HEMICELLULOSES EXTRACTION AND USES IN THE PULP INDUSTRY

J. O. Resende, J. Colodette, M.C.S.M. Soares, R.C. Oliveira, J.L. Gomide
Federal University of Viçosa
Viçosa, MG Brazil 36570.000, colodett@ufv.br

Abstract

The search for a better use of wood in the pulp industry has fuelled interest in a more rational use of its components, particularly xylans. This study investigates the impacts of auto-hydrolysis of wood chips for xylan removal prior to karft pulping as well as the redeposition of xylans onto fibers during kraft pulping (proprietary technology). Wood chips auto-hydrolyzed for 60 min at 170^{o}C allowed the removal of 60% xylans but subsequent kraft cooking produced 6% lower yield. The yield losses during auto-hydrolysis and kraft cooking added up 13.4% in relation to conventional kraft cooking. Kraft pulp derived from auto-hydrolyzed chips showed 75% efficiency across oxygen delignification compared with 43.6% of the reference-pulp, resulting in an subsequent ECF bleaching cost reduction of US$ 7.00 per ton of bleached pulp. The chip auto-hydrolysis process is seemingly not viable for the low xylan eucalyptus wood evaluated since it result in pulp of very low refinability/quality and the resulting acid hydrolizate containing xylan is to little concentrated for appropriate use in the manufacture of ethanol. Kraft pulping with xylan redeposition showed potential to increase overall pulping yield by 7.1% (from 51.1-58.2%) and increase pulp refinability and quality, but the process requires an external source of xylans.

Introduction

Xylans are eucalyptus main hemicelluloses and they are prone to significant degradation during kraft pulping due to their low molecular weight, branched and amorphous structure, richness in reactive groups, and large amounts of reducing end groups in relation to cellulose on a weight basis. However, they are protected by uronic acids. A significant fraction of eucalyptus wood xylans is lost during kraft pulping, reaching values in the range of 50-60% (uronic acids and acetyl groups included).This large fraction of material consumes a significant amount of the whiter liquor effective alkali. Thus, partial xylan removal from wood chips prior to pulping, through auto-hydrolysis with water, acid hydrolysis, alkali leaching and/or enzyme based processes, could potentially improve kraft pulping economics since the extracted xylans could be used to make high added value products such as biofuels, biopolymers, xilitol, etc. Would this approach make sense for eucalyptus wood?

During the kraft pulping process wood xylan is extensively modified. Part of the xylan is dissolved either as a polymer or after degradation to smaller fragments during the heating period of the cook. Towards the end of the cook part of this dissolved xylan is thought to be resorbed onto the fibres (Schönberg, 2001; Clark, 1985; Olm and Tistad, 1979). Some studies also reveal that the xylans retake can also improve paper properties such as tensile and other bonding strength of paper (Sihtola and Blomberg 1975, Schönberg 2001, Sjöberg 2002). Fibers rich in hemicelluloses tend to produce high density / low bulk paper sheets, which are not so interesting for tissue products. On the other hand, printing and writing (P&W) paper grades needs tensile strength and can benefit from high hemicelluloses contents in the fiber (Schönberg 2001).

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

This study aimed at determination of proper conditions for removal of eucalyptus wood xylans with water by the so-called auto-hydrolysis process, determination of proper kraft pulping conditions for processing auto-hydrolyzed wood chips, assessing bleachability and quality of kraft pulps derived from auto-hydrolyzed wood chips, determining proper conditions for xylan redeposition and its effect on pulp quality.

Experimental

1. Material

Ten *Eucalyptus urograndis* trees (7 yr old) were collected in the field. Five 50 cm long bolts were cut from each tree at different heights (0, 25, 50, 75, and 100%). All bolts were hand debarked and chipped in a laboratory chipper. The chips were screened (35x35mm and 8x8mm screens) and air dried to uniform moisture content of about 20%. These chips were mixed and they composed a single sample that was used

in the auto-hydrolysis studies and to prepare kraft pulp (kappa no. 21) for the xylan redposition studies. A bale (250 kg) of commercial bleached kraft pulp was used to extract the xylans for the redeposition studies. The pulp had 90% ISO brightness and contained 15.8% xylans and 83.4% glucans.

2. Xylan removal from wood chips via auto-hydrolysis

The auto-hydrolysis stage was carried out in a 20-L M&K digester with pressure and temeperatrue electronic controls, under the following conditions: water/wood = 3.5/1 L/kg, temperature= 165 °C, time to temperature= 60 min, time at temperature= 10, 20, 30, 40 and 60 min. After completion of the auto-hydrolysis stage, the cooking liquor was drained and collected for analysis, and the kraft cooking liquor was added to the digester. The volume of kraft liquor added was calculated to obtain an liquor/wood of 3.5/1 L/kg, considering the moisture that remained in the chips after drainage of the acid hydrolyzate. The kraft cooking simulated the Lo solids technology under the following conditions: Impregnation zone: 112°C, 60 minutes, 45% of total effective alkali (EA); upper coking zone: 155°C, 60 minutes, 30% of EA; lower coking zone: 156°C, 120 minutes, 25% of EA. A total sulfidity of 37% and H-factor of 680 was used. After completion of the kraft stage, the residual cooking liquor was drained, a sample was collected for analysis and the cooked chips were thoroughly washed with tap water and fiber separation was done in a 20-L hydrapulper. The pulp was screened using a l 0.2mm plate screener, dewatered to 30% consistency and stored for further studies. Reference cookings were carried out on regular chips (not auto-hydrolyzed) under similar conditions as above.The resulting pulps were evaluated for yield and chemical properties and further bleached to ISO brightness 90% with the O/O-D*-(PO)-D-P sequence and again evaluated for their physical-chemical properties. Tappi standard procedures were used to evaluate the brown and bleached pulps.

3. Xylan preparation and redeposition onto kraft pulp

Xylans were extracted from commercial bleacehd kraft pulp through the so-called *Cold Caustic Extraction* (CCE) stage. The pulp was extracted with NaOH 80g/L at 25°C for 30 minutos at 10% consistency. The pulp slurry was then filtered and the filtrate collected and stored at low temperature. This filtrate containing 9.5% of the pulp original xylan content (15.8%) was used in the xylan redeposition experiments. Xylans redeposition onto kraft pulps was carried out using a proprietary procedure developed at Federal University of Viçosa Pulp and Paper Laboratory, which is currently under licensing.

Results and discussion

1. Effect of xylans removal from chips on overall kraft process performance and pulp quality

It is observed that increasing auto-hydrolysis (AH) time results improved xylan removal from the wood chips with consequent yield losses (Table 1). The 10-min and 60-min treatments at 170^{o}C resulted 5 and 16.2% yield losses, respectively. The pH of water used for the AH treatment decreased to 3.4-3.0 due to the acetyl groups (2.6% on wood wt.) originally present in the wood. The original wood contained 25.3% lignin and its content increased slightly in the longer AH treatments (30 and 60 min) due the signficant xylan removal, which affected the mass balance. For the 60-min AH treatment wood xylan content decreased by 61.4% from 12.2 to 4.7% on wood wt. It is worth noting that any distillation process at end of ethanol fermentation requires energy, with a minimum 3% ethanol concentration in the liquor being desirable for the process economics. Assuming a 3.5:1 water to wood ratio and that all 7.5% xylose removed (60-min AH) is recovered and converted into ethanol at a rate of 45%, the concentration of ethanol in the liquid phase would be only 1%. Thus the xylan removed in the auto-hydrolysis stage would not be economically feasible for ethanol manufacture.

Table 1. Auto-hydrolysis (AH) results at 170 ºC and different reation times

AH reaction time, min	Yield, %	Wood xylans, %	Xylans Removal, %	Lignin, %	Spent liquor pH	Hydrolyzate solids, %
0	100	12.2	0	25.3	---	---
10	95.0	10.7	12.3	25.1	3.4	1.3
20	93.7	9.5	22.1	24.9	3.2	1.8
30	89.2	7.8	36.1	25.6	3.1	2.4
40	87.5	6.4	47.5	27.0	3.0	2.7
60	83.8	4.7	61.4	26.7	3.0	3.3

In order to pulp the auto-hydrolyzed chips to kappa number 16-17 an effective alkali (EA) charge ranging from 15.4% to 16.1% as NaOH was required (Table 2). Note that the EA requirement to pulp the original wood (not auto-hydrolyzed) to kappa 16.9 was only 15.9% as NaOH. As the intensity of hydrolysis increased (from 10 to 60 minutes) the EA demand decreased slightly, probably due to lower hemicelluloses content in the chips. The pulping yields were determined on the basis of the auto-hydrolyzed wood weight and and they ranged from 49.3 to 44.5% agains 53.9% for the untreated chips. Hence, the removal of

hemicelluloses from the wood prior to kraft pulping decreases pulping yield significantly. It is worth noting that the overall yield, including the yield in the auto-hydrolysis (AH) plus that in the pulping itself, is even lower for the pre-hydrolyzed chips (46.8-37.32%) in relation to the reference chips (53.9%). The xylan contents of the pulps derived from auto-hydrolyzed chips were quite low, ranging from 5.5 to 1.5% against 16.8% for the reference chips and, as a consequence, the HexA content of such pulps were also low.

The black liquor solids (BL) content and higher heating value (HHV) increased with increasing auto-hydrolysis time and this was expected given the low hemicelluloses heating value in relation to lignin and other wood components. The HHV and solids content were, respectively, 12.4% and 5.1% higher for the 60-min auto-hydrolyzed chips in relation to the reference ones.

Table 2. Kraft pulping results for refererence and auto-hydrolyzed (AH) eucalyptus chips

AH time, min	EA, % as NaOH	Kappa No.	Total pulping yield, %	AH+total pulping Yield,%	Pulp Viscosity, mPa.s	Xylans, %	HexA, %	BLS, %	BL HHV, kcal/kg BLS
0	15.9	16.9	53.90	53.9	78.4	16.8	0.97	13.8	3354
10	16.1	16.8	49.30	46.8	89.4	5.5	0.25	14.3	3521
30	15.8	17.3	47.00	41.9	81.1	2.5	0.14	14.4	3703
60	15.4	16.8	44.50	37.3	68.0	1.5	0.07	14.5	3771

The pulp samples described in Table 2 were treated with oxygen in a double-stage process (O/O-stage. The kappa drop across the O/O stage was substantially higher for the pulps produced from auto-hydrolyzed chips (Table 3) due to their lower HexA contents (0.25-0.07%) in relation to the reference (0.97%). Since HexA react sluggish with oxygen (4-6% removal – Table 3) and they account for kappa number, they negatively affect oxygen delignification efficiency when measured simply by kappa drop across the stage. It is worth noting that selectivity and brightness gain across the oxygen stage increased with increasing AH time, a fact that can be explained by the much higher efficiency of such stage on the pulps derived from auto-hydrolyzed chips. Oxygen stage yield was not much affected by AH time with the yield loss being in the range of 1.7-2.3%. In spite of the higher O-stage efficiency for the pulps derived from auto-hydrolyzed chips, no negative impact were observed in the O-stage yield in relation to the reference. Such result indicates that the oxygen stage was very selective to the pulp lignin fraction. The yield loss per kappa unit dropped across O/O-stage were low for pulps derived from AH chips because they had less xylans.

Table 3. Double-stage oxygen delignfication* perforamance for kraft pulps derived from auto-hydrolyzed (AH) chips

AH time, min	Kappa Drop, %	HexA removal, %	Viscosity drop,%	Brightness gain, % ISO	Selectivity**	Yield loss, %
0	41.6	5.9	35.9	16.6	1.10	2.3
10	62.9	5.0	47.2	21.1	1.26	2.1
30	66.7	4.6	49.2	23.1	1.35	1.9
60	73.0	3.9	53.3	27.3	1.43	1.7

*temp = 90/100°C; pressure= 600/400 kPa; time=15/60 min; consistency=2/11%; NaOH= 2/0%; O_2= 2.2/0 %.
**kappa drop (%)/viscosity drop(%).

The pulps were further bleached to 92% with the D*(PO)DP sequence under simialr conditions (Table 4). A kappa factor of 0.20 was applied in the first chlorine dioxide stage and chlorine dioxide dose was varied in the second D-stage. A fixed charge of 3 and 2 kg H_2O_2/odt pulp was applied in the (PO)- and last P-stage, respectively. The relative bleaching chemical costs varied from 136 for the reference pulp to 100 for the pulp derived from the 60-min auto-hydrolyzed chips. The longer the AH time, the lower the bleaching cost. However, the gains were not very significant at AH times higher than 10 minutes. The decrease in bleaching chemical costs caused by chip auto-hydrolysis derives from the much lower pulp kappa numbers entering the bleach plant, caused by more efficient oxygen delignification in such pulps that contained very low amounts of HexA. The pulps derived from auto-hydrolyzed chips showed lower bleachabilities than the reference pulp. In other words, they showed significantly lower kappa decrease per kg of active chlorine applied in relation to the reference. This was expected since lower kappa oxygen delignified pulps tend to consume more active chlorine per kappa unit than higher kappa ones because of low availability of phenolic hydroxyl groups. In this particular case, the reference pulp entered the bleach plant with a kappa number (9.9) that was almost twice as bigger as the ones (4.5-6.2) derived from pre-hydrolyzed chips.

Brightness reversion varied from 1.1% to 1.7% ISO, with the lowest value found for the pulp derived from the 60-min auto-hydrolyzed chips, which is explaiend by its low HexA content. Final viscosities of the pulps derived from auto-hydrolyzed chips were lower than that of the reference pulp, but still acceptable for

msot applications of eucalyptus pulps (21.2-28.4 mPa.s). Bleaching yield losses varied in the range of 4.3-4.9%, with the highest value for the reference and the lowest for the 60-min auto-hydrolyzed ones.

Table 4. D*-(PO)-D-P bleaching[@] of oxygen delignified kraft pulps derived from auto-hydrolyzed chips

Bleaching Parameter	**Auto-hydrolysis Time, min**			
	0	**10**	**30**	**60**
[1]Total Active Chlorine, %	4.01	2.92	2.75	2.46
Bleachability, K #/% act Cl	2.21	1.73	1.71	1.42
[2]Relative chemical costs	136	110	105	100
Brightness , % ISO	92.0	92.0	92.0	92.0
Reversion, % ISO	1.6	1.4	1.3	1.1
Pulp Viscosity, mPa.s	36.3	28.4	25.3	21.2
[3]Yield losses, %	4.9	4.7	4.5	4.3
O/O-stage Kappa No.	9.9	6.2	5.8	4.5

[@] **D*-stage**:10% consistency, 95°C, 120 min, 2.8 end pH; **(PO)-stage**:10% consistency, 90°C, 120 min, 500 kPa pressure, 3 kg H_2O_2/odt, 10.5 end pH; **D-stage**:10% consistency, 85°C, 120 min, 4.5 end pH; **P-stage:**10% consistency, 85°C, 120 min, 2 kg H_2O_2/odt,10.0 end pH.
1 Total active chlorine = (ClO_2*2.63 + H_2O_2*2.09 + O_3*2.5); **2** Calculated for a brightness target of 92.0 % ISO exactly ; **3**Includes yield loss across O/O stage.

The bleached pulps were tested for their refinability and strength properties (Fig. 1A-C). Pulp refinability (Fig 1A), tensile (Fig 1B) and tear (Fig 1C) strengths were largely impaired by chip auto-hydrolysis, with the negative impact being proportional to AH time. The low xylan contents of pulps derived from AH chips decreased their hydration and bonding potential. On the other hand, the pulps produced from auto-hydrolyzed chips showed very high bulk, a result explained by their low conformability (Fig. 1D).

Table 5. Refinability and physical properties of kraft pulps derived from auto-hydrolyzed chips conventional cooked to kappa 17 and bleached to 920% ISO with the O/O-D*-(PO)-D-P sequence

AH Time, min	PFI Rev.	°SR	Bulk cm³/g	M.O.E. MNm/kg	Tensile Index N.m/g	Burst Index kPa.m²/g	Tear Index mN.m²/g	Opacity, %
0	0	17	2.28	2.09	12.3	0.39	2.67	79.5
	1000	22	1.78	5.19	50.7	2.41	10.0	76.1
	2500	40	1.55	5.88	67.5	4.11	12.5	70.9
	3500	54	1.36	6.08	75.2	4.25	12.4	67.3
10	0	14	2.36	1.70	7.83	0.20	1.97	81.4
	3000	21	1.80	4.46	34.4	1.00	6.96	75.8
	5000	35	1.63	5.23	48.3	1.95	8.84	75.4
	6000	46	1.44	5.53	50.9	2.05	8.93	74.9
30	0	14	2.82	1.12	6.05	0.18	1.75	81.9
	3000	20	1.85	3.82	25.5	0.61	5.24	80.2
	5000	31	1.66	4.37	33.2	1.01	6.25	79.5
	6000	38	1.54	4.75	36.6	1.08	6.48	78.6
60	0	15	3.15	0.80	4.54	0.16	1.66	82.7
	3000	22	1.94	3.52	23.4	0.50	4.42	82.3
	5000	34	1.68	4.24	31.5	0.75	5.29	81.9
	6000	43	1.58	4.58	33.8	0.90	5.62	81.4

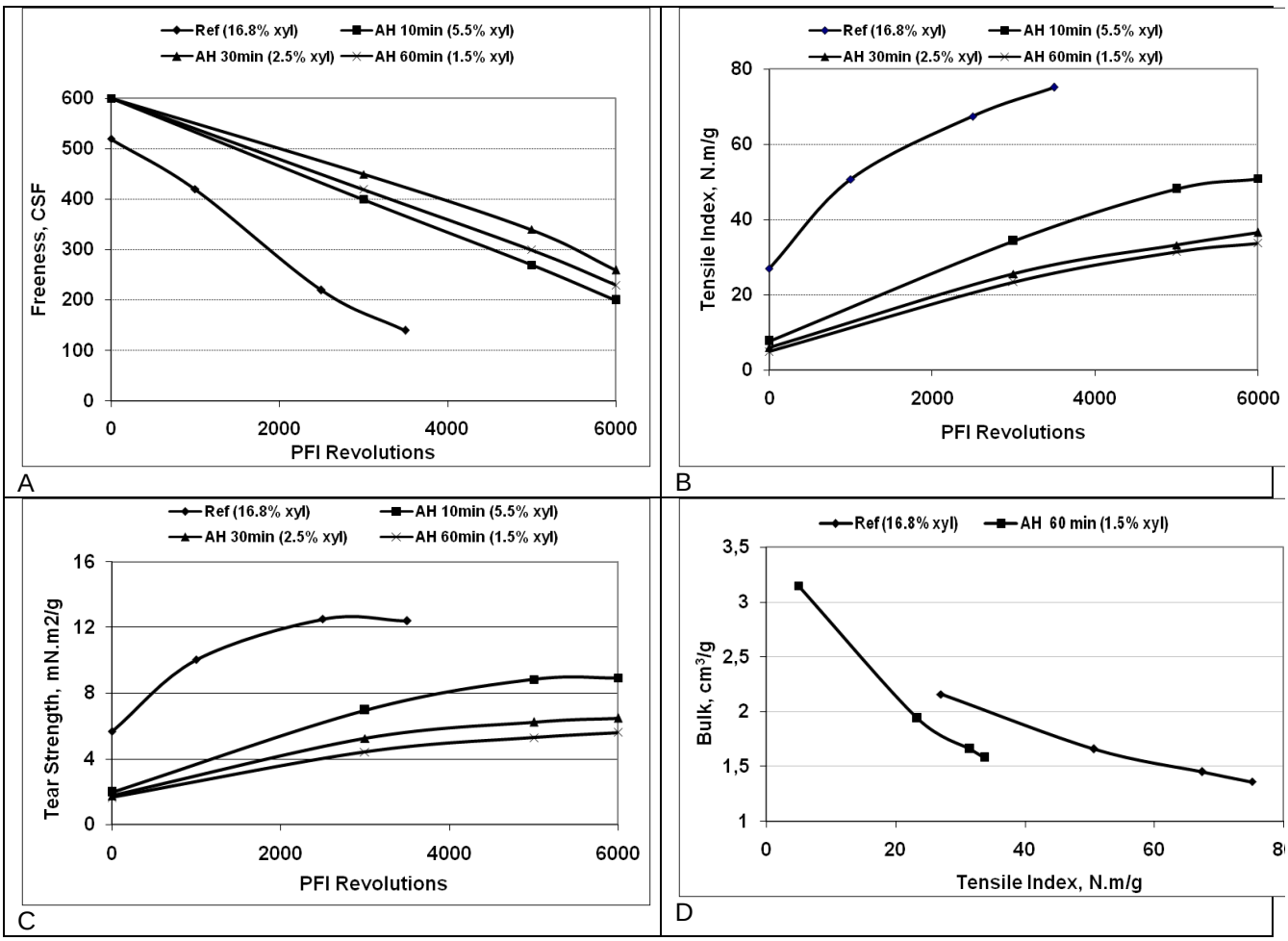

Figure 1. Effect of chip auto-hydrolysis time on kraft pulp refinability and physical properties.

2. Effect of xylan redeposition onto kraft pulp on its yield and quality

Xylans from an extra source were added to kraft pulp during the manufacturing process using a proprietary redeposition technique developed at UFV Pulp and Paper Laboratory. Pulp xylan content increased from original 16.9% to 21.3%, while overall yield increased from the 53.8 to 58.2% after xylan deposition. The added xylan showed Mw and polidispersities somewhat similar to those existing in the original pulp. The xylan rich pulps showed significantly higher refinability and bonding strength properties (tensile, tear, burst and MOE) in relation to the conventional kraft pulp (Table 5). On the other hand they showed poor drainability, lower bulk and opacity due to strong fiber consolidation and conformability.

Table 5. Refinability and physical properties of conventional and modified (with xylan redeposition) kraft pulps cooked to kappa 17 and bleached to 90% ISO with the O-A/D-(PO)-D sequence

Pulp Sample	PFI Rev.	°SR	Bulk cm³/g	M.O.E. MNm/kg	Tensile Index N.m/g	Burst Index kPa.m²/g	Tear Index mN.m²/g	Opacity, %
Conventional kraft (16.9% xylans)	0	15.0	2.38	1.91	10.08	0.24	1.90	81.12
	1000	28.0	1.76	4.50	42.51	2.27	9.08	77.93
	2000	45.0	1.52	5.32	61.78	3.73	9.98	74.60
	3000	65.0	1.34	5.66	67.69	4.46	9.38	72.10
Modified w/ redeposition (21.3% xylans)	0	17.0	2.25	3.38	22.16	0.77	4.04	81.37
	1000	33.0	1.68	5.21	60.91	3.41	9.36	75.85
	1500	43.0	1.52	5.46	68.58	4.05	10.00	72.65
	2000	50.0	1.43	5.79	72.68	4.55	10.42	70.81

Conclusions

The chip auto-hydrolysis process is not technically and economically viable for the low xylan eucalyptus wood evaluated since it result in pulp of very low refinability/quality and the resulting acid hydrolizate

containing xylan is to little concentrated for appropriate use in the manufacture of ethanol. The technique would be more appropriate to woods of large xylan contents.

Kraft pulping with xylan redeposition showed very high potential to increase overall pulping yield by 4.4% (from 53.8-58.2%) and increase pulp refianbility and quality, but the process requires an external and inexpensive source of xylans.

References

1. Olm, L., Tistad, G. Kinetics of initial stage of pulping. Svensk Papperstidning. 1979. v. 82, n.15, p. 458-464.
2. Schönberg, C.; Oksanem, T.; Suurnäkki, A.; Kettunem, H.; Bucghert, J. The importance of xylan for the strength properties of spruce kraft fibres. Holzforschung. 2001. v. 55, p. 639-644.
3. Shin, N. H. and Stromberg, B. Xylan´s impact on eucalyptus pulp yield and strength – Myth or reality?. Proceedings of the 3rd International Colloquium on Eucalyptus Pulp. 2007. Belo Horizonte. Brazil.
4. Sihtola, H.; Blomberg, L. Hemicelluloses precipitated from steeping liqour in the viscose process as additives in papermaking. Cellul. Chem. and Technol.1975. v. 9, n. 5, p. 555-560.
5. Sjöberg, J.; Kleen, M.; Dahlman, O.; Agnemo, R.; Sundvall, H. Analysis of carbohydrate and lignin in the surface and inner layers of softwood pulp fibers obtained employing various alkaline cooking process. Nordic Pulp and Paper Research Journal. 20002.v. 17, p. 295-301.

Acknowledgements

The research leading to these results has received funding from the European Community's Seventh Framework Programme FP7/2007-2013 under grant agreement no KBBE-2009-3-244362 LignoDeco (a EU/Brazil co-operation project), and from the Minas Gerais State Research Foundation.