Behavior of deposited xylans during oxygen delignification across pulp bleaching and refining, and their influence on paper properties

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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. 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.

Introduction

Xylans deposition during oxygen delignification is a good alternative to increase fiberline yield[1]. 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. [2] 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 [3]. The quantity, instead of the chemical nature of hemicelluloses seems to determine paper properties [4]. On the other hand, it has been reported that xylans deposited in kraft pulps result in increased tensile and bonding strengths [5-7]. 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 [8]. The increased flexibility and conformability increases fiber bonding (LAINE, 1996).Dahlman et al. [9] 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 [10,11]. Kim et al.[12] 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. [13], studying ramie hemicelluloses as a beating additive concluded that they improvepulp 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 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 previous paper [1] 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 [1]. 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–94and xylans content was measured by HPLC according to Wallis et al. [14].

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 (T205 sp-06,T220 sp-06, T410 om-08, T551 om-06, T494 om-06, T519 om-06, adapted from Skowronski and Bichard [15]) after pulp conditioning for 24 h in a room at 50±2% of relative humidity and temperature of 23±1°C.

Deposited xylans stability across bleaching and refining operations

After the final bleaching stage, the pulp was analyzed to its xylanscompostion, 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 theirxylans content by HPLC-PAD according to Wallis[14].

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 2.

Table 2.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$/odtpulp	**14.81**	**14.40**	**14.47**
Brightness , % ISO	89.9	90.5	90.3
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. [16] 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.

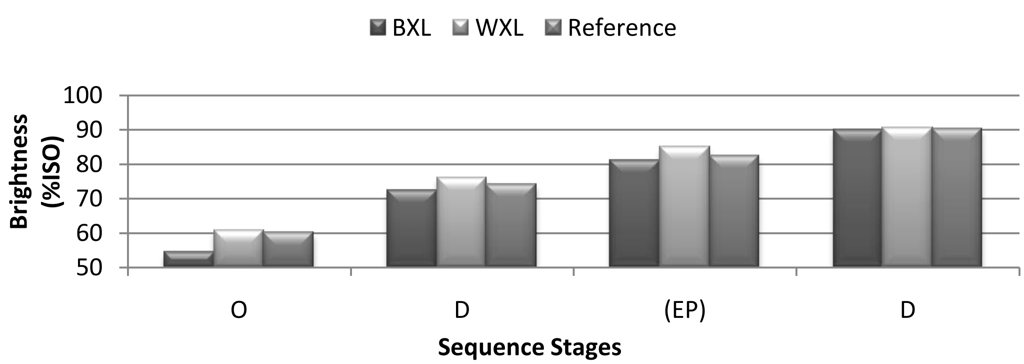

Figure 1.Brightness behavior across the bleaching sequence for processes with addition of brown pulp xylans (BXL), white pulp xylans (WXL) and no xylans (REF).

Deposited xylans stability across bleaching

The xylans content of the pulps were evaluated after the final bleaching stage. The results are shown in table 3.

Table 3: 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 substituted with side groups [1], 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 strengthto withstand the forces the paper undergoes during manufacturing in high speed machines and their use. 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 [13,17-18], 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 3). Figure 2 shows that the same schopperriegler degree was reached by the special pulps (WXL and BXL) with approximately 40% of the energy demanded by the reference.

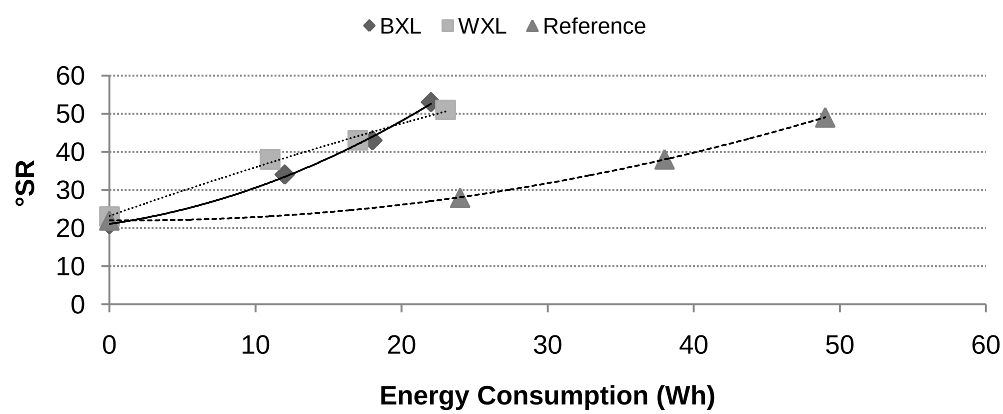

Figure 2.SchopperRiegler degree (ºSR) vs. Energy consumption for processes with addition of brown pulp xylans (BXL), white pulp xylans (WXL) and no xylans (REF).

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).

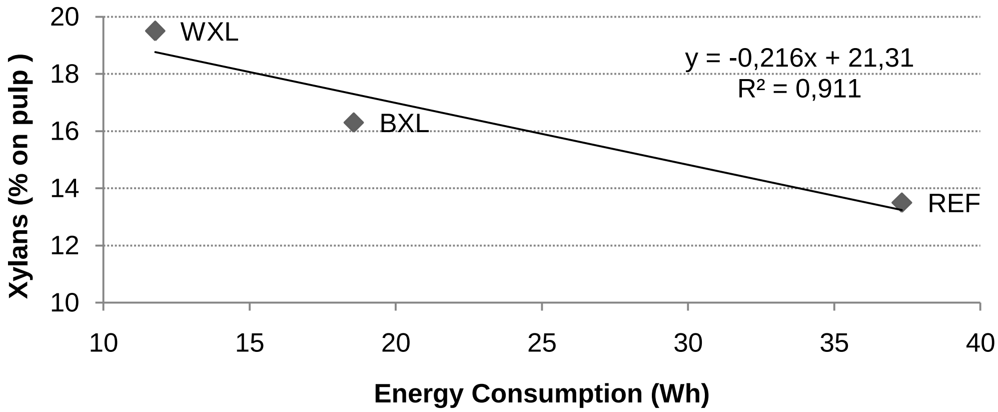

Figure 3.Energy consumption vs. xylans content at 60 N.m/g tensile indexfor processes with addition of brown pulp xylans (BXL), white pulp xylans (WXL) and no xylans (REF).

It has been reportedthat pulps with high hemicelluloses content tend to form papers with higher density and lower bulk [13,17-18]. Figure 4 indicates that for low energy demand, pulps with higher xylans content form denser papers and similar trends in the opposite direction were observed for paper bulk, as they are inversely correlated. 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.

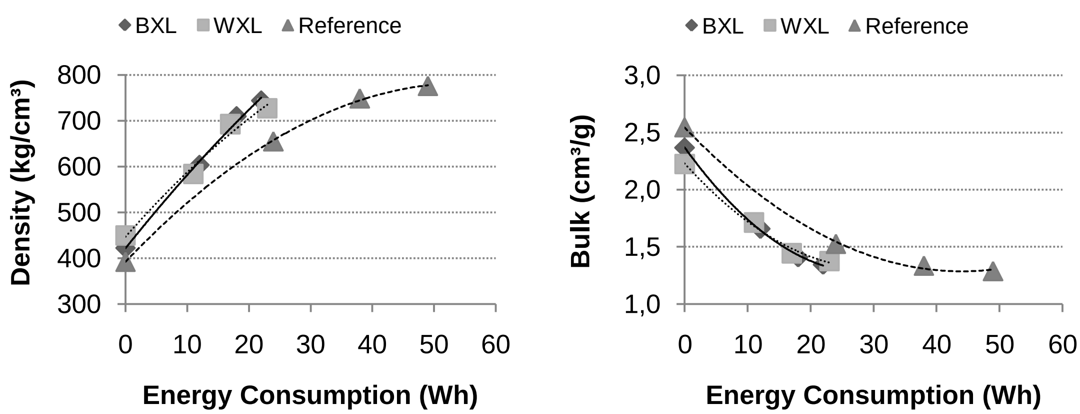

Figure 4. Density and bulk vs. energy consumption for processes with addition of brown pulp xylans (BXL), white pulp xylans (WXL) and no xylans (REF).

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 5 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.

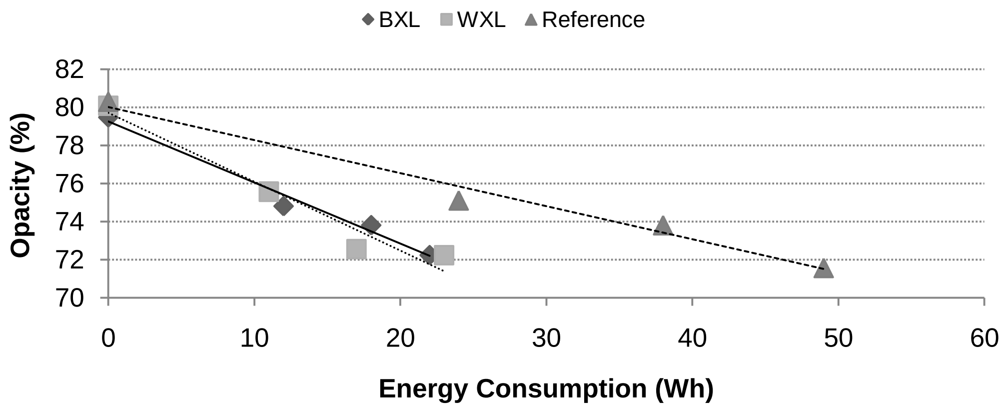

Figure 5.Opacity vs. energy consumption for processes with addition of brown pulp xylans (BXL), white pulp xylans (WXL) and no xylans (REF).

Many studies show that xylans increase tensile index [3, 5-7]. Tensile index can show how the paper will behave on its making process, that is based on traction forces. Figure 6 shows that at low energy consumption, both BXL and WXL increased tensile index. The same behavior can be seen in tensile energy absorption (TEA) (Fig. 7). 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 xylancontent , more tension is needed to rupture them. This result corroborates the theory of Liiti et al. [10] andKersavage[11], 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.

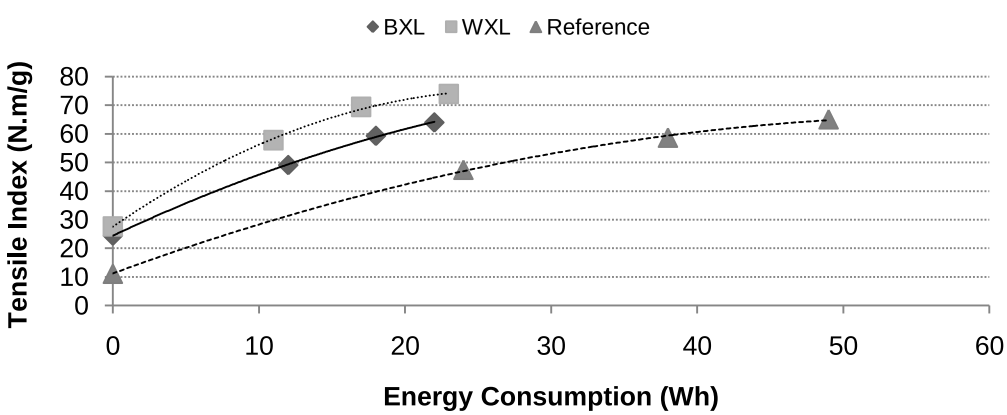

Figure 6.Tensile index vs. energy consumption and schopperriegler for processes with addition of brown pulp xylans (BXL), white pulp xylans (WXL) and no xylans (REF).

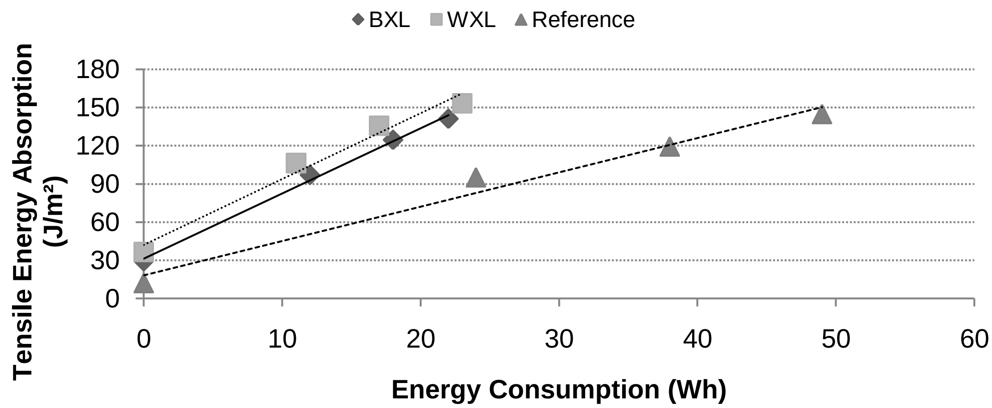

Figure 7.Tensile energy absorption vs. energy consumption and schopperriegler for processes with addition of brown pulp xylans (BXL), white pulp xylans (WXL) and no xylans (REF).

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 [19]. Figure 8 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.

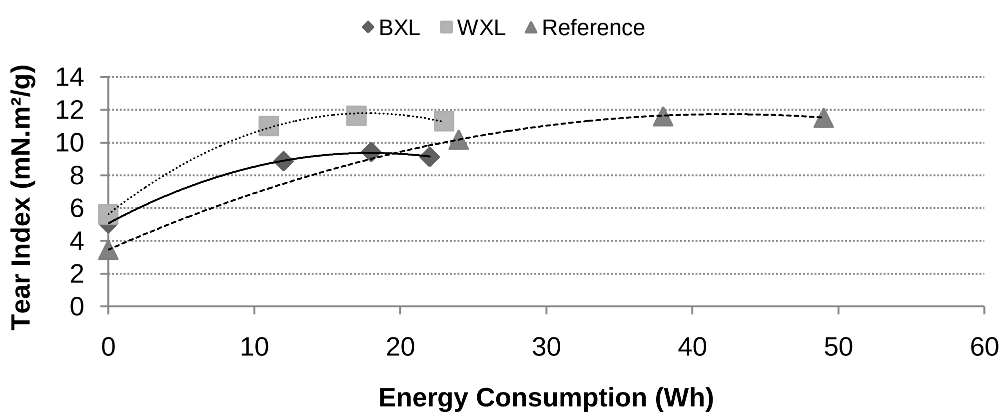

Figure 8. Tear index vs. energy consumption and schopperriegler for processes with addition of brown pulp xylans (BXL), white pulp xylans (WXL) and no xylans (REF).

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 paper sheet. Figure 9showsthat both BXL and WXL improved SEM values in relation to the reference, showing the role of xylansin making stiffer papers. It seems that the more linear structure, with less side chain groups of WXL xylans[1] helps turning the sheet stiffer. All the curves were statistically different according to the identity models test at 5% of probability.

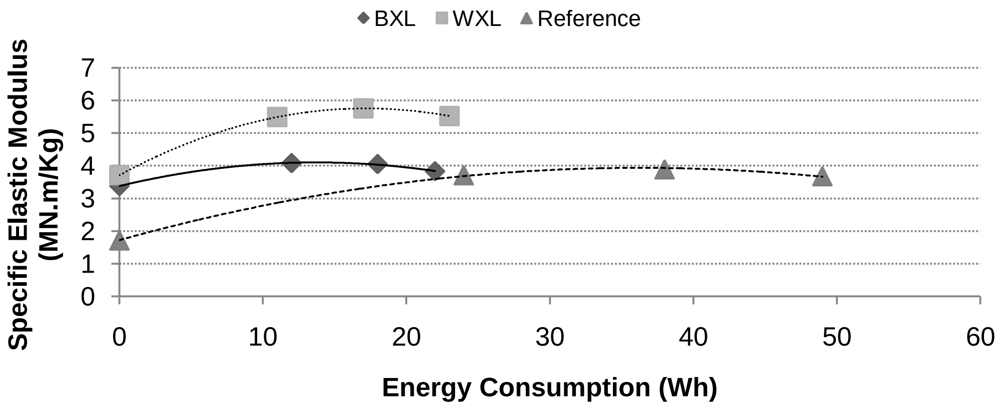

Figure 9.Specific elastic modulus vs. energy consumption and schopperriegler for processes with addition of brown pulp xylans (BXL), white pulp xylans (WXL) and no xylans (REF).

Liiti et al [10] andKersavage[11] 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 10 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.

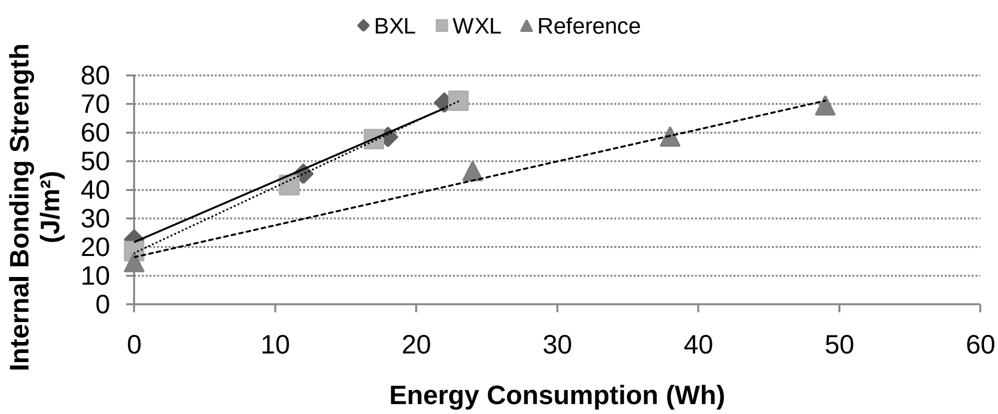

Figure 10.Internal bonding strength vs. energy consumption and schopperriegler for processes with addition of brown pulp xylans (BXL), white pulp xylans (WXL) and no xylans (REF).

Deposited xylans stability across refining

The xylan content was evaluated in papers with a schopperriegler degree around 35, which is industrially used to printing and writing paper grades. The results are shown in Table 4. The more linear and less substituted xylans seems to attach better to fibers, thus resisting more to the mechanical forces of the refiner. Figure 11 shows the stability of xylans across the whole process.

Table 4.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

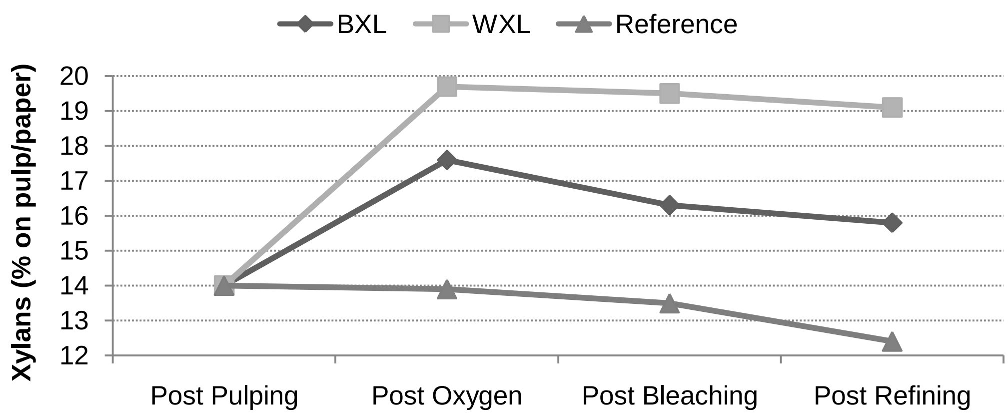

Figure 11.Xylans stability across processes with addition of brown pulp xylans (BXL), white pulp xylans (WXL) and no xylans (REF).

Conclusions

Pulp treated withWXL 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 xylansdeposited 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 xylansacross refining is very high, with the best results for the WXL.

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