extract (Table 2) were the responsible for such results.

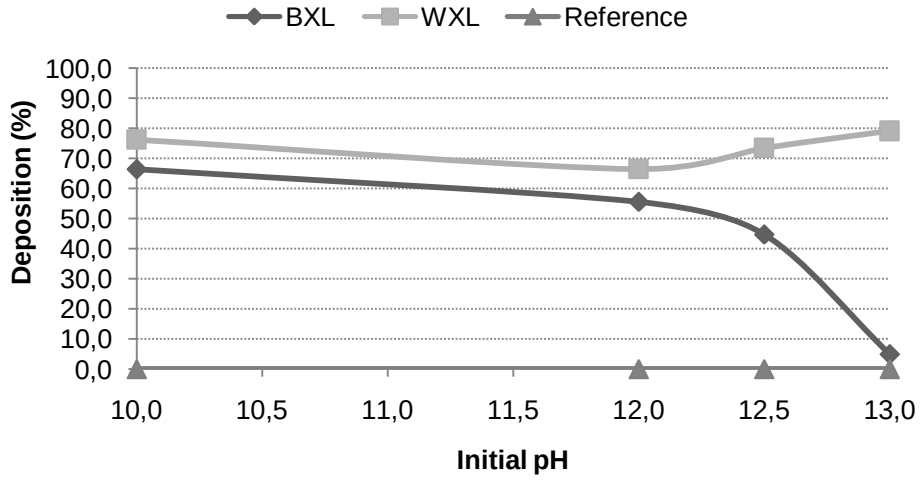

Figure 2: Deposition values expressed in percentage for processes with addition of brown pulp xylans (BXL), white pulp xylans (WXL) and no xylans (REF).

Impact of xylans deposition on oxygen delignification performance

The impact of xylan deposition (BXL and WXL) on end pH and pulp kappa number, brightness and viscosity as a function of the initial pH of the oxygen delignification are shown in Figures 3a-d. The reaction end pH correlated well with the initial pH as anticipated. No significant effect of the WXL and BXL xylan deposition on end pH was observed (Fig. 3a). This is an indication that reactions between

xylans and oxygen delignification chemicals (NaOH and O_2) are negligible. On the other hand, the presence of lignin in the xylan extract affected oxygen delignification efficiency, since the pulps treated with the BXL showed higher kappa numbers (Fig. 3b) and lower brightness (Fig. 3c) than those treated with WXL and reference. The xylan deposition with both BXL and WXL extracts resulted in decreased pulp viscosity due to the low molecular weight of these hemicelluloses in relation to cellulose (Fig. 3d). At the starting pH of 12, the viscosity of the xylan treated pulp was 70% lower than that of the reference. The xylan deposition increases pulp xylan/cellulose ratio, thus diminishing overall viscosity. The increase in the oxygen delignification initial reaction pH had the expected effect of decreasing pulp kappa number and viscosity and increasing brightness. The pulp viscosity was particularly penalized at pH 13 where alkaline hydrolysis of cellulose chains became severe, for both treatments without and with (BXL and WXL) added xylans.

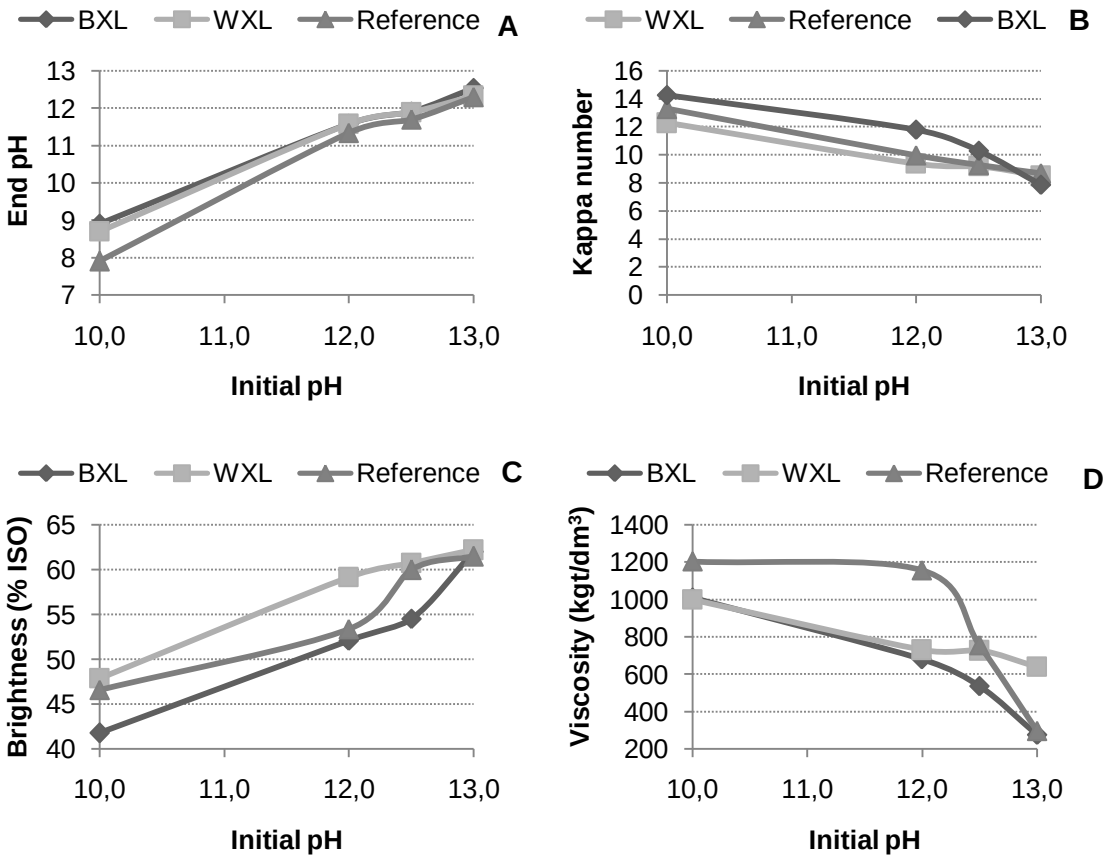

Figure 3: Effect of oxygen delignification initial reaction pH on end pH (a), and pulp kappa number (b), brightness (c) and viscosity (d), for processes with addition of brown pulp xylans (BXL), white pulp xylans (WXL) and no xylans (REF).

The lignin-xylan assembling before precipitation theory (Westbye et al. 2007) was confirmed in this study. The sample with BXL addition at pH 10 resulted in a pulp with lower brightness and higher kappa number when compared to the reference, indicating that lignin precipitation did occur.

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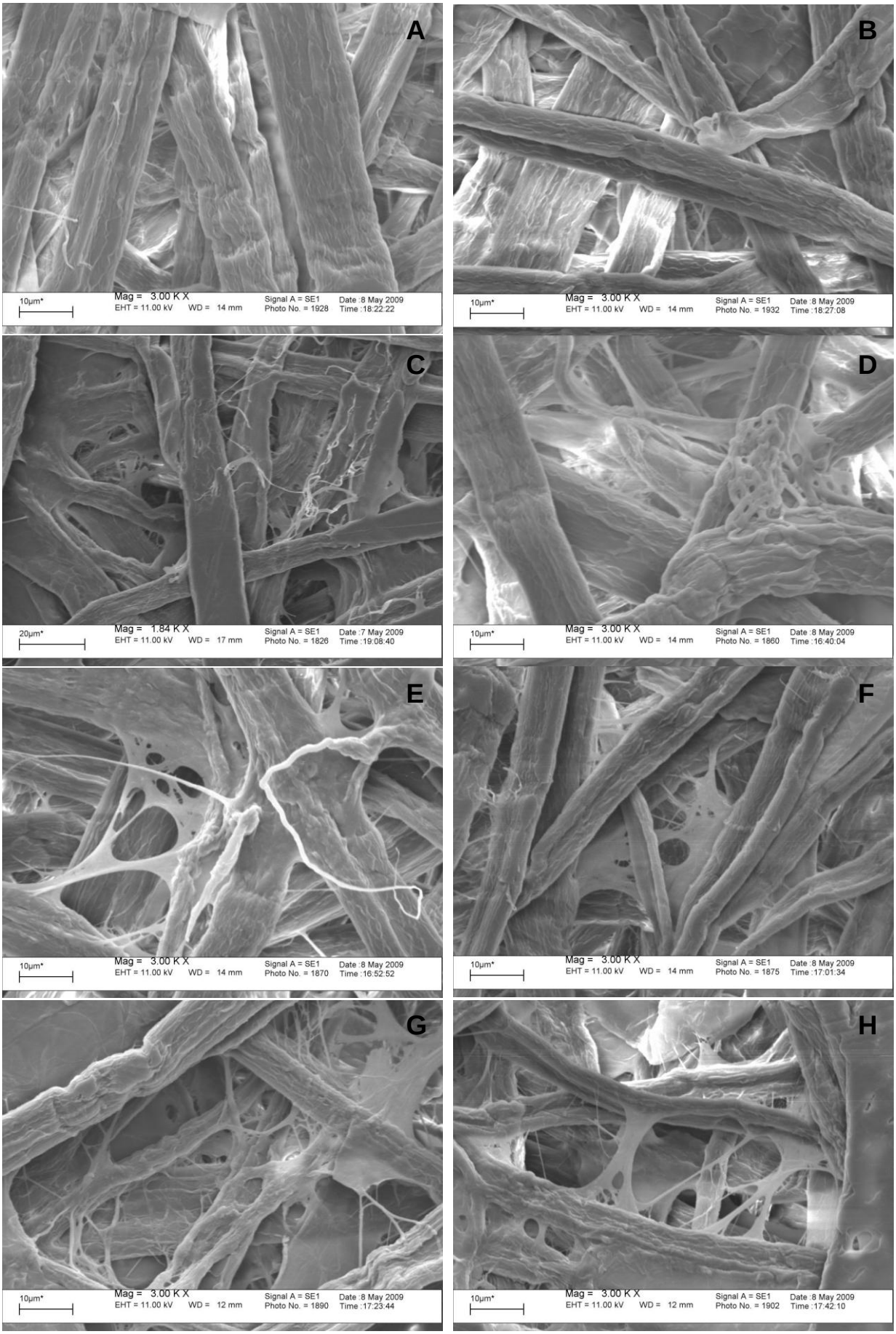
SEM images

SEM images of thin handsheets prepared with reference pulp and pulps treated with BXL and WXL extracts are presented in Figure 4. The xylan deposition onto pulp fibers is visible in all images obtained whit the pulps treated with BXL and WXL, regardless of pH, whereas those untreated do not show such pattern. The formation of xylan aggregates is visible, particularly seen in image 4d. This same kind of images was also seen by Linder et al. (2003).


A
10µm*
Mag = 3.00 K X
EHT = 11.00 kV WD = 14 mm
Signal A = SE1
Photo No. = 1928
Date :8 May 2009
Time :18:22:22
B
10µm*
Mag = 3.00 K X
EHT = 11.00 kV WD = 14 mm
Signal A = SE1
Photo No. = 1932
Date :8 May 2009
Time :18:27:08
C
20µm*
Mag = 1.84 K X
EHT = 11.00 kV WD = 17 mm
Signal A = SE1
Photo No. = 1826
Date :7 May 2009
Time :19:08:40
D
10µm*
Mag = 3.00 K X
EHT = 11.00 kV WD = 14 mm
Signal A = SE1
Photo No. = 1860
Date :8 May 2009
Time :16:40:04
E
10µm*
Mag = 3.00 K X
EHT = 11.00 kV WD = 14 mm
Signal A = SE1
Photo No. = 1870
Date :8 May 2009
Time :16:52:52
F
10µm*
Mag = 3.00 K X
EHT = 11.00 kV WD = 14 mm
Signal A = SE1
Photo No. = 1875
Date :8 May 2009
Time :17:01:34
G
10µm*
Mag = 3.00 K X
EHT = 11.00 kV WD = 12 mm
Signal A = SE1
Photo No. = 1890
Date :8 May 2009
Time :17:23:44
H
10µm*
Mag = 3.00 K X
EHT = 11.00 kV WD = 12 mm
Signal A = SE1
Photo No. = 1902
Date :8 May 2009
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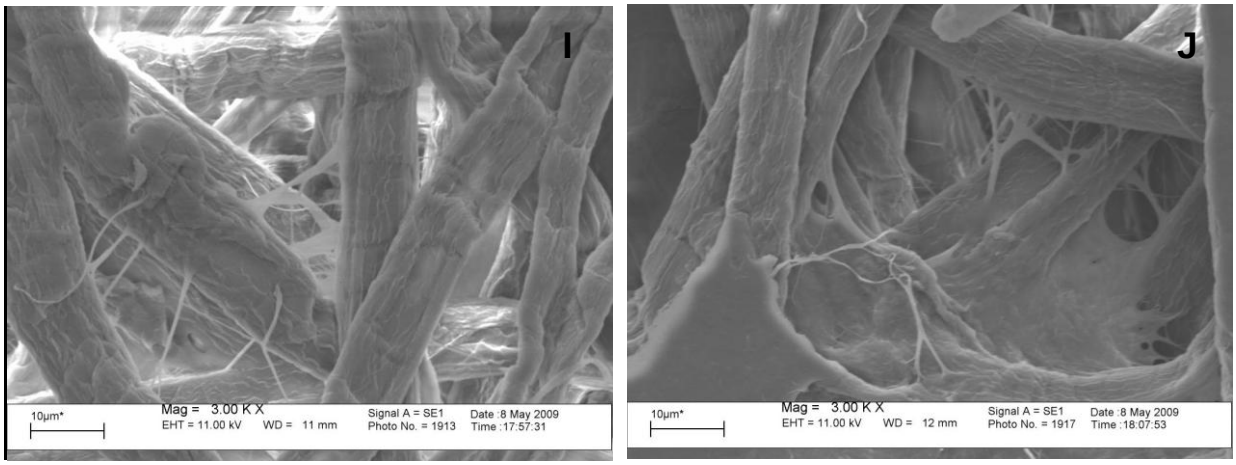

Figure 4: SEM images of the Reference at pH 12: A and B; BXL addition: pH 10 – C, pH 12 – D, pH 12.5 – E, pH 13 – F; WXL addition: pH 10 – G, pH 12 – H, pH 12.5 – I, pH 13 – J.

All images show that deposition occurred in greater extent with the WXL extract in relation to the BXL one. This trend was confirmed through the pulps carbohydrate composition analysis by HPLC (Fig. 1). In BXL images, slight differences are seen among samples prepared at different pH values. In image C, the xylans cannot be clearly visible as aggregates, but they are appearing like fiber coating, turning the surface smoother. In almost all images xylans appears aggregated to each other forming a web, thus bonding one fiber to another. This supports the theory that xylans can act as a stress transfer matrix (LIITI et al, 2005; KERSAVAGE, 1973).

Conclusions

Xylans deposition during oxygen delignification seems to be technically feasible in order to improve fiberline yield since there is no need of expensive additions/modifications to the already installed equipments in a mill. Xylans extraction was more efficient in bleached pulps than in brown pulps, showing that LCC's are not as soluble as pure xylans, turning them more challengeable to be removed from brown pulps. Deposition of xylans extracted from bleached pulps was not interfered by the media pH whereas deposition of xylans extracted from brown pulps was effective only at pH under 12. It could be seen that WXL xylans with less side chain groups and lower M_w tend to deposit more efficiently than BXL. For the BXL extract the highest deposition occurred at the lowest pH tested (10,0). Oxygen delignification performance was not influenced by WXL xylans deposition while negatively affected by BXL xylan deposition.

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CAPÍTULO III

Xylans deposition onto eucalyptus pulp fibers during oxygen delignification. Part 3: deposited xylans behavior across pulp bleaching and refining, and their influence on paper properties

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Key words: xylans, oxygen delignification, xylans deposition, xylans stability, paper properties, energy savings.

Abstract

Xylans deposition during oxygen delignification showed great potential for increasing fiberline yield. On the other hand, these deposited xylans must be stable during the pulp bleaching and refining operations, in order to maintain the yield gains. Thus, brown pulp samples were treated with two types of xylans extracts, one from bleached pulps (WXL – White Xylans Liquor) and another from brown pulp (BXL – Brown Xylans Liquor) and subsequently bleached to 90% ISO with the D(EP)D sequence, and refined in a PFI mill. The strength and absorption properties of the pulps were then evaluated against a reference not treated with xylans. It was concluded that pulp bleachability was not impaired by WXL xylan deposition but slightly negatively affected by BXL xylans. Pulp refinability was improved by both WXL and BXL xylan deposition. The deposited xylans were quite stable across bleaching and refining with the WXL xylans being slightly more stable than the BXL ones. The xylans structures affect their ability to deposit onto pulp fibers and their stability with the presence of lignin being negative. At low energy consumption, the deposited xylans increased almost all properties evaluated, such as tensile index, tear index, tensile energy absorption, and internal bonding strength. The same was not seen when comparing with schopper riegler. The results show that the deposited xylans increased pulp refinability.

Introduction

Xylans deposition during oxygen delignification is a good alternative to increase fiberline yield. On the other hand, the deposited xylans must be stable during the bleaching and refining operations, in order to assure these yield gains. Buchert et al. (1995) studied the effect of bleaching on the structure of xylan and concluded that bleaching decreases both carboxylic groups and xylan contents. It is seen that high xylans content in the pulp fibers, preferably increases tensile strength of papers, but does not affect the bonding strength of pulps with same density (MOLIN and TEDER, 2002). The quantity, instead of the chemical nature of hemicelluloses seems to determine paper properties (ANNERGREN et al., 1962). On the other hand, it has been reported that xylans deposited in kraft pulps result in increased tensile and bonding strengths (SIHTOLA and BLOMBERG, 1975; SCHÖNBERG et al., 2001; SJÖBERG et al., 2002). Xylan introduces new carboxylic groups into fibers. Fibers with higher acid group content swell more, exposing larger surface areas with more potentially reactive sites available for interaction (ERIKSSON and SJÖSTRÖM, 1968). The increased flexibility and conformability increases fiber bonding (LAINE, 1996). Dahlman et al. (2003) evaluated the molecular properties of hemicelluloses located in the inner and surface layers of hardwood and softwood pulps. The quantity of hemicelluloses, weight-average molar mass (M_w), number-average molar mass (M_n) are higher in the surfaces layers, indicating that these parameters could serve as a sensitive indicator for predicting the potential surface properties and bonding ability of the pulp fibers. Hemicelluloses may act as effective stress-transfer matrix (LIITI et al, 2005; KERSAVAGE, 1973). Kim et al. (1975) suggested that hemicelluloses in fibers allow cellulose fibrils to flow and organize more when fibers are dried, and this straightens dislocations and other potential weak spots. Xylans also diminish energy consumption during pulp beating, leading to energy savings, due to their high hydrophilicity. Bhaduri et al. (1995), studying ramie hemicelluloses as a beating additive concluded that they improve pulp strength properties and decrease energy consumption through reduced beating time. Strength properties, such as tensile index, folding endurance and burst index of paper sheets were significantly improved when xylans were added to the pulp.

Thus, the objective of this study was evaluating the impact of xylans deposition during the oxygen delignification (Chapter I and II) on pulp bleachability with the sequence D(EP)D, refinability

and paper properties. The stability of the deposited xylans across bleaching and refining was also evaluated.

Materials

Two pulps containing deposited xylans (WXL and BXL), according to experiments discussed in chapter II and one untreated pulp (reference) were bleached, refined and evaluated for their physical and mechanical properties. The WXL and BXL treated pulps were prepared by application of xylan extracts into the oxygen delignification stage run at pH 12.5. This pH value was chosen for it delivered pulps with low kappa number, high xylan content, good brightness and acceptable viscosity. The reference pulp was treated the same way (pH 12.5), except that xylan extracts were not added during the oxygen delignification stage. The characteristics of the pulps are shown in Table 1.

Table 1: General characteristics of the pulps used for the bleaching and refining experiments.

Characteristics	BXL	WXL	Reference
Kappa number	10.3	9.2	9.3
Viscosity (kg/dm^3)	536.5	728.0	759.4
Brightness (%ISO)	54.5	60.8	60.0
Xylans Content (% on pulp)	17.6	19.7	13.9

Methods

ECF Bleaching

The two special pulps and the reference were bleached to 90 %ISO brightness, with the sequence D(EP)D. In the first chlorine dioxide stage (D), a kappa factor of 0,12 was applied to all samples at 95 ^oC and final pH 3,0 for 120 min. The hydrogen peroxide reinforced extraction (EP) was carried out with 8 kg NaOH/odt and 1.5 kg H_2O_2/odt pulp at 80 ^oC and final pH 10.5 for 60 min. The last chlorine dioxide stage (D) was run with variable doses of ClO_2 in order to reach the 90% ISO brightness target at 75 ^oC and final pH 5.0 during 60 min. All three bleaching stages were carried out at 10% consistency. All the bleaching stages were made in a warm bath using plastic bags. After each stage, the pulps were washed with the equivalent to 9 m^3 of distilled water per ton of pulp. After each stage, brightness was measured according to Tappi T452 om-08. At the final stage brightness was measured before and after pulp aging according to Tappi UM 200 in order to determine reversion potential. Pulp viscosity was measured according to Tappi T230 om–94 and xylans content was measured by HPLC according to WALLIS et al. 1996.

Paper physical, mechanical and optical properties evaluation

For determination of pulp physical, mechanical and optical properties the samples were refined in the laboratory using PFI mill method at 10% of pulp consistency. Physical and mechanical tests were performed using laboratory handsheets according to TAPPI test methods (Table 2) after pulp conditioning for 24 h in a room at 50 $\pm$ 2% of relative humidity and temperature of 23 $\pm$ 1°C. Tensile tests were done according to TAPPI T494 om-96 using INSTRON tester (model 4204 computer controlled) under the following conditions: Cross head speed=25 mm/min.; Load cell capacity=1.0 KN; specimen dimension=160x15 mm; Grip distance=100 mm.

Table 2: Test methods for pulp beating and strength property evaluations

Laboratory beating of pulp	T248 sp-08
Forming Hand sheets for Physical Tests of Pulp	T205 sp-06
Physical Testing of Pulp Hand sheets	T220 sp-06
Grammage of paper	T410 om-08
Thickness (caliper) of paper and paperboard	T551 om-06
Internal Tearing Resistance of Paper (Elmendorf)	T414 om-04
Tensile Breaking Properties of Paper	T494 om-06
Opacity	T519 om-06
Internal Bonding Strength	Skowronski and Bichard, 1997 Adapted

Deposited xylans stability across bleaching and refining operations

After the final bleaching stage, the pulp was analyzed to its xylans compostion, in order to notice their stability across bleaching. Printing and Writing paper mills usually refine eucalyptus pulp to a drainage resistance value about 35 ºSR, thus papers refined to such value were chosen. Both pulps after bleaching and papers after refining were evaluated to their xylans content by HPLC-PAD according to WALLIS et al. 1996.

Results and Discussion

Bleaching

All the pulps were bleached to a final brightness of 90% ISO with the sequence D(EP)D. A summary of reagents quantities and costs required to reach the target brightness is presented in table 3. The experimental results obtained stage by stage of bleaching are represented in Table 1-3 (Appendix).

Table 3: Summary of bleaching results for reference, WXL and BXL treated pulp samples.

Reagents	BXL	WXL	REF
ClO_2, % as Cl_2	1.52	1.40	1.42
H_2O_2, %	0.15	0.15	0.15
O_2, %	2.00	2.00	2.00
NaOH, %	0.80	0.80	0.80
H_2SO_4, %	2.20	2.25	2.25
$MgSO_4$, %	0.00	0.00	0.00
ClO_2 , %	0.58	0.53	0.54
[1]Total Active Chlorine, %	1.83	1.71	1.73
Costs, US$/odt pulp	**14.81**	**14.40**	**14.47**
Brightness , % ISO	89.9	90.5	90.3
Reverted Brightness, % ISO	87.9	88.0	88.0
Brightness Reversion, % ISO	2.0	2.5	2.3
Final Viscosity, kg/dm[3]	444.1	624.8	653.1

[1]Total Active Chlorine = (ClO_2*2,63 + H_2O_2*2,09)

The amount of reagents needed to bleach the reference and WXL treated pup samples to 90% ISO were almost the same, with slight less chlorine dioxide needed for the WXL. The pulp BXL treated sample consumed larger amounts of active chlorine to reach 90% ISO brightness than the other two samples. This result was anticipated since the BXL extract contained sizeable amounts of lignin, which contaminated the pulp during the oxygen delignification stage to a point that the post-oxygen kappa number was one unit higher for this sample than for the other two (Table 1). This additional lignin consumed part of the alkali and oxygen required for the reaction. The brightness behavior of the three pulps across the bleaching sequence is shown in Figure 1 whereby the lower performance of the BXL sample is easily seen. Regarding to brightness reversion, Buchert et al. (1997) concluded that uronic acids enhance brightness reversion. The higher amount of uronic acid present in the BXL xylan could explain the higher brightness reversion of BXL sample.

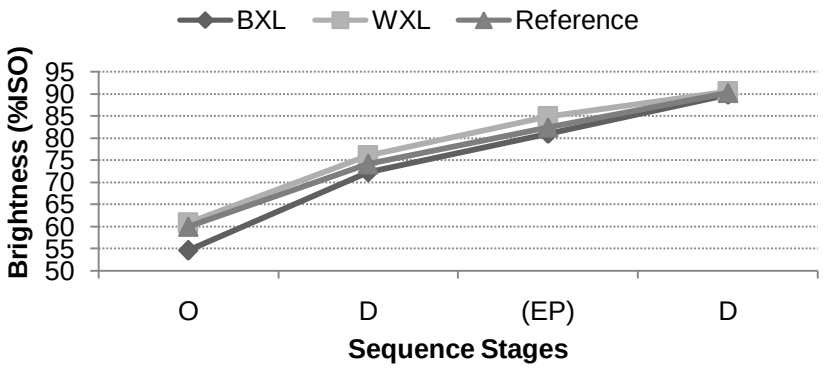

Figure 1: Brightness behavior across the bleaching sequence for processes with addition of brown pulp xylans (BXL), white pulp xylans (WXL) and no xylans (REF).

Deposited xylans stability across bleaching

The xylans content of the pulps were evaluated after the final bleaching stage. The results are shown in table 4.

Table 4: Bleached pulp xylans content and xylan losses across bleaching

Sample	Xylans Content (% on pulp)	Losses (%)
BXL	16.3	7.4
WXL	19.5	1.0
Reference	13.5	2.9

The xylans deposited from the WXL extracts were most stable during the bleaching than the ones from the BXL. This result is explained by the fact that the structure of the xylan from the WXL was less substitituted with side groups (Uronic acids – Chapter II), which favored a better attachment onto the pulp fibers, thus leading to a greater stability. These results are in accordance with the lower deposition values obtained by the BXL in comparison to the WXL.

Paper 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. Opacity is another important property since the printing processes occurs in both sides of the sheet. The role of xylans during refining and in paper properties has been widely studied and they seem very important to for P&W paper grades (ANJOS et al., 2005, MOLINA et al., 2008; BHADURI, et al., 1995), but has not been studied after deposition during oxygen delignification.

By the pulp composition analysis after the bleaching, it is seen that the deposited xylans were quite stable across the bleaching sequence. In other words, pulps with xylan content higher than usual entered in the refining process (Table 4). Figure 2 shows that the same schopper riegler degree was reached by the special pulps (WXL and BXL) with approximately 40% of the energy demanded by the reference.

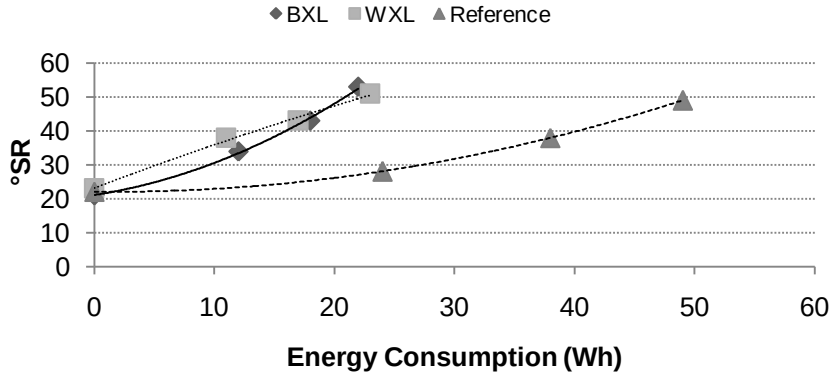

Figure 2: Schopper Riegler degree (ºSR) vs. Energy consumption for processes with addition of brown pulp xylans (BXL), white pulp xylans (WXL) and no xylans (REF).

This corroborates the fact that xylans has big affinity to water, making the fibers swelling easier, thus requiring less energy to reach a same drainage resistance value (^{o}SR). Figure 3 shows that pulps with higher xylan content (considering the content evaluated after bleaching) need much less energy to reach a same tensile index (60 N.m/g).

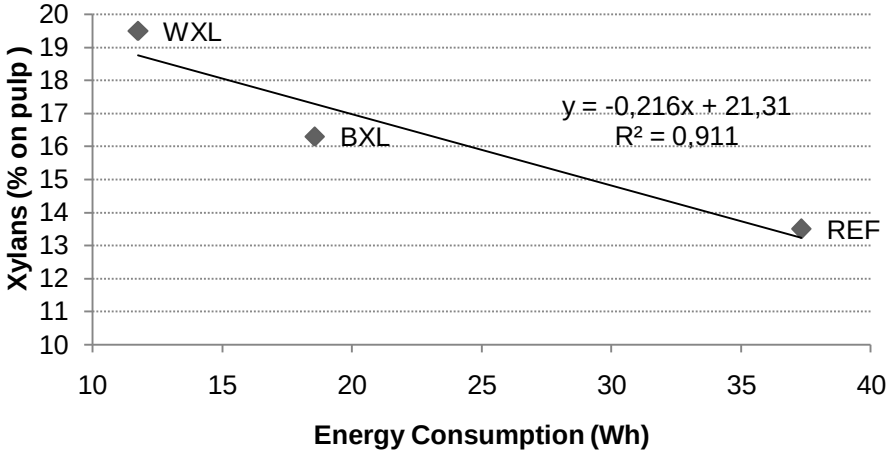

Figure 3: Energy consumption vs. xylans content at 60 N.m/g tensile index for processes with addition of brown pulp xylans (BXL), white pulp xylans (WXL) and no xylans (REF).

It has been reported (ANJOS et al., 2005, MOLINA et al., 2008; BHADURI, et al., 1995) that pulps with high hemicelluloses content tend to form papers with higher density and lower bulk. Figure 4 indicates that for low energy demand, pulps with higher xylans content form denser papers. On the other hand, this trend was not seen when the plot was made against schopper riegler. Similar trends in the opposite direction were observed for paper bulk (Fig. 5). One possible explanation is that, as the refining process was much more drastic for the reference, the formation of fines and the break of fibers leaded to losses of material, turning the paper denser.

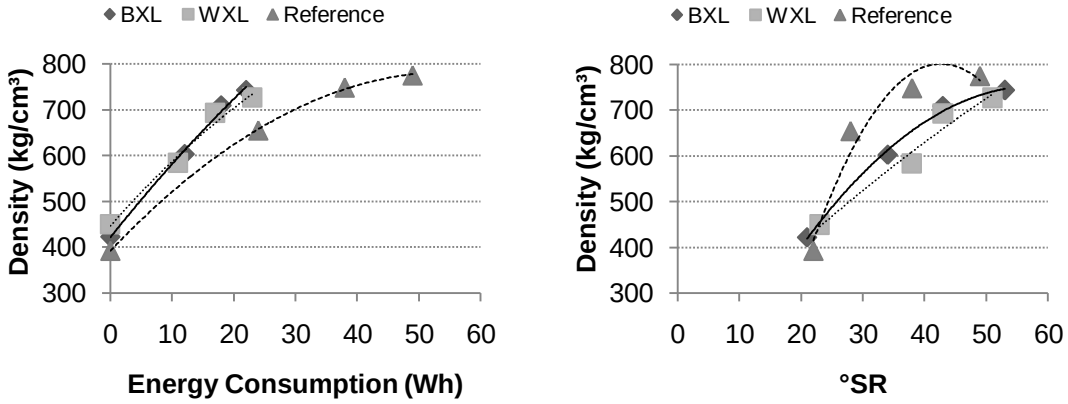

Figure 4: Density vs. energy consumption and schopper riegler for processes with addition of brown pulp xylans (BXL), white pulp xylans (WXL) and no xylans (REF).

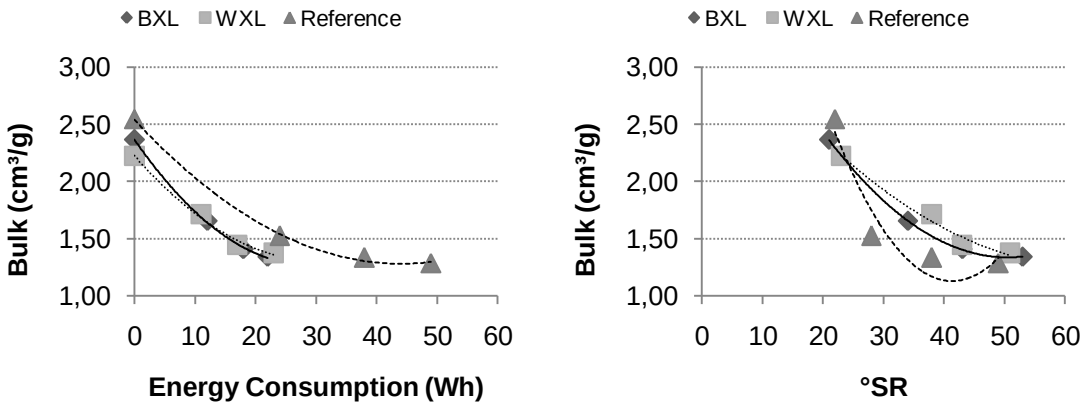

Figure 5: Bulk vs. energy consumption and schopper riegler for processes with addition of brown pulp xylans (BXL), white pulp xylans (WXL) and no xylans (REF).

.Opacity is an important property of P&W papers, since many of them pass in various printing processes, and they have to be opaque enough so that, what is printed in one side cannot be seen clearly on the other side of the sheet. It can be seen in figure 6 that high xylan content decreases opacity of the paper. This can be easily explained by the fact that as xylans turn the paper denser and, consequently less thick and opaque. All the curves were statistically different according to the identity models test at 5% of probability.

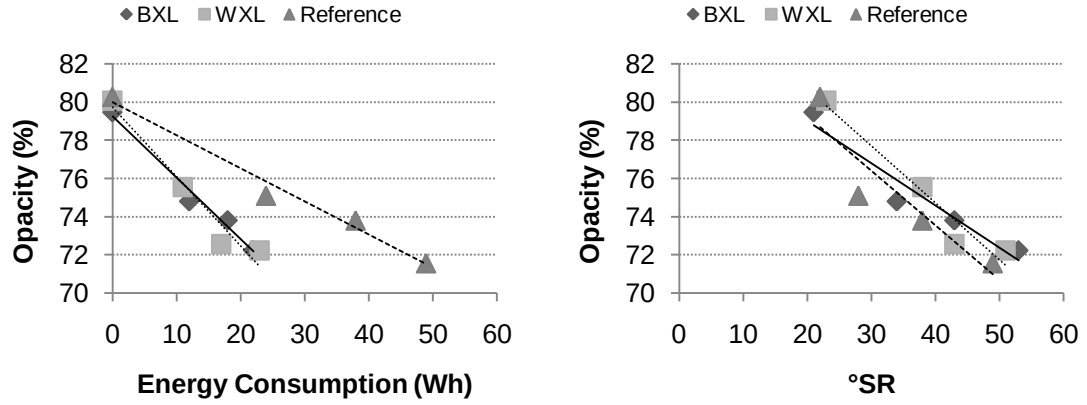

Figure 6: Opacity vs. energy consumption and schopper riegler for processes with addition of brown pulp xylans (BXL), white pulp xylans (WXL) and no xylans (REF).

Many studies (MOLIN and TEDER, 2002; SIHTOLA and BLOMBERG, 1975; SCHÖNBERG et al., 2001; SJÖBERG et al., 2002) show that xylans increase tensile index. Tensile index can show how the paper will behave on its making process, that is based on traction forces. Figure 7 shows that at low energy consumption, both BXL and WXL increased tensile index, but this trend is not clear when comparing with schopper riegler. The same behavior can be seen in tensile energy absorption (TEA) (Fig. 8). TEA shows the work done when a paper specimen is stressed to rupture in tension under prescribed conditions. It can be seen that for papers with high xylan content , more tension is needed to rupture them. This results corroborates the theory of Liiti et al (2005) and Kersavage (1973), where they say that hemicelluloses can act as a stress transfer matrix. It seems that the externally deposited xylans divide the tension applied, thus more work is needed to rupture the sheet. All the curves were statistically different according to the identity models test at 5% of probability.

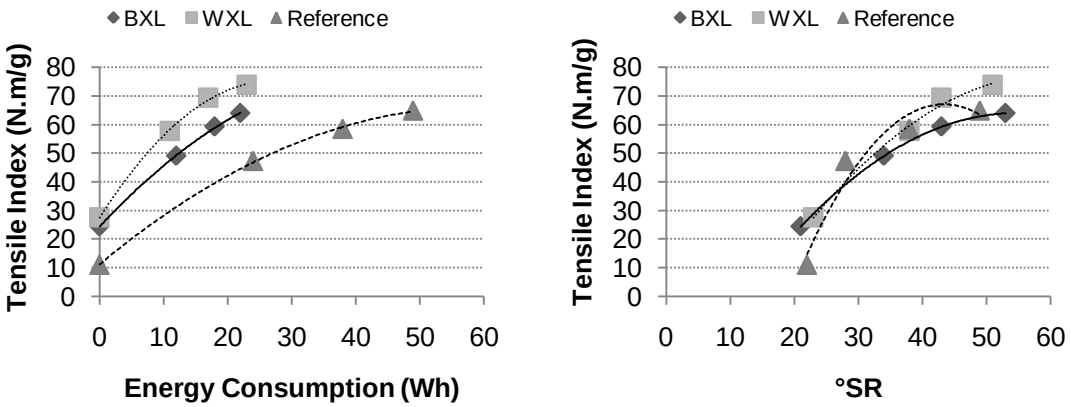

Figure 7: Tensile index vs. energy consumption and schopper riegler for processes with addition of brown pulp xylans (BXL), white pulp xylans (WXL) and no xylans (REF).

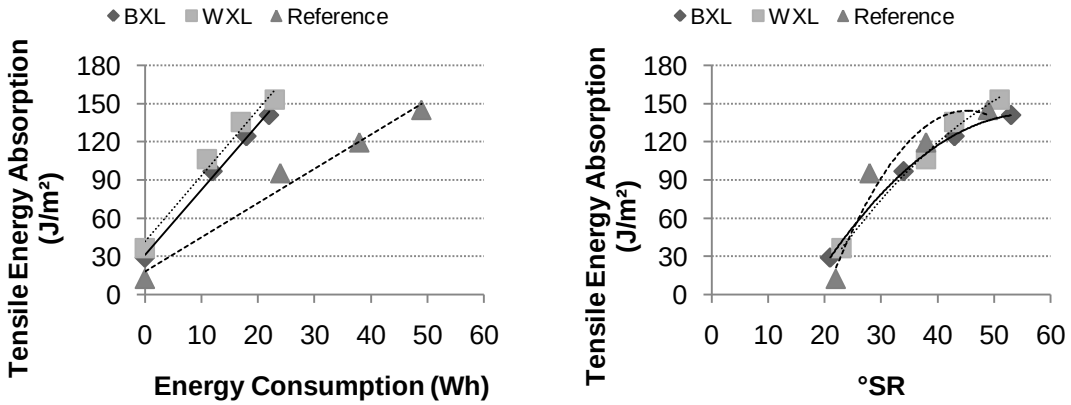

Figure 8: Tensile energy absorption vs. energy consumption and schopper riegler for processes with addition of brown pulp xylans (BXL), white pulp xylans (WXL) and no xylans (REF).

Another property that shows important role for printing and writing paper grades is tear index. Tear index is closely related to the integrity of the fiber wall, number of fibers, internal fiber bonds (CASTANHO and OLIVEIRA, 2000). Figure 9 shows that BXL treated pulps had, in general, the lowest values of tear index. This can be partly related to the lower viscosity of this pulp in relation to the others. Viscosity is highly affected by xylans content of the pulp. When the content of xylan increases, viscosity tends to decrease. In other words, if BXL and WXL had the same fiber wall integrity, WXL would have a lower viscosity, what did not occur, showing a better integrity of the fiber for the WXL, which was confirmed by the values of tear index. At low energy consumption, tear index of both xylans treated pulps were higher than the reference. This could not be seen in high energy consumptions. At more drastic refining operations, the integrity of the fiber starts to be lost, thus low values are encountered. All the curves were statistically different according to the identity models test at 5% of probability.

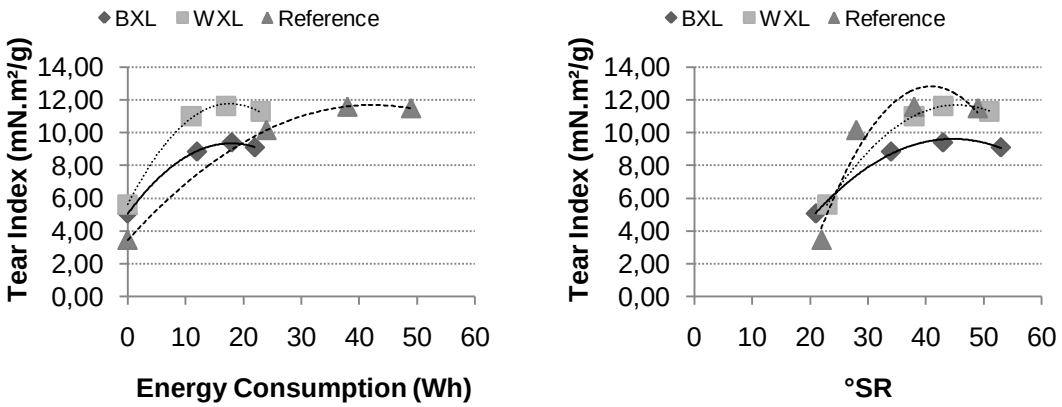

Figure 9: Tear index vs. energy consumption and schopper riegler for processes with addition of brown pulp xylans (BXL), white pulp xylans (WXL) and no xylans (REF).

The role of the deposited xylans can be visible when seeing the specific elastic modulus (SEM). As xylans make the sheet denser, it turns it stiffer. Specific elastic modulus shows the stiffness of the sheet. Figure 10 shows that both BXL and WXL improved SEM values in relation to the reference, showing the value of xylans for making stiffer papers. It seems that the more linear structure, with less side chain groups of WXL xylans Chapter II) helps turning the sheet stiffer. All the curves were statistically different according to the identity models test at 5% of probability.

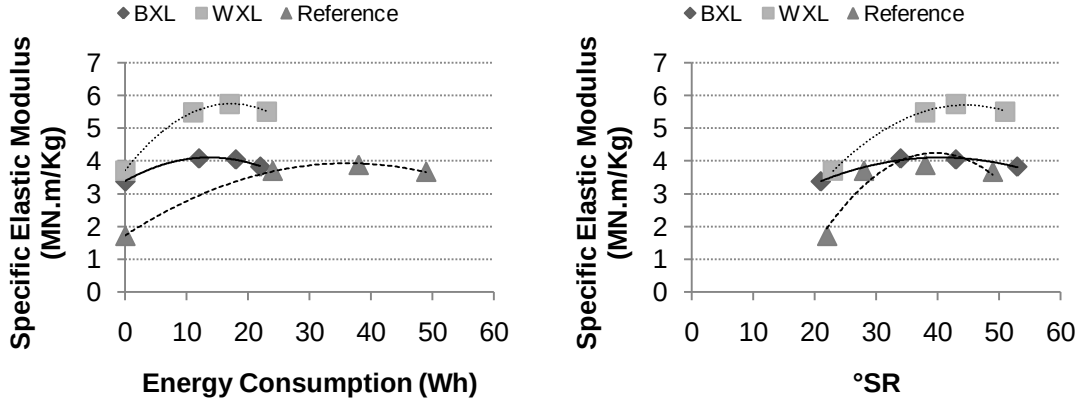

Figure 10: Specific elastic modulus vs. energy consumption and schopper riegler for processes with addition of brown pulp xylans (BXL), white pulp xylans (WXL) and no xylans (REF).

Liiti et al (2005) and Kersavage (1973) stated that hemicelluloses can act as stress transfer matrix. In this work, the internal bonding strength was evaluated in order to verify the effect of deposited xylans. Figure 11 shows that the values of internal bonding strength are much higher for the xylans treated pulps than the reference. All the curves were statistically different according to the identity models test at 5% of probability.

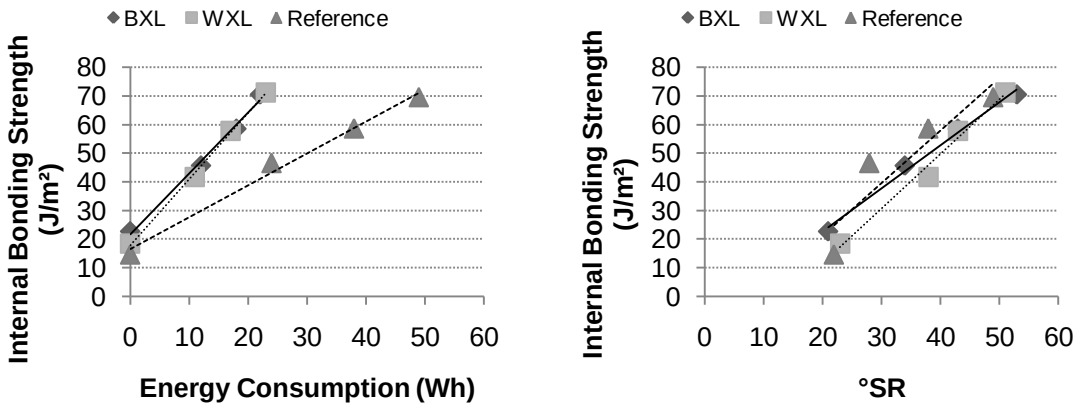

Figure 11: Internal bonding strength vs. energy consumption and schopper riegler for processes with addition of brown pulp xylans (BXL), white pulp xylans (WXL) and no xylans (REF).

Deposited xylans stability across refining

The xylan content was evaluated in papers with a schopper riegler degree around 35, which is industrially used to printing and writing paper grades. The results are shown in Table 5. The more linear and less substituted xylans seems to attach better to fibers, thus resisting more to the mechanical forces of the refiner. Figure 12 shows the stability of xylans across the whole process.

Table 5: Xylans content and losses after the refining process to reach a 35 °SR.

Sample	Xylans Content (% on pulp)	Losses (%)
BXL	15.8	3.1
WXL	19.1	2.1
Reference	12.4	8.1

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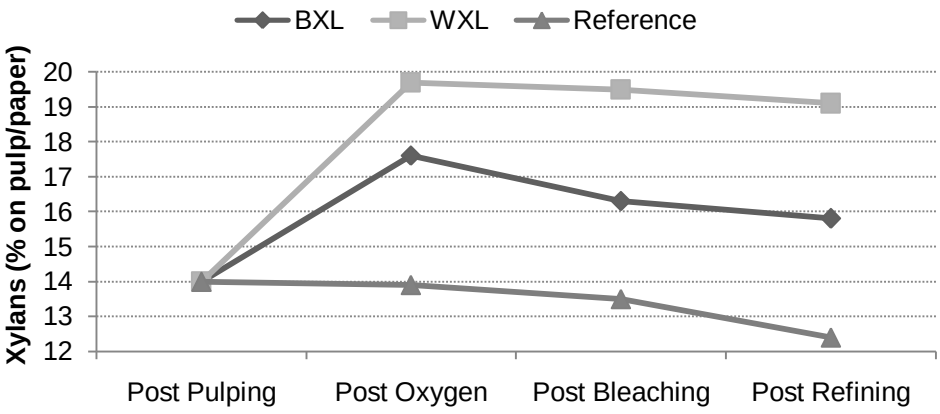

Figure 12: Xylans stability across processes with addition of brown pulp xylans (BXL), white pulp xylans (WXL) and no xylans (REF).

Double line concept

Pulps with high xylans content tend to form papers with high density, high tensile and bonding strength, low air resistance, and such properties fit better to P&W papers. On the other hand, pulps with low xylan content tend to form papers with high bulk, leading to high liquid absorption due to capillarity and softness, and such properties fit better to tissue papers. We are proposing a double line concept (Figs. 13 and 14), since all the liquor extracted from one line, can be used in another, with no need of make-ups. Such concept will lead to a recovery boiler relief, since lower organic matter will be sent to it. In addition, different final high-quality products will be created.

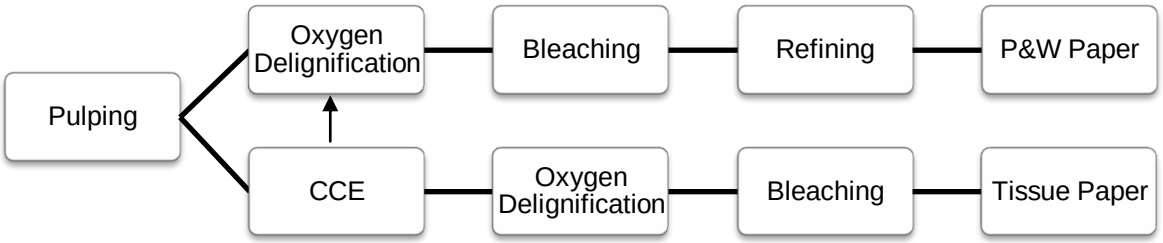

Figure 13: Proposed BXL double line concept in order to create different high-quality final products.

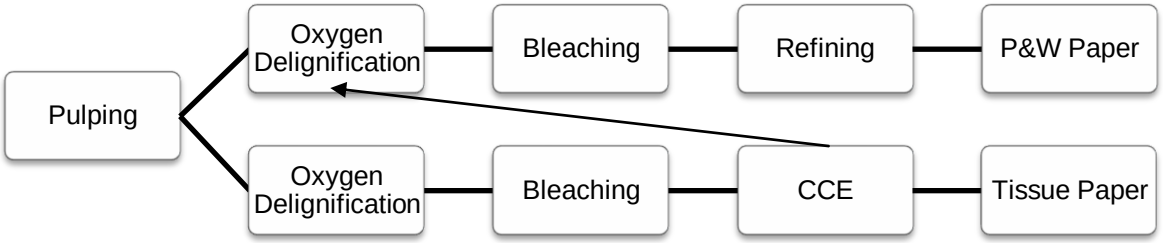

Figure 14: Proposed WXL double line concept in order to create different high-quality final products.

The forest biorefinery concept proposes to investigate new reasonable methods to utilize fibrous material and consequently, extract more value from them and it has been widely studied over the last years, since mills are being environmentally pressured to minimize their wastes, loads and pollution. One option to minimize wastes from pulp and paper mills and agricultural activities would be to use them as a source of xylans (Fig. 15). Part of these wastes (xylans) would not go to environment directly, since they would be extracted using the CCE method aforementioned, and subsequently deposited onto eucalyptus fibers, being now part of a high-quality product.

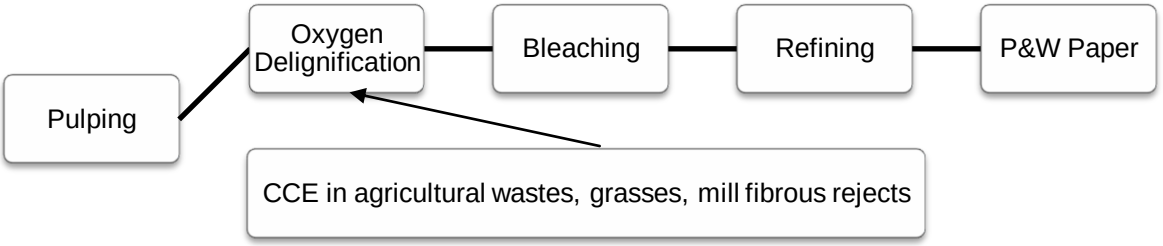

Figure 15: Biorefinery concept using agricultural wastes, grasses and mill fibrous rejects as a cheap source of xylans in order to create high-quality final products.

Conclusions

Pulp treated with WXL extracts showed the outstanding performance during bleaching, with low bleaching chemical costs and good brightness. BXL had the worst bleaching performance among the pulps tested, likely related to the presence of lignin in the extract used for the oxygen delignification experiments. The highest NaOH charge used in the oxygen delignification improved pulp bleachability, what can be seen by the quite low ClO_2 demand. The added xylans seemed to increase brightness reversion. The xylans deposited from WXL and BXL were reasonably stable across the bleaching sequence, with the best results achieved for WXL. Xylans containing less substitution are more stable when deposited over the fibers. The added xylans increased almost all paper properties, except for opacity and bulk using low refining energy. Deposited xylans increase pulp refinability. The stability of deposited xylans across refining is very high, with the best results for the WXL.

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CONCLUSÕES GERAIS

A deposição de xilanas durante a deslignificação com oxigênio mostrou ser tecnicamente atrativa para aumento de rendimento na linha de fibras e diminuição de consumo de energia na etapa de refino da produção de papel.

Nos níveis avaliados, as condições operacionais da deslignificação com oxigênio tais como tempo (30-60 min.), temperatura (85-105^{o}C) e dosagem de álcali (10-30 kg/odt) não tiveram efeito sobre os níveis de deposição de xilanas extraídas de polpa branqueada (WXL).

Para xilanas extraídas de polpa marrom (BXL), a deposição foi prejudicada em valores altos de pH, indicando influência negativa da presença de lignina.

A estrutura das xilanas teve grande influência na deposição, branqueamento e no comportamento durante o refino e propriedades físicas. Estruturas com maior teor de xilose e menor teor de grupos urônicos (WXL) proporcionaram melhor taxa de deposição e melhor estabilidade durante o branqueamento e refino, tendo menores perdas durante o processo.

Para baixos valores de consumo de energia, as polpas com elevado teor de xilanas obtiveram melhores propriedades do que a referência, tendência não encontrada quando comparada com schopper riegler. A partir disso, foi visto que as xilanas depositadas aumentaram a refinabilidade das polpas.

APÊNDICES

APÊNDICE A

Quadro 1. Condições gerais dos estágios de branqueamento pela seqüência D(EP)D das polpas BXL pH 12,5.

Condições e Resultados	Estágios de Branqueamento				
	D*	**(EP)**	**D**	**D**	**D**
Consistência, %	10	10	10	10	10
Tempo, min	120	60	60	60	60
Temperatura, ^{0}C	95	80	75	75	75
Pressão, bar	-	-	-	-	-
O_2, Kg/tas	-	-	-	-	-
Fator kappa	**0,12**	-	-	-	-
ClO_2 como Cl_2 , kg/tas	12,2	-	1,5	3	4,5
H_2O_2, kg/tas	-	1,5	-	-	-
NaOH, kg/tas	-	8	-	-	-
H_2SO_4, kg/tas	20	-	3	2,5	2
pH final	3,2	10,7	4,4	4,7	4,7
Consumo de Reagentes, %	100	100	100	100	100
Número Kappa		3,2	-	-	-
Alvura A.D., % ISO	72,3	81	86,9	88,1	89,9
Alvura O.D., % ISO	-	-	84,2	82,1	87,4
Reversão de Alvura, % ISO	-	-	2,7	6	2,5
Viscosidade, cP	-	-	-	-	6,4

Quadro 2. Condições gerais dos estágios de branqueamento pela seqüência D(EP)D das polpas WXL pH 12,5.

Condições e Resultados	Estágios de Branqueamento				
	D*	**(EP)**	**D**	**D**	**D**
Consistência, %	10	10	10	10	10
Tempo, min	120	60	60	60	60
Temperatura, ^{0}C	95	80	75	75	75
Pressão, bar	-	-	-	-	-
O_2, Kg/tas	-	-	-	-	-
Fator kappa	**0,12**	-	-	-	-
ClO_2 como Cl_2 , kg/tas	11,0	-	1,5	3	4,5
H_2O_2, kg/tas	-	1,5	-	-	-
NaOH, kg/tas	-	8	-	-	-
H_2SO_4, kg/tas	20	-	3	2,5	2
pH final	3,1	10,8	4,5	4,7	4,8
Consumo de Reagentes, %	100	100	100	100	100
Número Kappa	-	2,6	-	-	-
Alvura A.D., % ISO	76,1	84,9	89,4	90,5	91,1
Alvura O.D., % ISO	-	-	86,9	85,74	88,7
Reversão de Alvura, % ISO	-	-	2,5	4,76	2,4
Viscosidade, cP	-	-	-	9,9	-

Quadro 3. Condições gerais dos estágios de branqueamento pela seqüência D(EP)D das polpa referência pH 12,5.

Condições e Resultados	Estágios de Branqueamento				
	D*	**(EP)**	**D**	**D**	**D**
Consistência, %	10	10	10	10	10
Tempo, min	120	60	60	60	60
Temperatura, ^{0}C	95	80	75	75	75
Pressão, bar	-	-	-	-	-
O_2, Kg/tas	-	-	-	-	-
Fator kappa	**0,12**	-	-	-	-
ClO_2 como Cl_2 , kg/tas	11,2	-	1,5	3	4,5
H_2O_2, kg/tas	-	1,5	-	-	-
NaOH, kg/tas	-	8	-	-	-
H_2SO_4, kg/tas	20	-	3	2,5	2
pH final	3,1	10,8	4,6	4,5	4,7
Consumo de Reagentes, %	100	100	100	100	100
Número Kappa		2,8		-	-
Alvura A.D., % ISO	74,1	82,4	89,1	90,3	90,9
Alvura O.D., % ISO	-	-	86,5	85,25	88,3
Reversão de Alvura, % ISO	-	-	2,6	5,05	2,6
Viscosidade, cP	-	-	-	10,6	-

APÊNDICE B

Quadro 4: Resultados dos testes físicos, mecânicos e óticos para a polpa BXL branqueada.

	BXL			
Revolutions number	0	1000	1500	2000
Energy Consumption (Wh)	0	12	18	22
°SR	21	34	43	53
Grammage (g/m²)	63,39	63,37	63,86	63,22
Tensile Index (N.m/g)	24,45	49,1	59,31	64
Burst	75,7	196,26	239,86	269,18
Tear	321	561	601	576
Burst Index (Kpa.m²/g)	1,19	3,10	3,76	4,26
Tear Index (mN.m²/g)	5,06	8,85	9,41	9,11
Strain (%)	2,41	4,43	4,88	5,26
Air Resistance (s/100cm³)	0,54	2,52	7,3	22,32
Thickness (µm)	150	105	90	85
Density (kg/cm³)	422,60	603,52	709,56	743,76
Bulk (cm³/g)	2,37	1,66	1,41	1,34
Tensile Energy Absorption (J/m²)	29,27	96,94	124,47	141,01
Internal Bonding Strength (J/m²)	22,66	45,63	58,49	70,46
Specific Elastic Modulus (MN.m/Kg)	3,38	4,08	4,05	3,83
Opacity (%)	79,47	74,81	73,81	72,24
Scattering Coefficient, m²/kg	43,78	34,81	32,85	31

Quadro 5: Resultados dos testes físicos, mecânicos e óticos para a polpa WXL branqueada.

	WXL			
Revolutions number	0	1000	1500	2000
Energy Consumption (Wh)	0	11	17	23
°SR	23	38	43	51
Grammage (g/m²)	66,12	64,23	62,33	63,25
Tensile Index (N.m/g)	27,69	57,74	69,39	73,87
Burst	85,56	193,82	241,5	273,07
Tear	371	707	725	715
Burst Index (Kpa.m²/g)	1,29	3,02	3,87	4,32
Tear Index (mN.m²/g)	5,61	11,01	11,63	11,30
Strain (%)	2,68	3,97	4,46	4,99
Air Resistance (s/100cm³)	0,63	3,44	7,42	22,64
Thickness (µm)	147	110	90	87
Density (kg/cm³)	449,80	583,91	692,56	727,01
Bulk (cm³/g)	2,22	1,71	1,44	1,38
Tensile Energy Absorption (J/m²)	36,59	106,34	135,65	153,23
Internal Bonding Strength (J/m²)	18,59	41,68	57,73	71,15
Specific Elastic Modulus (MN.m/Kg)	3,71	5,49	5,75	5,52
Opacity (%)	80,07	75,56	72,55	72,23
Scattering Coefficient, m²/kg	44,23	36,25	32,92	31,67

Quadro 6: Resultados dos testes físicos, mecânicos e óticos para a polpa referência branqueada.

	Reference			
Revolutions number	0	2000	3000	4000
Energy Consumption (Wh)	0	24	38	49
°SR	22	28	38	49
Grammage (g/m²)	64,8	65,5	63,64	62,07
Tensile Index (N.m/g)	11,16	47,42	58,61	65,01
Burst	40,31	188,8	239,73	281,06
Tear	224	667	739	715
Burst Index (Kpa.m²/g)	0,62	2,88	3,77	4,53
Tear Index (mN.m²/g)	3,46	10,18	11,61	11,52
Strain (%)	2,1	4,42	4,76	5,41
Air Resistance (s/100cm³)	0,51	3,03	8,15	26,77
Thickness (µm)	165	100	85	80
Density (kg/cm³)	392,73	655,00	748,71	775,88
Bulk (cm³/g)	2,55	1,53	1,34	1,29
Tensile Energy Absorption (J/m²)	12,22	95,27	119,48	144,98
Internal Bonding Strength (J/m²)	14,8	46,62	58,65	69,54
Specific Elastic Modulus (MN.m/Kg)	1,72	3,71	3,89	3,68
Opacity (%)	80,29	75,11	73,81	71,57
Scattering Coefficient, m²/kg	45,21	34,07	33,43	31,17