

XYLAN'S IMPACT ON EUCALYPTUS PULP YIELD AND STRENGTH – MYTH OR REALITY?

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ABSTRACT

Many studies for improving pulp yield and pulp strength have been conducted by increasing the amount of hemicelluloses, especially xylan, in the pulp. However, inconsistencies exist within the published data. This may be due to differences in xylan structure, nature of cellulose, and/or experimental conditions.

From mill experiences using alkali profile cooks on hardwoods, it was noticed that higher yield and tensile strength were obtained without a corresponding increase of xylan content. As a result, two laboratory studies using multiple white liquor additions and multiple black liquor extractions were carried out to investigate the impact of cooking conditions on pulp yield and pulp strength. Results of studies indicate that cellulose yield shows a good correlation with pulp yield and is significantly affected by alkali profiles. A higher alkali charge in the beginning of cook shows the most negative impact on cellulose yield at a given cooking chemical charge. There is no significant difference in xylan yield between different alkali profiles used in our studies. A positive effect of higher H-factor at a higher cooking temperature on pulp yield and pulp viscosity is also reported.

Both unbleached pulp cellulose yield and pulp viscosity affect the bleached pulp tensile index. However, unbleached pulp cellulose yield shows a better correlation than pulp viscosity. Xylan content of pulp does not show any effect on tensile index of either unbleached or bleached pulps.

INTRODUCTION

During conventional kraft cooking, part of the hemicellulose dissolves in the liquor. The hemicellulose dissolves steadily throughout cooking, and at the same time the dissolved hemicellulose undergoes degradation. For hardwood, the concentration of xylan in the cooking liquor reaches a maximum (about 8% of the wood weight) and then slowly decreases as the cooking is continued (1). For softwood, the maximum concentration is reached at a later stage of cooking and the concentration of dissolved xylan is lower compared with hardwood (2,3). The decrease in concentration of xylan in the black liquor may be attributed in part to redeposition on the fibers. Adsorption of birch and spruce xylyns on cellulose fibers (cotton and cotton linters) has been

demonstrated under ordinary kraft cooking conditions (4,5), although the amount of xylan in the birch pulp has not been found to increase at any stage of kraft cooking (1). An earlier study on radial distribution of hemicellulose through the cell wall of unbleached and bleached spruce kraft pulps concluded that the major portion of kraft hemicellulose, especially xylan, were located in the outermost layers of the fiber (6). Recent surface layer studies (5,7,8,9,10,11) also demonstrated that larger quantities of xylan were found in the surface layer materials isolated from both hardwood and softwood mill kraft pulps than in the inner layer material. These studies presumed that a large increase in the amount of xylan in the fiber surface resulted from xylan redeposition. However, Asunmaa and Lange (12) also found that the cellulose is most densely packed around the lumen of spruce and birch undelignified fibers, while the relative packing density in the outermost layers is roughly half of that around the lumen. They also found that hemicellulose is about half or more of the original carbohydrate material in the outermost regions. Around the lumen, 10 to 20% of the carbohydrate material is hemicellulose. If it is assumed that there is a redeposition of xylan during cooking, the amount is quite small, as was demonstrated by measuring radioactivity of tritium labeled xylan on the fiber (13). The decrease in the amount of xylan in the liquor must therefore be explained mainly by the degradation of the dissolved xylan (1,5).

It has been shown that the dissolution (or degradation) and redeposition of xylan are strongly affected by the cooking conditions. At the beginning of cooking (below 140°C), the amount of degraded xylan is small. This subtle stability against primary peeling is due to the presence of 4-O-methylglucuronic acid substituents predominantly in the C-2 position and arabinose in the C-3 position. As the temperature increases, the rate of alkaline hydrolysis of glycosidic bonds, including the bonds connecting the 4-O-methylglucuronic acid to the xylan chain, increases. As a result, xylan degradation during the heat-up period to the cooking temperature becomes significant. Earlier studies (1,14) also reported that the alkali charge has a strong influence on the degradation of xylan. The degradation of xylan is more pronounced at a higher alkali concentration, which promotes the dissolution of xylan. Our recent alkali profiling cook study (15) clearly demonstrated that the amount of dissolved xylan in the cooking liquor entirely depends on the alkali concentration of the cooking liquor. The amount of xylan dissolved in the cooking liquor decreased with lowering initial alkali concentration. It is also interesting to note that the dissolved xylan profile during alkali profile cooks behave differently compared to conventional cooks which showed a peak dissolved xylan concentration of 14g/l. However, an alkali profile cook with a cooking liquor concentration below 20 g/L EA as NaOH during the heating-up phase did not show the same peak concentration of

dissolved xylan in the cooking liquor at any stage of cooking. It was maintained at less than 5 g/L throughout the cook.

As a xylan molecule with fewer substituents at both the C-2 and C-3 positions is more susceptible to peeling reactions, the degradation of xylan in the pulp and the cooking liquor is accelerated. Degradation of the dissolved xylan in the cooking liquor can be shown by reduction of molecular weight or Degree of Polymerization (DP_n) (1,5). The solubility of xylan is clearly related to the substituents, especially uronic acid content and alkali concentration of the cooking liquor (5,13,14,16). Decreased alkali concentration during cooking, coupled with less substituted linear xylan, creates favorable conditions for redeposition to occur. It was also shown that xylan redeposition is influenced by cooking temperature and the amount of xylan in the cooking liquor (4,5,13,17,18). According to Hansson's study (13), the rate of sorption increases with increasing temperature, and higher sorption of birch xylan and pine glucomannan on cotton fiber was obtained at a higher temperature (18). But Clayton and Stone (13) reported contradictory results. When white birch chips were cooked with tritium labeled xylan under ordinary kraft cooking conditions, pulps of higher radioactivity were obtained at lower temperatures at a given amount of xylan. This presumably indicates that at lower temperatures, less xylan is decomposed and more dissolved xylan is available for sorption. A possible reason behind the differences between Hansson and Clayton's results is the amount of xylan used in the experiments. In Hansson's work, the amount of hemicellulose added in alkali solution was two times more than the amount of cotton, while the amount of xylan Clayton added was only 0.78% of the wood used during white birch cooking. However, a recent Danielsson study using birch black liquor concluded that temperature did not significantly affect xylan redeposition at a given alkali concentration (5). Meanwhile, results of the Clayton and Danielsson studies showed that compared to cooking temperature, alkali concentration in the cooking liquor had a greater effect on the xylan redeposition. The xylan redeposition is facilitated by a lower alkali concentration.

For many years, it has been claimed that pulp yield and pulp strength properties can be improved by increasing hemicellulose retention in the pulp. Since it is known that the change in alkalinity of the cooking liquor and temperature during the cook greatly affects the effectiveness of the hemicellulose retention, there is an increasing interest in developing new cooking processes that adapt flexible cooking conditions. Lo-Solids® Cooking is a unique pulping method maintaining both an even alkali concentration and lower dissolved wood solids throughout the cook. In Lo-Solids cooking, the multiple white liquor additions and multiple black liquor extractions can be arranged in many different ways, depending on each individual

digester. The inherent flexibility of the Lo-Solids cooking allows for independent control of chemical reaction environments within the various zones of a continuous digester.

Previously, the effect of the amount of xylan in the fiber on pulp yield and pulp strength properties was primarily studied using softwood under conventional cooking conditions. From mill experiences using alkali profile cooks on hardwoods, it was noticed that higher yield and tensile strength were obtained without a corresponding increase of xylan content. As a result, we decided to investigate the effect of changing alkalinity in the various cooking zones on the amount of carbohydrate in Eucalyptus pulps and its impact on pulp yield and pulp strength properties.

EXPERIMENTS

Eucalyptus Urogandis chips from Brazil were used for both the first and second studies. For the first study, three sets of laboratory cooks using total effective alkali (EA) charges of 18, 20, 22, and 24% were conducted for producing various kappa number pulps. In the first set of cooks, total EA charge was varied by varying the EA charge in the impregnation stage (8, 10, 12, and 14% EA) while adding the fixed EA charges at the first cook stage (6% EA) and wash zone (4% EA). In the second set of cooks, the EA charge to the impregnation stage (8% EA) and wash zone (4% EA) were fixed and the first cook stage EA charges were varied (6, 8, 10, and 12% EA). The third set of cooks was designed to vary the EA charge to the wash zone (4, 6, 8, and 10% EA) while adding a fixed EA charges to the impregnation (8% EA) and the first cook stage (6% EA). All cooks were done at 155 °C and 680 H-factor. For the second study, two different cooking temperatures (145°C and 155°C) were used for H-factor study under the same cooking conditions as the second set of cook in the first study.

RESULTS AND DISCUSSIONS

Effect on Pulp Yield and Kappa Number

It is shown that lignin-free yield is strongly affected by white liquor profiling (Figure 1). The yield loss is

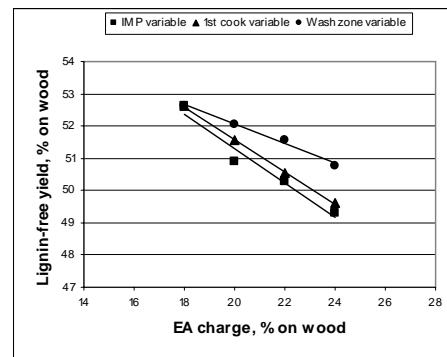


Figure 1. Impact of alkali profile on lignin-free yield

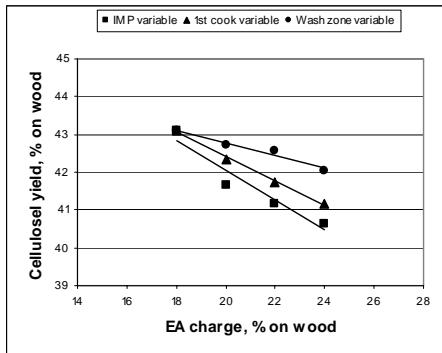


Figure 2. Impact of alkali profile on cellulose yield

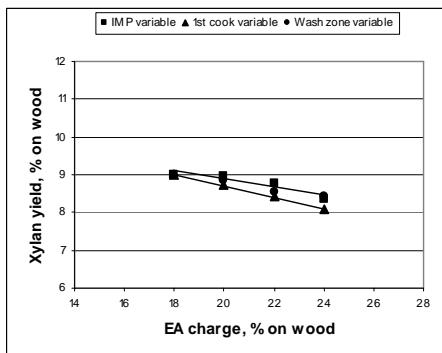


Figure 3. Impact of alkali profile on xylan yield

more pronounced with increasing alkali concentration in the beginning of cook (in the impregnation stage) than in the later stage of cooking (in the wash zone).

Under a constant alkali concentration in the impregnation stage, increasing alkali concentration during the heat-up period (the first cook stage) also showed the similar effect on pulp yield as increasing alkali concentration during the beginning of cook. This result clearly indicates that adding more cooking chemical in the initial and bulk delignification stages increases carbohydrate degradation, especially cellulose degradation (Figure 2). Comparably small differences in xylan yield were found between different white liquor profiles (Figure 3). This is somewhat unexpected as cellulose, which is more crystalline than hemicellulose, is more resistant to alkaline hydrolysis (19). However, this result can be explained by the stability of xylan against primary peeling reaction due to substituents in the C-2 and C-3 positions, and lower dissolution of xylan at a lower alkali concentration due to white liquor profiling (15). This is one of the factors which explains why lignin-free yield is primarily affected by the cellulose yield. This result is in agreement with earlier findings (20, 21). It is also found that xylan content in pulp cannot be used as an indicator of pulp yield. As seen in Figure 4, no relationship is found between the content

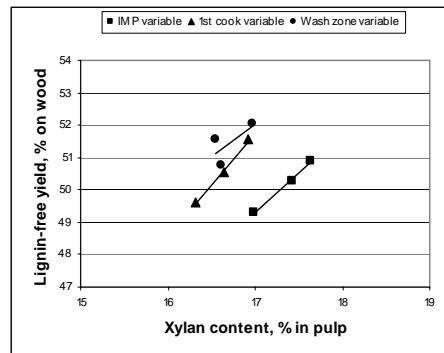


Figure 4. Impact of xylan content on lignin-free yield

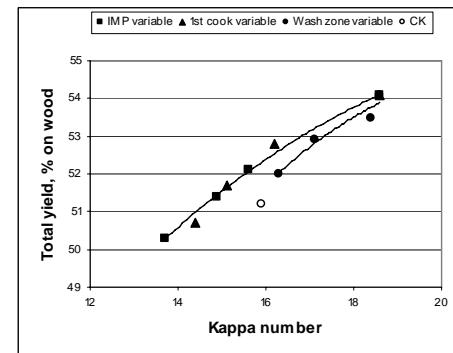


Figure 5. Impact of alkali profile on total yield as a function of kappa number

of xylan in the pulps and the lignin-free yield obtained from the series of cooks using different alkali profiles. In addition, when alkali charges were varied in a given stage of the cook, the variation of xylan content does not fully explain the variation of lignin-free yield.

Because the cooking conditions are mainly controlled by the target kappa number, the impact of alkali profiling on pulp yield should be compared at a given kappa number. When total yield is plotted as a function of kappa number (Figure 5), increasing the white liquor charge in the wash zone shows the most negative effect on pulp yield at a given kappa number.

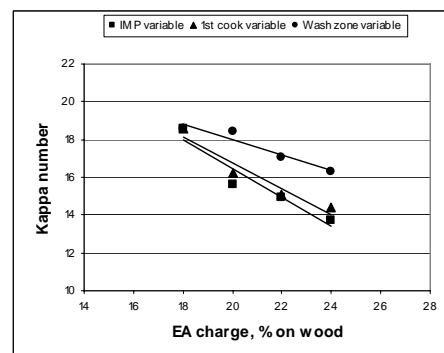


Figure 6. Impact of alkali profile on kappa number as a function of EA charge

This result is completely opposite compared to the results from Figure 1. This negative effect on pulp yield at a given kappa number is explained by the lower delignification rate. As seen in Figure 6, the alkali profile has quite a different influence on delignification compared to pulp yield. For a given total EA charge, increasing cooking liquor charges in the wash zone results in a higher kappa number. This indicates that for better delignification, white liquor charge should be higher in the initial or bulk delignification stages.

Due to the lower delignification rate, the alkali charge in the wash zone requires larger changes to obtain the same kappa number reduction than the changes needed in the impregnation and 1st cook stages. This higher alkali charge in the wash zone results in lowering the total yield at a given kappa number.

Tensile Index

Paper is a network of fibers bonded at fiber-fiber crossings. Tensile strength is mainly influenced by the strength of the fibers and the bond strength between them (22).

In general, fiber strength is significantly affected by cellulose fibrils, microfibrillar angle, mechanical and chemical fiber damages, and fiber defects.

During pulping and bleaching, fiber deformations such as fiber curls, kinks, and dislocations likely occur, and the influence of the deformations on fiber strength properties of the fiber network is significant (23). A lower tensile index is obtained with curled fibers. Meanwhile, kinks mainly affect the wet strength of the pulp.

For many decades, it has been known that hemicellulose improves paper strength by acting as an adhesive and binder (24,25,26). The function of hemicellulose as strength promoters is attributed to their high hydrophilic properties. Due to the high affinity for water, hemicellulose enhances swelling of the fiber, leading to fiber flexibility. This improves fiber conformation during sheet formation and increases inter-fiber bonding. Hence, paper properties correlated to fiber network strength properties such as tensile index is improved (27,28,29,30).

The contribution of hemicellulose to fiber strength is not clear. Hemicellulose may act as an effective stress-transfer matrix and mechanical damage to the fibers may impair the stress transfer matrix (31,32). Kim et al. (33) suggested that hemicellulose in fibers allows cellulose fibrils to flow and organize more when fibers are dried, and this strengthens dislocations and other potential weak spots.

According to Spiegelberg, xylan is the most significant hemicellulose for improving fiber strength. It has been

previously shown that the removal of xylan from the fiber decreases fiber strength (34,35,36).

Most earlier studies reporting the positive effect of xylan on paper and fiber strength were conducted under a constant amount of cellulose (load bearing element) in the fiber. In other words, only the amount of hemicellulose in the fiber was varied. However, a recent study employing different cooking conditions which vary the amount of both hemicellulose and cellulose in the fiber reported that the fiber strength and bond strength were not influenced by the hemicellulose content of fiber. However, tensile and tear index were linearly affected by the cellulose/hemicellulose ratio (37). The study on birch pulps produced under the ordinary kraft cooking conditions with and without hemicellulose promoting conditions (black liquor recirculation with and without lowering pH) at three different alkali charges concluded that at a given alkali charge, redeposited hemicellulose on fiber did not influence tensile index (Aurell's data table II). Results from this study also indicated that a higher tensile index is obtained from lower alkali cooking without hemicellulose promoting conditions than from higher alkali cooking with hemicellulose promoting conditions (17). This may indicate that minimizing degradation of cellulose and hemicellulose is more important than increasing the amount of hemicellulose in the fiber.

Recently, the influence of the location and the charge of xylan in the fiber on tensile strength was reported by several investigators (5,8,38). Results showed that higher xylan content was found in the fiber surface layer than in the inner layer, which may be due to xylan redeposition on the fiber. It was reported that this higher surface xylan content, but not inner layer xylan content, showed a positive correlation with tensile index. In addition, it was also reported that the surface xylan had a higher DP than the corresponding xylan in the inner layer (9). This is a quite interesting statement because if higher xylan content in the surface layer is the result of redeposition of dissolved xylan, the DP should be lower than the DP of xylan in the inner layer.

It might be possible that the higher xylan content in the surface layer leads to higher surface swelling, which leads to stronger inter-fiber bonds (39), but this increase in surface swelling may not be significant to the total fiber swelling and corresponding shrinkage in drying. The study on fiber surface charge of unbeaten regenerated cellulose (rayon) suggested that surface charge had no significant influence on the swelling whereas an increase in bulk charge had a large effect (38). However, the strength of the fiber-fiber joints and the paper tensile properties are mostly affected by the surface charge. This effect is due to an increase of the contact area with increasing charge.

Effect of white liquor profiling cooks on tensile strength

In order to study the effect of cooking conditions on tensile strength at a given H-factor, the tensile index at 3000 PFI revolutions was plotted as a function of unbleached pulp kappa number (Figure 7). For unbleached pulps, all pulps at different kappa numbers show a similar tensile index. It seems the variation in cooking conditions does not affect the unbleached pulp tensile index. In contrast, the bleached pulps

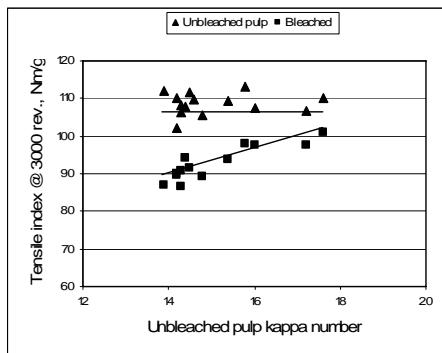


Figure 7. Impact of degree of cooking on tensile strength (cooking under the same HF).

show quite different results. A lower bleached pulp tensile index is obtained from a lower kappa unbleached pulp. This finding was unexpected because both 13.9 and 17.6 kappa unbleached pulps have a similar tensile index and the 13.9 kappa unbleached pulp is delignified under milder oxygen bleaching conditions than the 17.6 kappa pulp. In addition, both oxygen delignified pulps were bleached to 90% ISO under identical bleaching conditions. This clearly indicates that the variation of cooking conditions has a great influence on bleached pulp strength properties.

If the improvement of the pulp tensile strength is primarily explained by improving inter-fiber bonding strength with increasing xylan content in the fiber, a higher tensile strength should be obtained from pulps that have higher xylan content. However, as shown in Figure 8, the variation of xylan content in neither unbleached pulps nor bleached pulps affects the tensile index. For the unbleached pulp, despite a variation of xylan content of the pulp from 16.1 to 14.9%, the same tensile index is obtained. A similar trend can also be observed with the fully bleached pulps. The variation of xylan content from 15.4 to 14.5% does not affect tensile index. All bleached pulps show a similar tensile strength. As discussed in the previous section (15), the small variation of xylan yield was found between different white liquor profiling cooks. This small difference is due to the lower dissolution (or degradation) of xylan under low alkali concentration throughout the cook. Meanwhile, the difference of cellulose yield was significant. This means that the variation of xylan content in the fiber is more affected

by changing the amount of cellulose than by changing the amount of xylan itself in the fiber. This may be why no correlation between xylan content and tensile index was found. Another possible reason is, as described by other studies (5,40,41), the amount of xylan in these pulps is over the critical limit, and thus no longer affects the tensile index. Recently it was also reported that 4-O-methylglucuronoxylan shows very little effect on the change of handsheet properties (40). Both unbleached and bleached pulp show a wider variation of tensile index at a given xylan content. The range of variation in the tensile index is from 87 to 100 Nm/g. This means factors other than xylan content significantly affect the tensile strength of pulp.

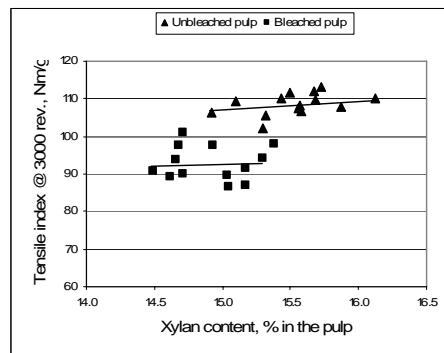


Figure 8. Impact of xylan content of pulp on tensile strength (cooking under the same HF).

Since the variation of pulp yield depends mainly on the cellulose yield under different cooking conditions, the impact of unbleached pulp cellulose yield on tensile strength of the bleached pulp is plotted in Figure 9. The bleached pulp tensile strength shows a good linear correlation with the unbleached pulp cellulose yield. A higher tensile index of bleached pulp is obtained from a higher unbleached pulp cellulose yield. When unbleached pulp cellulose yield increases from 41 to 43%, the tensile index of bleached pulp increases from 86 to 101 Nm/g. As shown in Figure 10, the tensile index of pulps is also affected by pulp viscosity. For unbleached pulps,

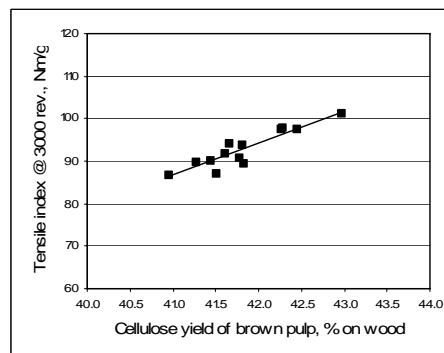


Figure 9. Impact of unbleached pulp cellulose yield on tensile strength of the bleached pulp (cooking with same HF).

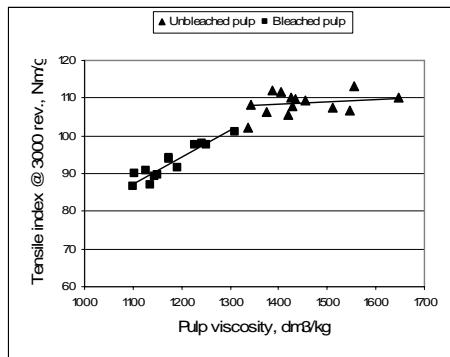


Figure 10. Effect of pulp viscosity on tensile strength (cooking under the same HF).

tensile strength decreases slightly as pulp viscosity decreases from 1640 to 1340 dm³/kg. However, bleached pulps show a quite different trend. Tensile strength of bleached pulp is directly proportional to bleached pulp viscosity. Changing bleached pulp viscosity from 1310 to 1100 dm³/kg decreases the tensile strength by 15 units from 101 to 86 Nm/g. This clearly indicates that decreasing the viscosity value below a certain level significantly affects the tensile strength due to a loss of fiber strength. When pulps were produced using the same H-factor, both unbleached cellulose yield and bleached pulp viscosity showed a good correlation with bleached pulp tensile strength. Since the effect of lower alkali concentration on tensile strength was found to be significant (17), higher H-factor cooks using a lower alkali concentration and higher cooking temperature was investigated. It was shown that despite using the

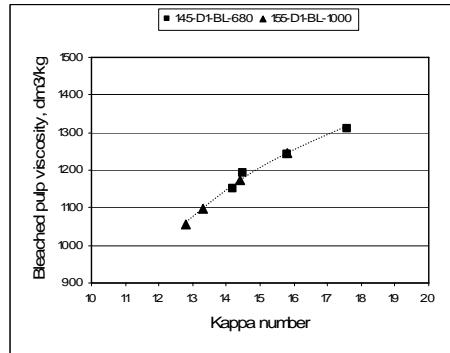


Figure 11. Effect of H-factor on bleached pulp viscosity (cooking under different HF).

higher temperature, lower alkali cooks maintained the same bleached pulp viscosities as lower H-factor cooks (Figure 11). However, as shown in Figure 12, bleached pulps produced from high H-factor cooking show a higher unbleached cellulose yield at a given kappa number than those produced from low H-factor cooking. When the bleached pulp tensile index was plotted as a function of unbleached cellulose yield and bleached pulp viscosity (Figures 13 and 14), the unbleached cellulose yield showed a better correlation with the tensile index of the bleached pulp.

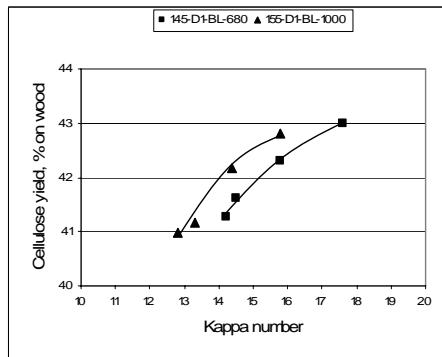


Figure 12. Effect of H-factor on unbleached pulp cellulose yield (cooking under different HF).

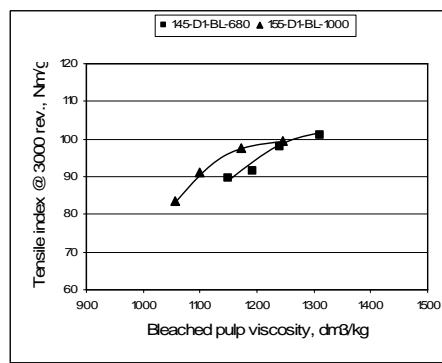


Figure 13. Effect of bleached pulp viscosity on bleached pulp tensile strength (cooking under different HF).

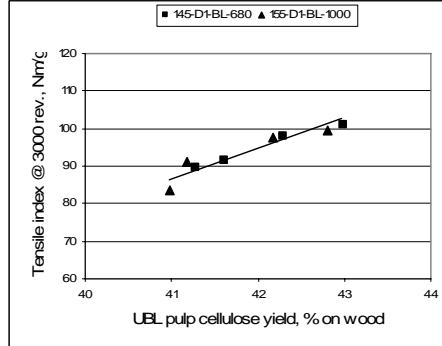


Figure 14. Effect of unbleached pulp cellulose yield on bleached pulp tensile strength (cooking with different HF).

This study suggested that the bleached pulp tensile strength is more dependent on cellulose characteristics than xylan content. Pulp viscosity does not adequately describe the cellulose characteristics, so there is a need to better understand the relationship between cellulose and tensile strength.

CONCLUSIONS

Our works on alkali profile cooks showed that

1. Pulp yield depends mainly on cellulose yield, and cellulose yield is significantly affected by alkali profiles.
2. Xylan content in pulp does not show any correlation with pulp yield.
3. Xylan content in pulp does not affect tensile index.
4. Unbleached pulp cellulose yield shows a better correlation with bleached pulp tensile index than pulp viscosity.
5. Selection of cooking conditions that produce higher unbleached pulp cellulose yield is a key factor to improve bleached pulp tensile index.
6. Cellulose yield is more affected by alkali distribution throughout the cook than by the cooking temperature.

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