UTILIZATION OF BLACK LIQUOR XYLAN TO INCREASE TENSILE PROPERTIES OF KRAFT PULP

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ABSTRACT

Xylan is the main hemicellulose in many eucalyptus species. During kraft pulping, xylan is partly dissolved in the cooking liquor but part of it will be redeposited onto the fibers in the later parts of the cook. In earlier studies, we have shown how dissolved xylan in black liquor can be used to increase both tensile stiffness and tensile index of the produced paper. This can be done without increasing the density of the produced paper too much if the xylan used has a rather high molecular weight distribution and low degree of substitution of charged uronic acids. In this study, the possibilities to increase the tensile strength of *Eucalyptus urograndis* kraft pulp by black liquor addition were investigated. All additions of black liquor to the kraft cook increased both the tensile strength and the sheet density, independent on the history of the black liquors, i.e. temperature and retention time.

INTRODUCTION

During kraft cooking, lignin, a large portion of the hemicelluloses, and a small portion of the cellulose, are dissolved in the cooking liquor. Although some of the dissolved hemicelluloses, particularly xylan, can be redeposited onto the fiber surface (Yllner and Enström 1956), a large part of the hemicelluloses remain dissolved. Glucuronoxylan can be isolated from the kraft cooking liquor as oligo- and polysaccharides, whereas dissolved glucomannan is degraded into smaller units under kraft pulping conditions (Saarnio and Gustafsson 1953; Yllner and Enström 1957; Simonson 1963).

The effect of the hemicellulose content of the pulp was discussed early on, and it was suggested that hemicelluloses increase the strength of the fiber–fiber joint by either increasing the swelling capacity of the fiber or acting as a "glue" between the fibers (Pettersson and Rydholm 1961). Recently, it has been shown that the increase in the tensile strength of the sheet due to xylan addition can be fully explained by the higher content of xylan on the fiber *surface*, whereas xylan located in the inner part of the fiber affects neither tensile strength nor tear resistance (Sjöberg et al. 2004). It is commonly believed that surface xylan adds flexibility to the cell wall/fiber surface, resulting in stronger fiber–fiber joints or greater contact area between the fibers (Rydholm 1965; Bhaduri et al. 1995).

In an industrial study, it was shown that it is possible to improve the tensile properties of the manufactured pulp significantly by exchange of black liquors to increase the amount of dissolved xylan present (Dahlman et al. 2003). It has been shown that the highest improvements in tensile strength and tensile stiffness achieved by addition of hardwood black liquor to the kraft cook of softwood was seen when the retention time of the black liquor was low i.e. withdrawn early in the kraft cook. This was explained by the higher molecular weight of the added xylan (Danielsson and Lindström 2005). This study investigated the importance of the history of xylan added to the later parts of the *Eucalyptus urograndis* kraft cook. Temperature and replacement times were varied when black liquor was manufactured. These liquors were later used as replacement liquors in subsequent cooks when 40 minutes remained of cooking. The manufactured pulps were strength evaluated. The purpose was to develop the cooking process towards higher cooking yield and pulp strength.

EXPERIMENTAL

Materials

The pulps were manufactured from industrially chipped and screened *Eucalyptus urograndis* wood originating from Aracruz, Brazil. Chips with knots and bark were removed by hand. Cooking liquors were prepared from technical grade Na_2S(s) and NaOH(s) to reach the alkalinity of 18% and sulfidity of 30%. Air dried chips were pre-steamed at 15 bar for 5 min and subsequently delignified in a laboratory forced circulation digester with a cooking vessel volume of 16 dm^3 and a circulation flow rate of 15 dm^3/s.

Table 1. Cooking parameters of black liquor manufacturing cooks.

Cook	Temp (°C)	H-factors	Cooking time (min)*	Yield (%)	Kappa no	$[OH^-]_{res}$ (mol/l)
1	150	450	143	50.7	15.3	0.138
2	130	362	832	52.0	16.7	0.138
3	130	27	54	66.6	-	0.286
4	150	35	0	61.0	-	0.292

*At final temperature

Manufacturing of black liquors
The temperature in the digester was increased by 1°C/min from 70°C to the final temperature and then held constant at this temperature for particular lengths of time (see Table 1). After cooking, all pulps were washed for 12 h in deionized water and defibrated in a water jet NAF defibrator (Nordiska Armatur Fabriken, Sweden). The total amounts of oxidizable structures in all pulps was determined as the kappa number (SCAN C 1:00). The residual hydroxide ion (SCAN N 33:94) and hydrogen sulfide ion concentrations (SCAN N 31:94) of all spent black liquors were determined.

Xylan was isolated from the black liquors manufactured in the cooks outlined in Table 1 using a method described in Axelsson et al. (Axelsson et al. 1962), but with one modification: in the last washing step, acetone was used instead of ethyl ether. The amounts of Klason lignin in the wood, pulps, and precipitated black liquor xylan were determined using Tappi method T222 om-83 and the carbohydrate composition was determined after acid hydrolysis and GC detection according to Tappi T249 cm-00.

Kraft cooks with black liquor addition
Spent black liquor from cooks 1-4 was used in a new set of kraft cooks. The chips and white liquor was the same as above. The liquor-to-wood ratio was 4:1 and the amount of chips was 1 kg BD. The cooking device used was a circulation digester and the pre-steaming procedure was the same as described above. The cooking temperature was increased by 1°C/min from 70°C to 150°C and then held constant for 1h 34 min; 2 l of the cooking liquor were then withdrawn from the cook. Thereafter, 2 l were withdrawn at the same time as 2 l of a replacement liquor were added. The remaining 2 l of the replacement liquor were finally added to the cook. The replacement liquor used was the spent kraft black liquor corresponding to samples 1-4 in Table 1 with an adjusted hydroxide ion concentration of 0.4 mol/l, a hydrogen sulphide ion concentration of 0.2 mol/l, ionic strength measured as sodium ion concentration of 2.5 mol/l and xylan concentration of 4.8 g/l. One reference cook was carried out with white liquor as a replacement liquor with the same concentrations except the xylan concentration which was zero. The duration of the liquor exchange was 10 min in total. The cook continued for a total duration of 2h 14 min at 150°C. All pulps had a final kappa number of 14.5 ± 0.1. These pulps were wet disintegrated (ISO 5263) and beaten in a PFI mill (ISO 5264) in four portions using 0, 500, 1000 and 3000 revolutions. Drainability (SR number) was determined for all beaten pulps using Shopper-Riegler testing according to SCAN-C 19:65. Hand sheets were prepared using the Rapid-Köthen method (ISO 5269-2) with deionised water and added NaCl to a final conductivity of 2.5 mS. The tensile strength properties were evaluated according to ISO 5270. Sheet thickness was determined using the SCAN P88:01 method. At least 12 test strips were evaluated for each pulp sample, and the standard deviation was always less than 3 units.

RESULTS AND DISCUSSION

Figure 1 shows the xylan concentration in the four spent black liquors manufactured in cooks 1-4 from Table 1.

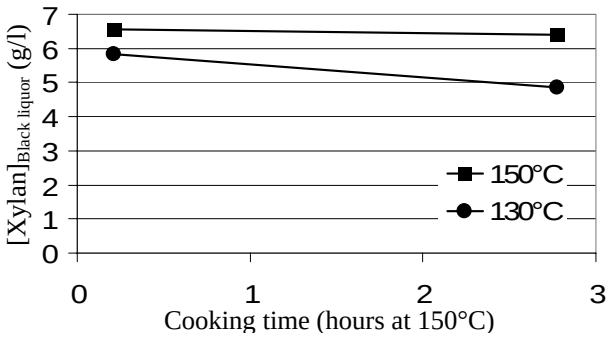

Figure 1. The xylan concentration in the black liquor at different cooking times and cooking temperatures. The cooking time was corrected to the cooking temperature of 150°C by using the energy of activation for the bulk delignification of eucalyptus, 118 kJ/mol (Santos et al. 1997).

It is seen that higher cooking temperature gives higher concentrations of xylan in the black liquor. The reason for the decrease in concentration with cooking time is degradation reactions and to some extent redepositon of xylan on the fiber surfaces. Compared to the behavior of birch xylan in the cook, the concentrations are here lower due to smaller amounts of xylan in the wood. It is also seen that the dissolved xylan is more stable throughout the cook, which has been seen before and can be explained by the lower cooking times and differences in molecular structure (Pinto et al. 2005). It has been shown for birch pulping that high cooking temperatures gives a dissolved xylan with higher amounts of total uronic acids (Danielsson et al. 2006).

Effect of xylan on pulp strength
The liquors in figure 1 were added to a subsequent kraft cook when 40 minutes of the cooking time remained. The retention time of the dissolved xylan in the black liquor affects the molecular weight and the cooking temperature affects the degree of substitution of uronic acids. The effect of these different kinds of xylan on the pulp strength was evaluated. Figure 2 shows the tensile strength of the pulps manufactured with addition of the different black liquors as response to beating. The amount of added xylan was the same for all the different additions.

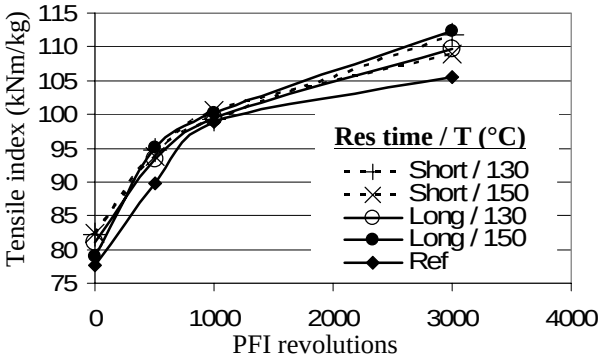

Figure 2. Tensile strength of pulps manufactured with addition of black liquor. The added black liquors were withdrawn from cooks after long or short cooking time and at 130 or 150°C cooking temperature. The reference was manufactured using white liquor as replacement liquor.

As seen in figure 2, the black liquor additions to the later parts of the cook significantly increased the beatability of the manufactured pulp. The history of added xylan seems to have no significant influence on the capacity of increasing the strength of the pulp. There are several possible reasons for this. The retention times were rather short for all these cooks compared to birch or softwood pulping so neither the molecular weight nor the degree of substitution of uronic acids have much time to be affected to any large extent. It has been showed that the molecular weight of dissolved xylan in *Eucalyptus globulus* is only slightly affected by cooking time (Lisboa et al. 2005). The four different xylans manufactured in the first part of this study may end up being not very different from each other and therefore there is no significant difference in the increase in strength between the different black liquor additions.Xylan increases the pulp strength as seen here and elsewhere but it also affects other parameters such as drainability and sheet density. It is therefore of interest to evaluate the tensile strength properties at different SR numbers (Figure 3) and sheet densities (Figure 4). Also compared at a given drainability, the tensile strength was increased by all different black liquor additions. The history of the black liquors was again not of any significant importance.

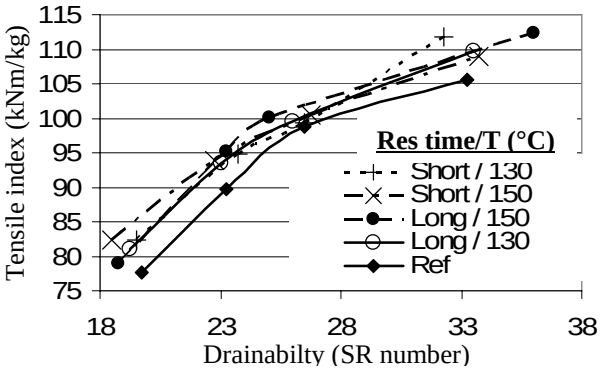

Figure 3. Tensile strength at different SR numbers for the same set of pulps as in figure 2.

Compared at a given sheet density however, the reference now had the highest tensile strength. Black liquor addition increased the sheet density to such an extent as eliminating the strength increase and ended up at lower tensile strength than the reference. Also the densification was similar for all the different xylan additions.

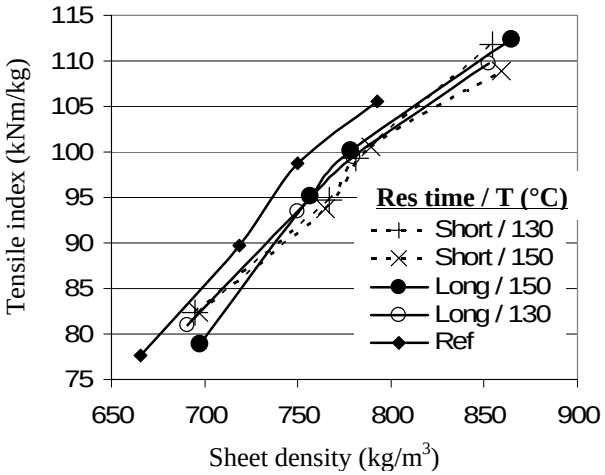

Figure 4. The tensile strength at different sheet densities for the same set of pulps as in Figure 2.

We have seen in an unpublished study for softwood cooking with addition of hardwood black liquor that a very high total amount of uronic acids also leads to a high densification of the sheet and the gain in strength will not be seen when compared at a given sheet density. The degree of substitution of dissolved xylan is decreased throughout the cook but is relatively high for eucalyptus (Lisboa et al. 2005) compared to birch xylan found in black liquor (Danielsson et al. 2006). Although no uronic acids have yet been quantified in this study, it is likely that all the additions above contain xylan with such high amounts of total uronic acids that all of them give high densification when sheets are manufactured. As the molecular weight of dissolved xylan is very slowly decreasing in eucalyptus kraft cooking and the degree of substitution is faster decreasing, the potential of this method is large when right cooking temperatures and retention times have been found.

We have earlier showed (Danielsson and Lindström 2005) that also the tensile stiffness can be significantly increased by an addition of xylan rich black liquor to the later parts of the kraft cook of softwood and that the increase correlates well to the replacement time of the dissolved xylans. In the case of eucalyptus no such effect was seen but they all ended up at around 11.5 MNm/kg in tensile stiffness index and the value was not affected much by beating.

CONCLUSIONS

When using black liquor xylan addition to the kraft cook of *Eucalyptus urograndis* in order to increase the pulp strength, the history of the black liquor does not seem to have any effect on the performance, within the studied interval. Black liquor addition increased both tensile strength and sheet density to such an extent so the overall tensile properties were negatively affected. We believe this has to do with the high amount of uronic acids in the added xylan.

ACKNOWLEDGEMENT

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