Influence of Alkali Charge on Hexenuronic Acid Formation and Pulping Efficiency for Lo-Solids® Cooking of Eucalyptus

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ABSTRACT

The goal of this work was to study the influence of the alkali charge on the hexenuronic acid content and pulping efficiency for the Lo-Solids® cooking process. Woods from 2 hybrids of 7-year-old *Eucalyptus grandis* x *Eucalyptus urophylla* (basic density of 0.499 and 0.559g/cm^3) were evaluated and the pulping process was conducted by applying active alkali charges (as Na_2O) of 13%, 15%, 17%, 19%, 21%, 23%, 24%, 25%, 27% and sulfidity of 30%. The results showed that in varying the alkali charge, it is possible to obtain unbleached pulp with different yields, carbohydrate composition, hexenuronic acid content from 10 to 65µmol/g and kappa numbers from 8 to 30. Although the hybrids studied presented different basic wood density, the pulping results obtained were not different, showing that both raw materials could be used for pulp production with Lo-Solids® pulping process, as it seems not to be significantly affected by basic wood density.

INTRODUCTION

It has been found that hexenuronic acid (HexA) formation occurs under alkaline and temperature conditions during kraft pulping, when 4-O-methylglucuronic acid from xylan is converted into hexenuronic acid; this conversion occurs through the elimination of the 4-O-methoxyl group after the loss of the hydrogen atom attached to the 5th position of the glucuronic acid residue (1). Figure 1 shows the conversion of 4-O-methylglucuronoxylan to hexenuronoxylan and hexenuronic acid formation under alkaline and temperature conditions.

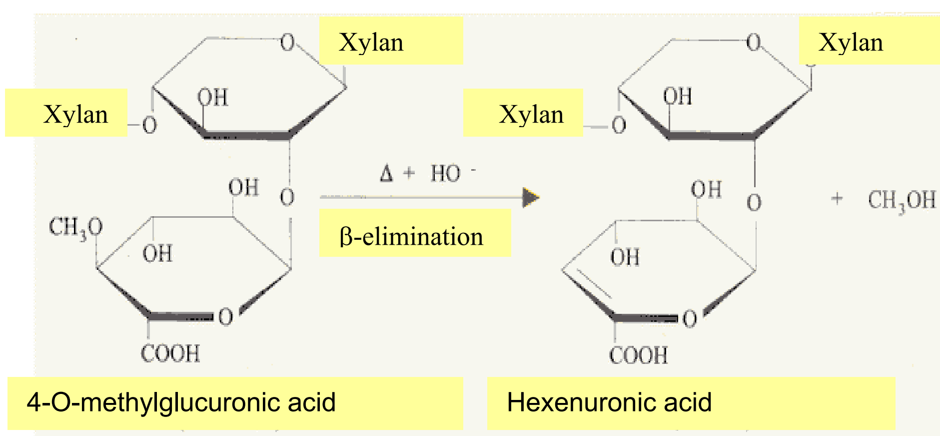

Figure 1 – The conversion of 4-o-methylglucuronoxylan to hexenuronoxylan during Kraft pulping as suggested by Clayton in 1962.

In alkaline pulping processes, the intensity of the delignification reactions is evaluated through the kappa number. Hexenuronic acids generated during the kraft pulping process consume potassium permanganate used in the determination of the kappa number, thus influencing the result of the analysis (2). These authors also studied the generation of these composites for different wood species and delignification levels and verified that 11.9 mmol of

Ahexs/kg of pulp corresponds to a unit of the kappa number. Therefore, depending on the type of cooking used, pulps from hardwoods may present up to 75 mmolHexs/kg pulp, contributing about 6 kappa units.

Hexenuronic acids form covalent bonds with the lignin and consume electrophilic chemical reagents during bleaching (chlorine, chlorine dioxide, ozone and peracids). They also bond to ions and provoke the brightness reversion of the bleached pulps. Hexenuronic acids have functional enol-ether and unsaturated carboxyl groups, which provide their stability and reactivity. These composites are relatively stable under alkaline conditions, and, for this reason, hexenuronic acid protects xylan against terminal depolymerization reactions, thus, preserving the yield of the pulping process. However, in drastic conditions of temperature and alkali dosage, these composites, as well as other polysaccharides, suffer alkaline hydrolysis and are degraded. Hexenuronic acid also suffers hydrolysis under acid conditions, being prone to the attack of electrophilic oxidants. Therefore, since the discovery of hexenuronic acid structures in kraft pulps, some technologies have been proposed for removing the composites from the pulp during the bleaching phase, which are basically based on the use of a stage with an acid hydrolysis at a temperature of about 80 to 100°C and a pH of about 3.

The alkali charge and the H-factor are the main variables that influence the formation of hexenuronic acid during Kraft pulping (3). Considering the *E. globulus* wood as raw material for kraft pulp, the alkali charge is the main factor that contributes to the formation and degradation of hexenuronic acid during pulping. The increase of the alkali charge promotes the xylan dissolution and degradation and, consequently, reduces the amount of hexenuronic acid in the pulp, once these groups of acid are bonded to xylan chains. The studies show that the formation of hexenuronic acid increases for kappa number between 11 and 18. These composites are reduced when kappa numbers are above these values due to degradation of hemicelluloses.

EXPERIMENTAL

Woods from two *Eucalyptus grandis* x *Eucalyptus urophylla* clone plantations, aged 7, with different basic densities – 0.499 **(hybrid P4299)** and 0.559g/cm^3 **(hybrid C085)** - were studied. Screened chips were obtained from 10 different trees; chip fractions of 2-10 mm thickness and 10-22 width were used; knots and bark were removed by hand prior to cooking.

The lab cooks were performed in a system that consists basically of a set of vessels, metering pumps and other accessories connected to a M/K digester. The treatments were conducted in triplicates following the pulping conditions presented on Table 1.

Table 1. Pulping conditions

Parameters	Condition
Amount of chips	800g
Liquor to wood ratio	4:1
Active alkali charge (as Na_2O)	13%, 15%, 17%, 19%, 21%, 23%, 25% e 27%
Sulfidity	30,0%
H-Factor	2045

Table 2. time/temperature and alkali profiles

Phases	Time (min.)	Temperature (°C)	Alkali split (%)
Steaming	15	100	-
Impregnation	40	120	50
Liquor Substitution	90	158	35
Cooking	70	158	-
Washing	200	158	15

For each cook, the total yield, screened yield and rejects content (0.2mm screen) were measured; for the pulps, the residual lignin, kappa number and viscosity were determined according to TAPPI Methods; hexenuronic acids were measured following the method proposed by Chai (3); carbohydrates were analyzed by HPLC-IC using and Dionex DX500 system.

RESULTS AND DISCUSSION

Table 3 shows the main characteristics of the wood used in this work.

Table 3. Wood characteristics for the materials studied

	E. grandis x E. urophyllla P4299			*E. grandis x E. urophylla* C085		
	Average	S.D.	C.V.	Average	S.D.	C.V.
Wood density (g/cm³)	0.499	0.0121	2.43	0.559	0.0123	2.20
Total lignin (%)	28.81	0.97	3.36	29.33	1.08	3.67
Cellulose and hemicellulose (%)	68.81	1.20	1.75	68.15	1.23	1.80
Extractives (%)	2.30	0.44	18.94	3.02	0.75	24.78
Acetyl groups (%)	3.29	0.14	4.33	3.39	0.17	5.13
Glucuronic acid (%)	1.48	0.07	4.84	1.55	0.08	5.41
Glucan (%)	45.10	1.67	3.71	45.83	0.92	2.01
Xylan (%)	12.94	0.38	2.95	13.02	0.31	2.41
Arabinan (%)	0.19	0.04	23.11	0.21	0.07	34.17

Apart from the basic density, the studied materials presented similar and typical characteristics for the wood used in the study for pulp production.

In the kraft pulping process, the kappa number is an important parameter once it is directly related to the yield and is an indicative of the amount of lignin in the pulp, which, for bleachable pulps, determines the strategies involved in the bleaching phase. Characteristics of the wood, such as the content of lignin, content of extractives, basic density and the chips thickness directly influence the kappa number of the pulp. The alkali charge applied and H-factor are the main parameters in the kraft pulping process used to control the variations provoked by the raw material in order to keep the delignification level of the pulp relatively constant.

Figure 2 shows that the kappa numbers are slightly higher for the C085 hybrid, especially for alkali dosages of less than 19% of active alkali and kappa number above 14. Such behavior of this material may be due to its higher basic density, which may have offered more resistance to the chips impregnation by the cooking liquor and decreased the delignification level (4).

The kappa number is influenced by the hexenuronic acid content of the pulp. Hexenuronic acids consume the potassium permanganate, which is the reagent used in the determination of the kappa number of the pulp, contributing to an increase in the kappa number value (5). Some studies suggest some conversion factors for the calculation of the corrected kappa number. The use of the proposed factor is considered by Li (2), in which a unit of the kappa number corresponds to 11.9 mmol of Ahexs/kg of pulp.

The results in Figure 2 show significant differences between the kappa values of the pulp without and with the correction, pointing out the importance of the quantification of hexenuronic acid in the definition of strategies in the bleaching phase. One must consider the influence of these composites in the bleaching phase: consuming the chemical reagents, such as chlorine, chlorine dioxide, ozone, bonding to metallic ions and causing reversion of the brightness of the bleached pulps.

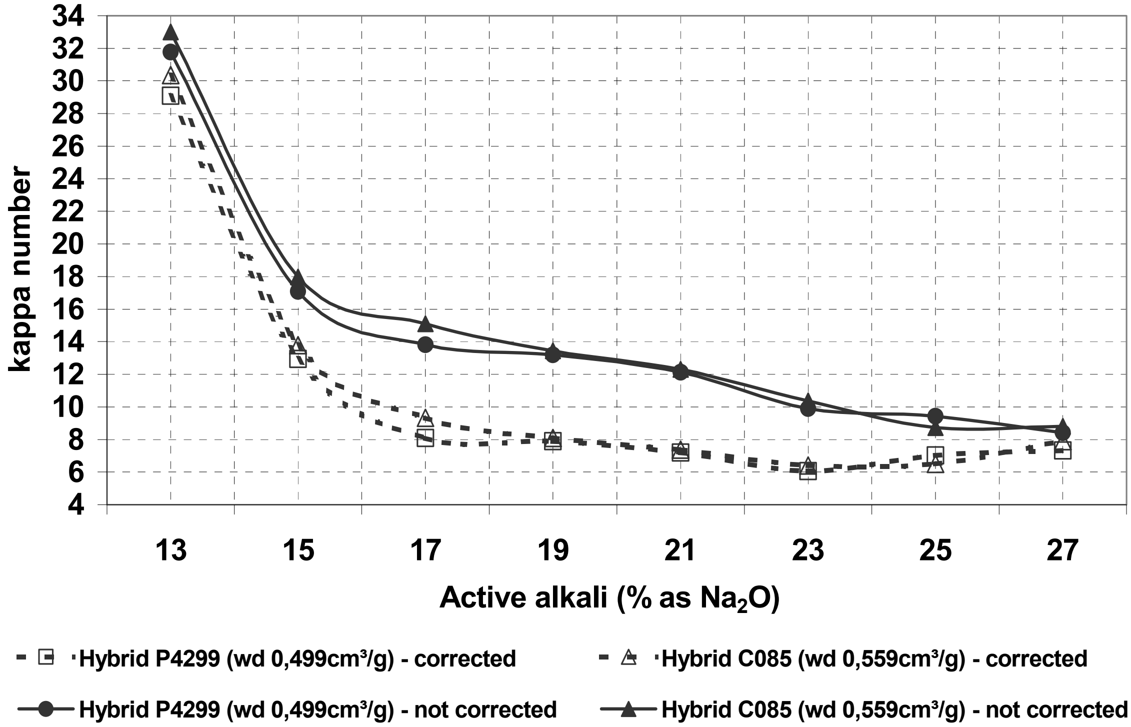

Figure 2 – Kappa number (corrected and not corrected) x active alkali

Considering that the "corrected" values for kappa number represent only the lignin content in the pulp, Figure 2 shows that an increase of the alkali charge beyond 20% does not lead to an increase in the delignification efficiency. The lignin profile as a function of the alkali charge suggested by the kappa number "corrected" in figure 2 is very similar to the profile presented in figure 3.

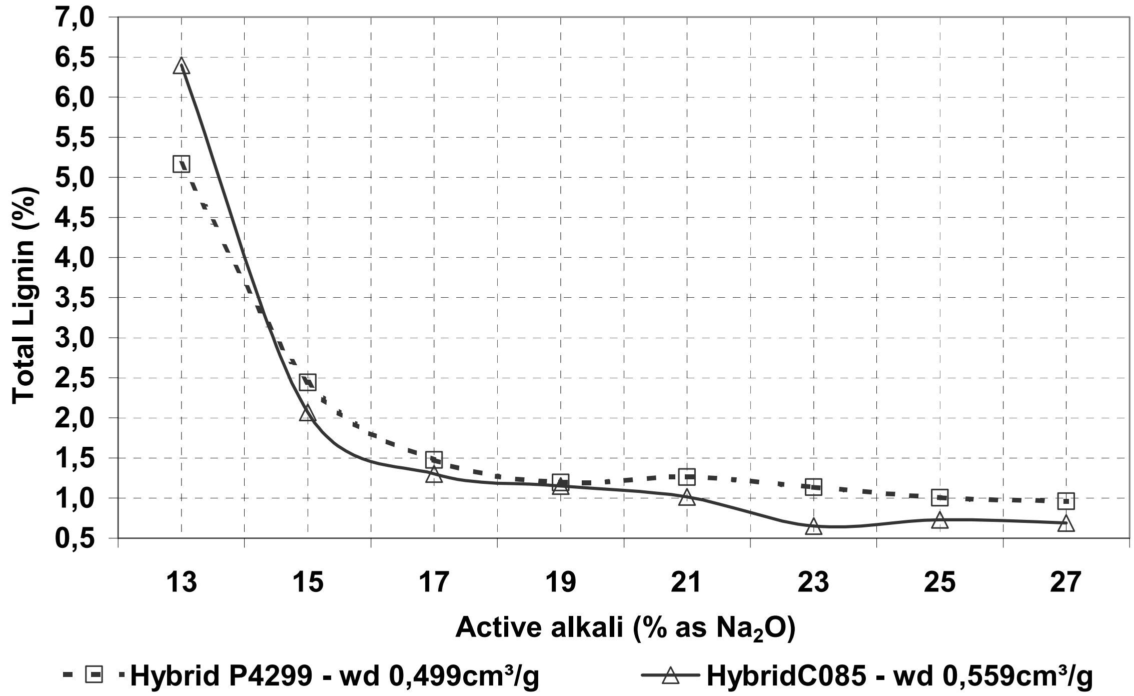

Figure 3 – Total lignin x active alkali

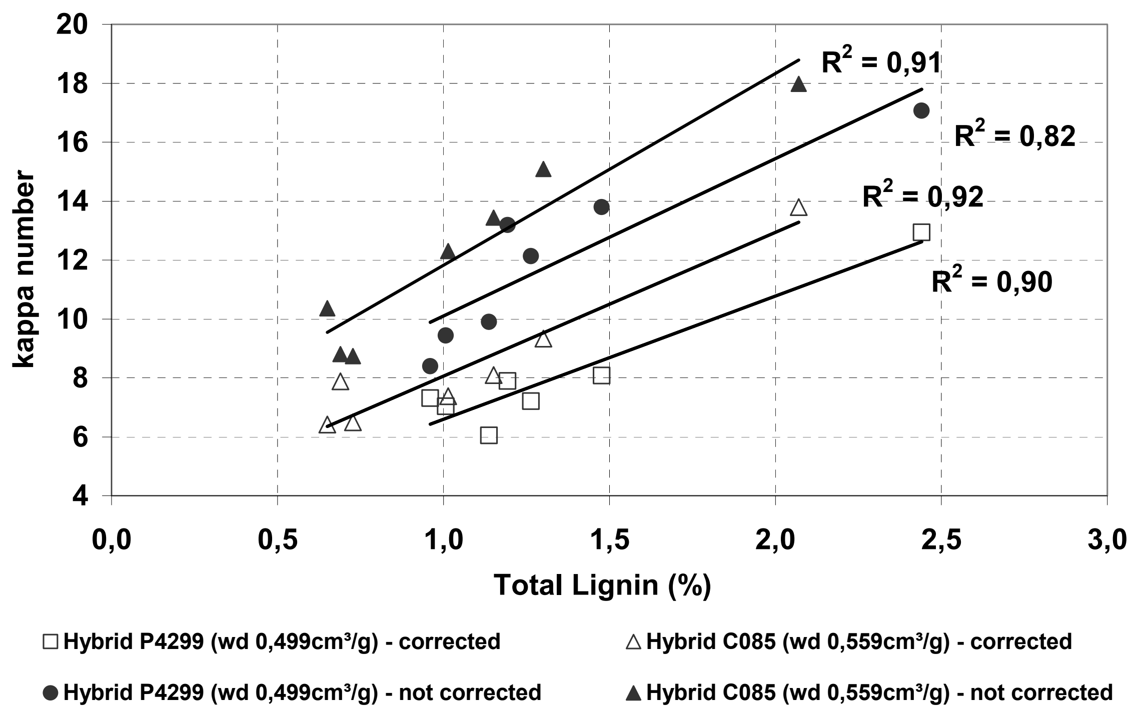

Figure 4 – Total lignin x kappa number

Figure 5 shows the effect of the alkali charge on the screened yield of the pulping process for materials P4299 and C085. Considering the inverse relation between the kappa number and the screened yield, the results presented in figure 3 show that for the materials considered in this study, for kappa number values of over 20, there is not an increase in the delignification efficiency. However, there is a significant reduction in the screened yield.

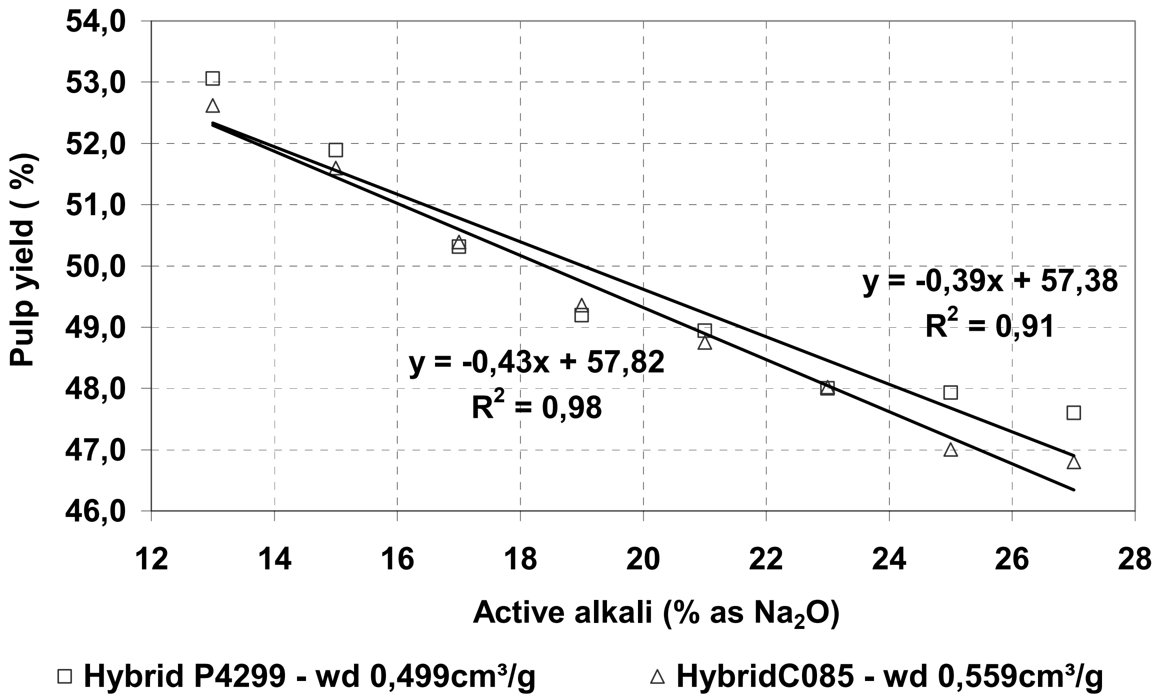

Figure 5 – Yield x active alkali

A significant reduction in the screened yield is observed as the alkali charge of the pulping process is increased. Such behavior is associated with carbohydrates loss, mainly the polysaccharides of low molecular weight, provoked by the degradation reactions.

The screened yield is an extremely important parameter for the pulp manufacturer considering the economic aspects related to the wood consumption, once the raw material is accountable for most of the pulp production cost.

Besides the negative aspect concerning the higher specific consumption of wood due to the lower yield, a low yield also generates a higher content of solids in the liquor, possibly resulting in a lower production rate, if the recovery boiler is running at its full capacity.

The kappa number and the screened yield are directly related process parameters. Figure 6 shows the effect of the delignification level (kappa number) on the screened yield of the pulping process for materials P4299 and C085.

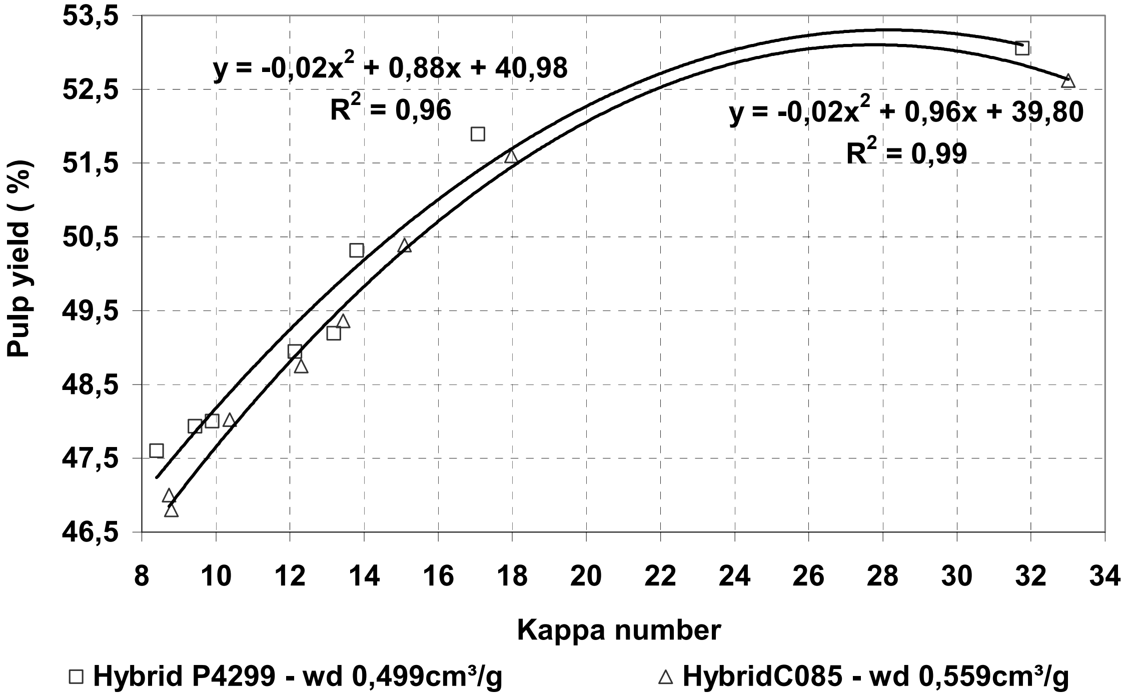

Figure 6 – Yield x kappa number

Figure 6 shows that for a kappa number of 18 or less, there is practically a linear effect of the kappa number on the screened yield of the pulping process, pointing out the importance of the non-isolated evaluation of parameters such as yield, alkali charge and, consequently, delignification level. As to kappa number values of about 30, there is also a screened yield reduction due to the higher amount of rejects, which are associated to the low alkali charge applied during the cooking. Similar values are also verified for materials P4299 and C085, which are possibly associated to the chemical composition similarity between the materials.

The viscosity of the pulp is a widely used parameter to control the pulp quality in the different phases of the production process. The pulp viscosity parameter is associated with the average polymerization degree and the corresponding molecular weight of the cellulose and hemicellulose polymers. This measure is used to indirectly estimate the carbohydrates degradation level during the phases of the pulping process.

Figure 7 shows the viscosity values obtained for both the materials studied when submitted to the different doses of active alkali.

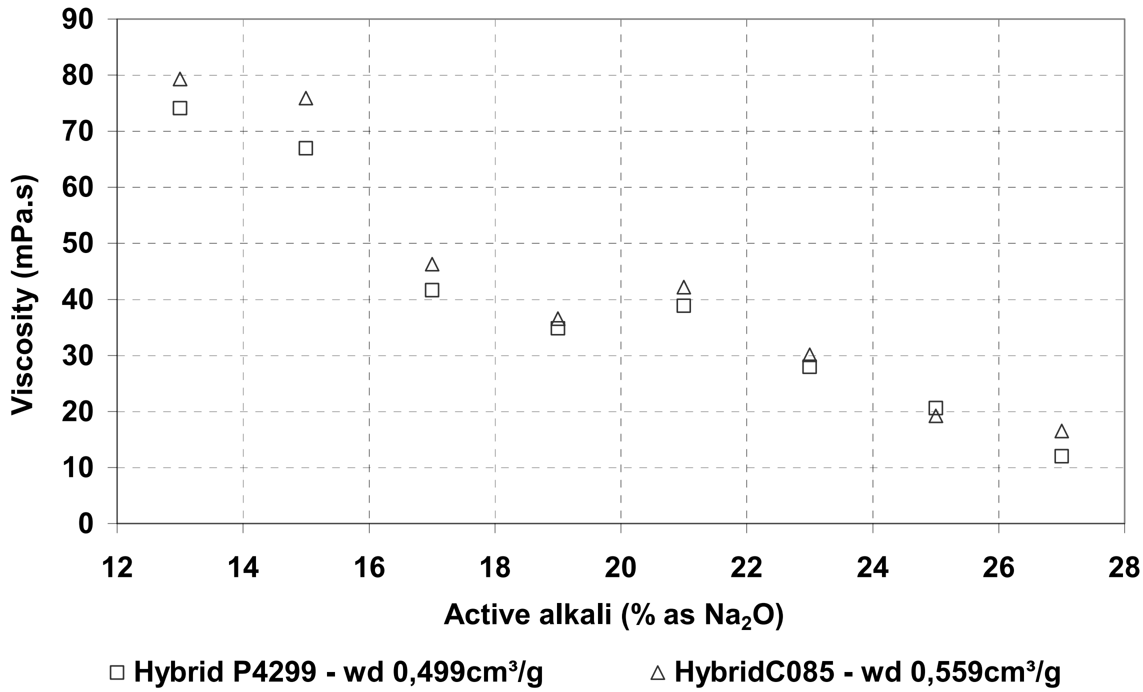

Figure 7 – Viscosity x active alkali

Figure 7 shows that no reduction is verified in the viscosity value of the pulp for alkali charges between 17% and 21%, which may be a transition region. A hypothesis would be that, although there is a low-molecular-weight polymer removal for this alkali level, the high-molecular-weight polysaccharides (cellulose) are preserved, allowing the maintenance of the average polymerization degree of the carbohydrates and the viscosity of the pulp. If confirmed in more detailed studies, these results can be interesting for the pulp production for sanitary uses, for it indicates an alkali charge limitation and delignification level for which hemicelluloses can be removed from the pulp without compromising the viscosity. A significant reduction in the pulp viscosity value for active alkali dosages of over 21% is shown in Figure 7, indicating polysaccharide degradation, resulting in pulps with lower physical resistance properties.

Figure 8 shows the hexenuronic acid contents of the pulp for materials P4299 and C085, when submitted to the different dosages of active alkali.

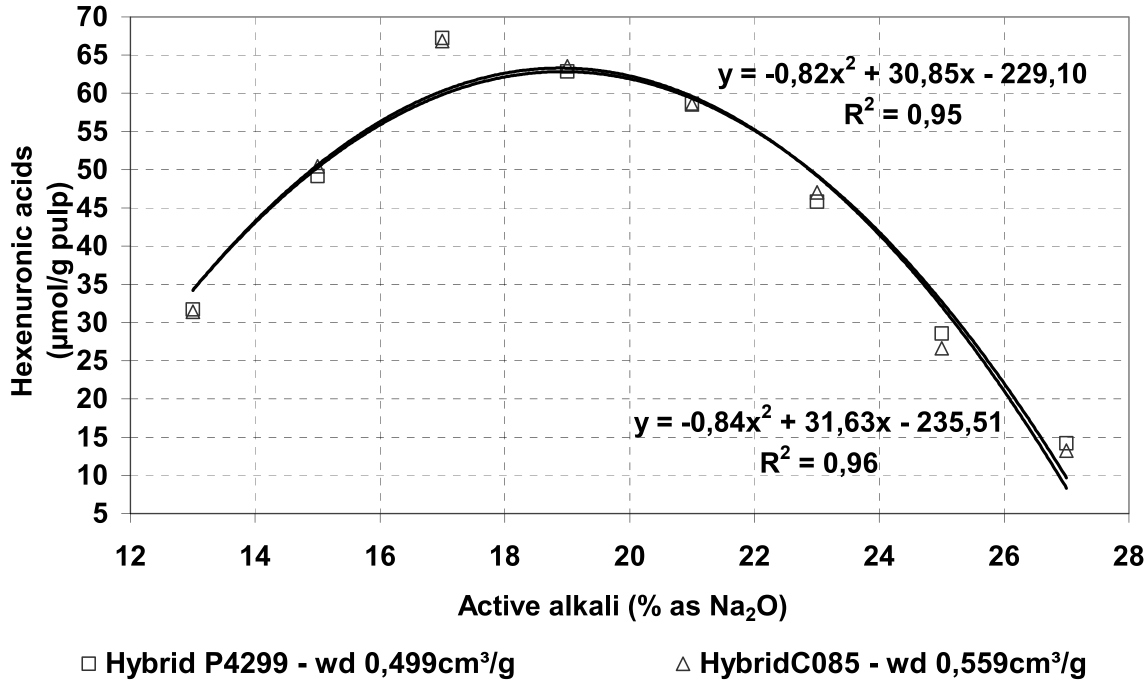

Figure 8 – Hexenuronic acid content x active alkali

Figure 8 shows that the hexenuronic acid formation is influenced by the alkali level used in the cook, confirming Chai's results (4), who described that the alkali charge and the H-factor are the main variables that influence the formation of hexenuronic acids during kraft pulping.

Figure 8 shows that an increase of 100% in the content of hexenuronic acids of the pulp when the alkali charge rises from 13% to 17%. As to alkali charges of above 17% of active alkali, we observe a significant reduction in the hexenuronic acids of the pulp, possibly due to dissolutions of hemicelluloses and/or degradation of hexenuronic acids.

The pulp kappa number, as said before, is a parameter that defines the strategies involved in the bleaching phase, such as charge of chemical reagents, number of stages, and sequence to be used. Therefore, it is important to analyze the existing relation between the kappa number and content of hexenuronic acid in the pulp in order to find out the influence of these acids on the bleaching phase, as discussed.

Figure 9 shows the correlation between the kappa number and content of hexenuronic acids of the pulp for both the materials studied, when submitted to different dosages of active alkali.

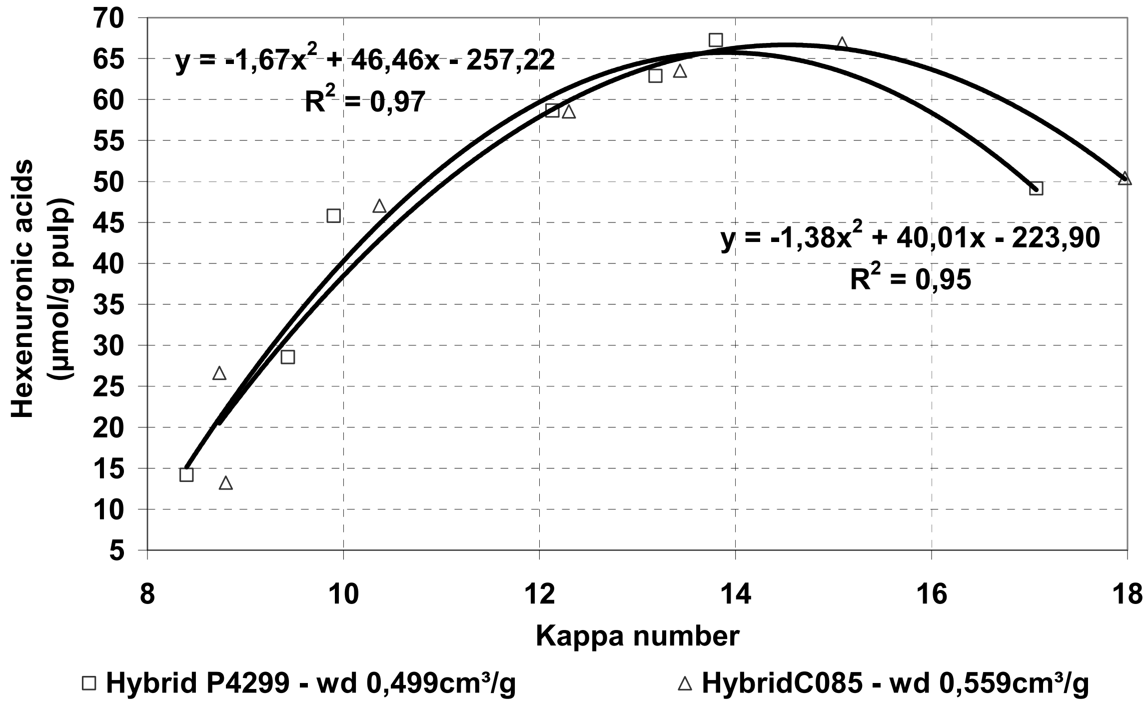

Figure 9 - Hexenuronic acid content x kappa number

Figure 9 shows that the amount of hexenuronic acid is also related to the kappa number of the pulp, considering the very association of the latter with the alkali charge applied in the pulping process, and consequently, the delignification level of the pulp.

The results show that the content of hexenuronic acid of the pulp significantly reduces to kappa numbers lower than 13, what is related to their degradation and the alkali dosages, as discussed. The content of hexenuronic acid is observed to increase when the kappa number of the pulp varies between 12 and 15, reaching a maximum kappa number of approximately 15. Kappa values above 16 present a reduction in the content of hexenuronic acids of the pulp, when related to a lower alkali charge used in the cooking. The results obtained are similar to Ek's et al. (2001), who studied conventional kraft pulping for *E. globulus*.

The content of hexenuronic acid in short fiber kraft pulp (*Liquidambar Styraciflua* L) obtained from different delignification levels decreases quickly when the delignification is brought to a kappa number under 14 (6).

Hemicelluloses are important chemicals present in the final pulp. Their presence, within certain limits, facilitates the refining of the fibers and also improves the physical properties of the paper. In the refining process, the fiber receives a mechanical treatment, which causes the removal of the primary wall of the fibers and allows their hydration, thus, increasing the flexibility and the bonding capacity of the fibers, and, consequently, the physical resistance properties of the paper.

Figure 10 shows the percentage of xylans removed from the wood during the pulping process for the different dosages of active alkali.

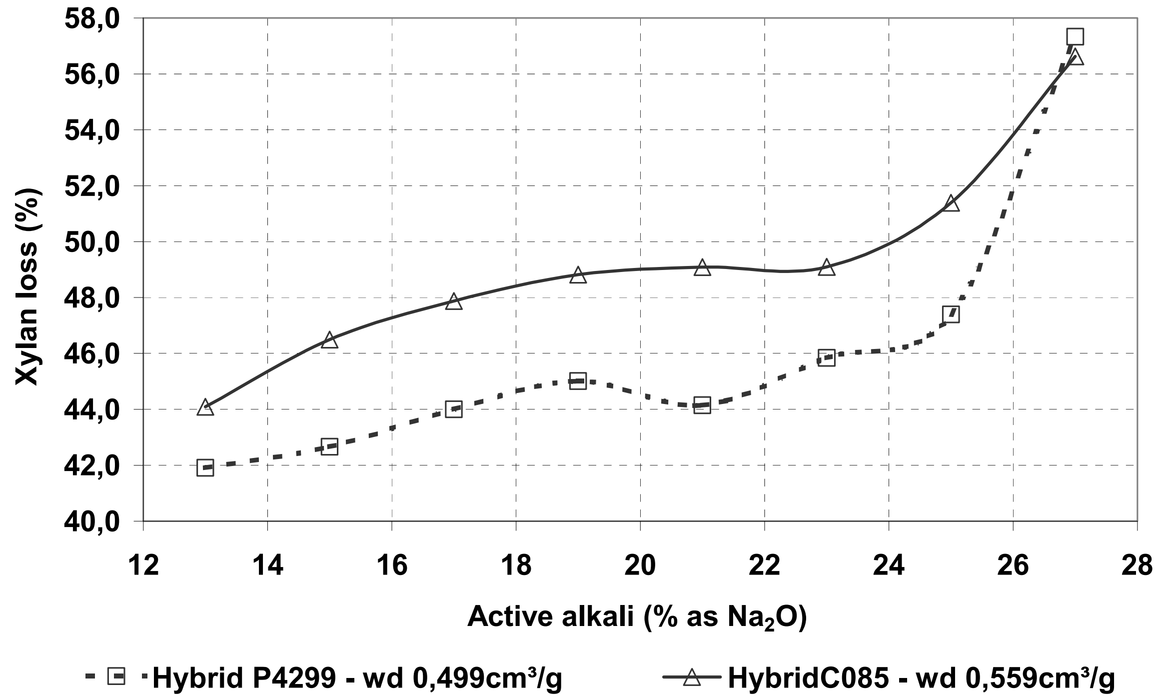

Figure 10 – Xylan loss x active alkali

Figure 10 shows that for an alkali charge of 15% active alkali and kappa number around 17, there is a removal of more than 40% of the xylans from the wood, showing more sensitivity of the low-molecular-weight polysaccharides to the increase of the alkali charge.

Figure 11 presents the percentage of glucans lost during the pulping process for the studied materials.

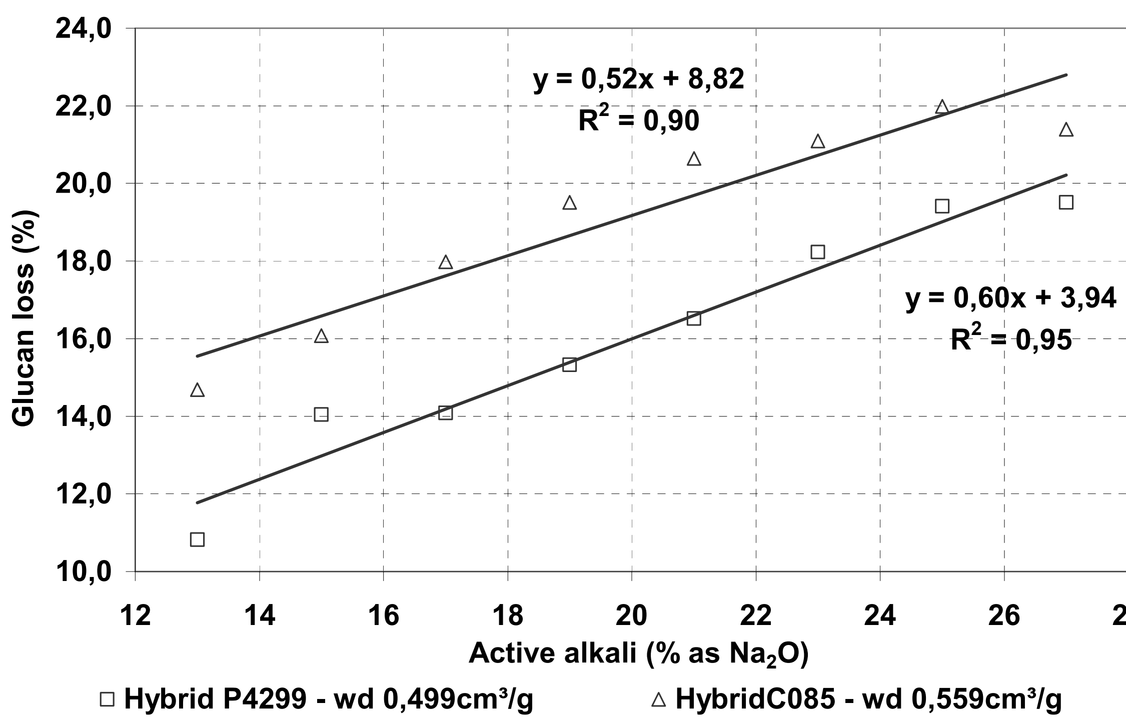

Figure 11 – Glucan loss x active alkali

Although glucans are less sensitive to the alkali charge than xylans, their removal from the pulp is observed as the alkali charge increases during the pulping process. Such behavior also occurs due to the terminal depolymerization reactions as well as the hydrolysis of cellulose polymers. These results are in accordance with the lower yield and viscosity values due to the increase in the alkali dosage, as previously observed.

Figure 12 presents the glucuronyl group percentage removed during the pulping process for materials P4299 and C085.

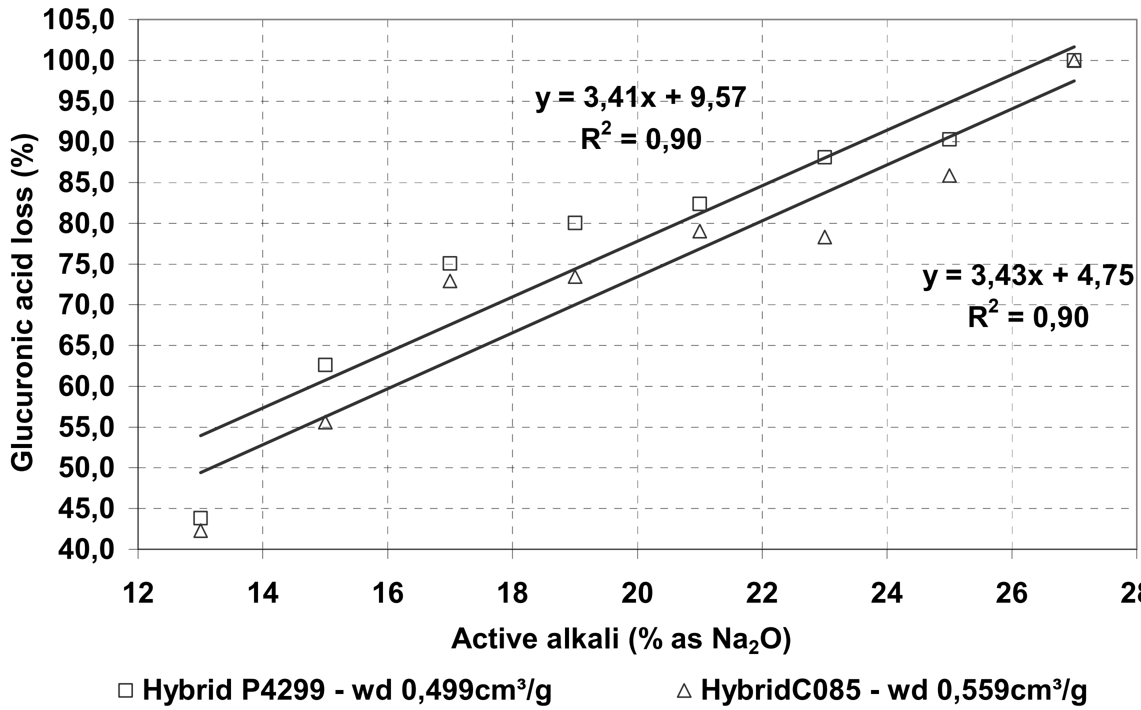

Figure 12 – Glucuronic acid loss x active alkali

The results shown in Figure 12 indicate that the alkali dosage also affects glucuronyl groups, which are reduced by 70% for an alkali charge of 17% of active alkali, which is likely associated with carbohydrate degradation.

Conclusions

From the results obtained in this research, the following conclusions can be established:

- the materials considered in this research (hybrid of *E. grandis* x *E. urophylla*), despite the basic density difference, showed the same performance under de Lo-Solids cooking; this fact may be related to the efficiency of the impregnation phase of this pulping process;

- the increase in the alkali charge leads to a reduction on the screened yield and in the kappa number; alkali charges above 19% did not show an increase in the delignification level;

- the maximum screened yield is obtained at kappa number 27;

- the hexenuronic acid formation is a function of the alkali charge; the hexA content increases up to an alkali charge of 18% and then decreases; the maximum hexA content is reached at kappa number 15;

- an increase in the target kappa number for bleachable grades (kappa 17 – 18) of eucalyptus pulp can lead in an increase in yield and also to a reduction in hexenuronic acid formation.

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