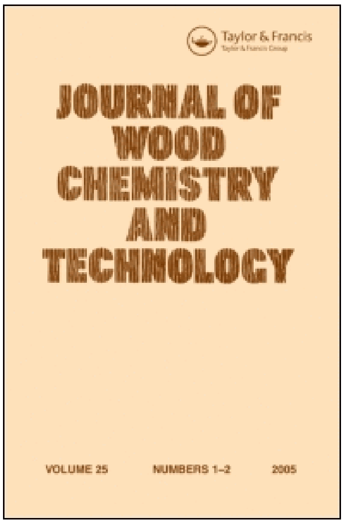

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Modification of Loblolly Pine Chips with *Ceriporiopsis subvermispora* Part 2: Kraft Pulping of Treated Chips

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Abstract: Loblolly pine (*Pinus* taeda) chips treated with *Ceriporiopsis subvermispora* for two or four weeks were pulped with different combinations of kraft pulping conditions to obtain a better understanding of the interaction between the fungal action and the pulping variables. Two different levels of effective alkali (18 or 22%), two times at maximum T_{max} (60 or 90 min), 22% sulfidity, and a T_{max} of 170°C, were used. The best delignification without adversely affecting pulp viscosity was found in pulps made from chips treated with the fungus for 2 weeks and at the mildest pulping conditions. At all pulping conditions there was a substantial decrease in the amount of rejects with 2 weeks of fungal treatment. Pulps from fungally-treated chips refined more easily than the control pulp and strength properties of pulps of fungally-treated chips were superior to those of the control pulp.

Keywords: *Ceriporiopsis subvermispora*, white-rot fungus, loblolly pine, kraft pulping, kappa number, lignin, carbohydrates, viscosity, refining, strength properties

INTRODUCTION

Early in the 1950's, Lawson et al.[1] considered the potential use of white-rot fungi in the pulp and paper industry. Most of the early attention was focused on the use of white-rot fungi to treat chips prior to mechanical pulping. With mechanical pulping the main efforts were focused on reduction of refining

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energy. These efforts were followed by consideration of fiber property improvement and improved bleaching response.

Kraft pulping and the papermaking properties of *Phanerochaete chrysosporium*-degraded oak were investigated in 1991 by Oriaran et al.[2] They followed the mycelial growth on the wood chips and found significant changes in the pulp yield, kappa number, water retention value, and handsheet properties. The pulps were more hydrophilic, responded faster to beating, and at comparable freeness levels had higher tensile, burst, and fold properties than pulps prepared from non-treated wood. Kraft pulps from *P. Chrysosporium*-degraded aspen chips also exhibited improved paper strength properties, such as burst and tear.[3]

Structural changes of residual lignin in decayed wood samples seem to affect the delignification process more than the extent of removal of individual wood components. Ferraz et al.[4] characterized the residual lignin of *Pinus taeda* chips treated with *C. subvermispora*. An extensive depolymerization of lignin was confirmed by the reduction in aryl-ether linkages from 10.6% (based on Klason lignin content) to 3.7% as a function of biodegradation time. In the preceding paper[5] we reported on the changes that occurred on treating loblolly pine (*Pinus taeda*) chips with *Ceriporiopsis subvermispora* for 2 and 4 weeks. In this paper we report on the effect that this type of treatment had on kraft pulping of the treated chips.

EXPERIMENTAL

Experimental Design

A split plot design was used with duplicates for each condition. This experimental design is suitable when one factor requires more experimental material for its evaluation than a second factor in factorial experiments. The larger treatment plot (the whole plot) or the kraft pulping set of conditions was split into smaller subplots corresponding to the different levels of fungal treatment.[5] For each level of fungal treatment time (0, 2, and 4 weeks), low and high levels of the pulping factors, effective alkali and time at maximum temperature, were studied.

Table 1 shows the different components of the design and the levels of the factors (low and high). The different combinations of the variables in the kraft pulping were arranged in 4 plots: low chemical/short time (LS), low chemical/long time (LL), high chemical/long time (HL), and high chemical/short time (HS). These 4 plots and their replicates gave rise to 2 blocks. Analyses of results were performed using the statistical software JMP version 4.

Kraft Pulping

After determining the chip moisture content, duplicate samples of loblolly pine chips from each level of fungal treatment time were placed in sealed

Table 1. Experimental plan corresponding to split plot design

Whole plot	Block	Fungal treatment	Time at T_{max}	Effective alkali	Kraft pulping designation
1	1	0	-1	-1	LS6
1	1	2	-1	-1	LS6
1	1	4	-1	-1	LS6
2	1	0	1	1	HL1
2	1	2	1	1	HL1
2	1	4	1	1	HL1
3	1	0	1	-1	HS2
3	1	2	1	-1	HS2
3	1	4	1	-1	HS2
4	1	0	-1	1	LL3
4	1	2	-1	1	LL3
4	1	4	-1	1	LL3
1	2	0	-1	-1	LS7
1	2	2	-1	-1	LS7
1	2	4	-1	-1	LS7
2	2	0	1	1	HL5
2	2	2	1	1	HL5
2	2	4	1	1	HL5
3	2	0	1	-1	HS8
3	2	2	1	-1	HS8
3	2	4	1	-1	HS8
4	2	0	-1	1	LL4
4	2	2	-1	1	LL4
4	2	4	-1	1	LL4

storage bags and stored in a freezer prior to pulping. Pulping was performed in a 4-L capacity M&K digester equipped with indirect heating through heat exchangers with forced liquor recirculation and a time-temperature program controller. The digester's basket was filled with 3 horizontal layers of chips separated by 48-mesh wire screens. The layers were chips subjected to 0 (control), 2, and 4 weeks of fungal treatment. The variables were effective alkali (18 or 22%) and time at maximum temperature, T_{max} (60 or 90 min). The other cooking variables, kept constant for all the experiments, were 22% sulfidity, 4:1 liquor-to-wood ratio, 90 min to T_{max}, and a T_{max} of 170°C. Table 2 summarizes the kraft cooking conditions. At the end of the cook, the different layers or fractions were kept in separate containers and thoroughly washed, as indicated by clear wash liquid. Each sample was then refined using a laboratory mixer and screened using a Williams type vibratory slotted screen (0.10 cut). The accepted pulps were then crumbed and kept in plastic bags in a refrigerator for further analysis.

Table 2. Kraft cooking conditions of control and biotreated chips

Conditions	Active alkali (AA), (%)	Effective alkali (EA), (%)	Time at 170°C[a] (min)	Sulfidity (%)
High chemical long time (HL)	22	19.5	90	22
High chemical short time (HS)	22	19.5	60	22
Low chemical Long time (LL)	18	16	90	22
Low chemical short time (LS)	18	16	60	22

[a] Time to T_{max} was always 90 min.

Analyses

The degree of delignification (kappa number) of the pulps was determined using TAPPI T236 cm-85. Klason lignin of kraft pulp samples was determined in accordance with TAPPI T222 om-88, "Acid-insoluble lignin in wood and pulp." The acid soluble lignin fraction was determined using TAPPI UM 250, "Acid-soluble lignin in wood and pulp." The total lignin content of a pulp sample was calculated as the sum of the Klason and acid-soluble lignins.

Refining of the never-dried kraft pulps was done in a PFI mill according to TAPPI T 248 cm-85. Samples of the pulp were collected at predetermined intervals (every 3,000 rev) from 0 to 12,000 revolutions of the refiner for a freeness (CSF) determination in accordance to TAPPI T 227 om-94, "Freeness of pulp."

The viscosities of the pulps were determined using a Cannon-Fenske capillary viscometer with 0.5M cupriethylenediamine (Cuen) as a solvent according to TAPPI T 230 om-32.

Handsheets for strength properties were prepared according to TAPPI T 205 om-88. Strength property measurements were performed on handsheets refined at 12,000 PFI revolutions. Test samples were conditioned and tested in a controlled humidity and temperature environment as outlined in TAPPI T 402 om-93. The tensile strength of a standard handsheet was determined as described in TAPPI T 220 om-88. The tear strength of a standard pulp handsheet was as described in TAPPI T 414 om-88.

RESULTS AND DISCUSSION

Pulp Yield

Because kraft pulping typically produces a relatively low yield, any modification of the conventional process should ideally be associated with a yield

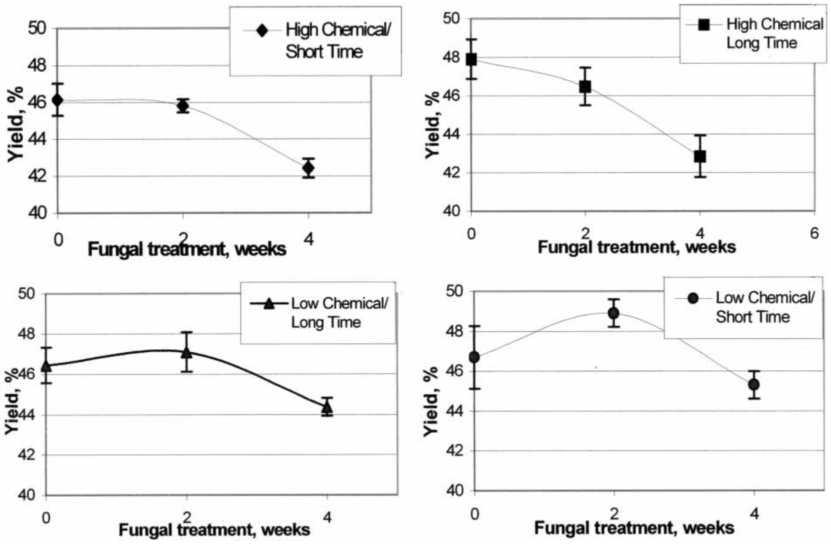

Figure 1. Effect of the chip fungal treatment time and kraft pulping conditions on pulp yield.

improvement. The combination of the fungal treatment and the cooking variables should affect the pulp yield, since it is related to lignin removal. The yield data for the 4 combinations of cooking treatments at different levels of biological treatment are shown in Figure 1. Except for the mildest pulping conditions (low chemical/short time) for which a yield increase was obtained there was no significant difference in the pulp yield between the control chips and those with 2 weeks of fungal treatment. For the four week treatment, the yield decreased significantly in all cases except the mildest conditions of low chemical and short time.

Rejects

The effects of kraft pulping variables and incubation time on the pulp rejects are shown in Figure 2. There was a substantial decrease in the rejects content as the incubation time increased from 0 to 2 weeks, regardless of the kraft pulping conditions. Although the harshest combination of variables (high chemical charge/long cooking time, HL) produced the smallest proportion of rejects, the mildest set of conditions (low chemical charge/short time, LS) resulted in the largest absolute decrease in pulping rejects with the fungal pretreatment.

Poor penetration and diffusion of cooking chemicals can cause nonuniform pulping and result in screened rejects. In this case, the exterior of the wood chip is overcooked and the interior is undercooked. From the results, it appears that fungal pretreatment of the chips improved the penetration of

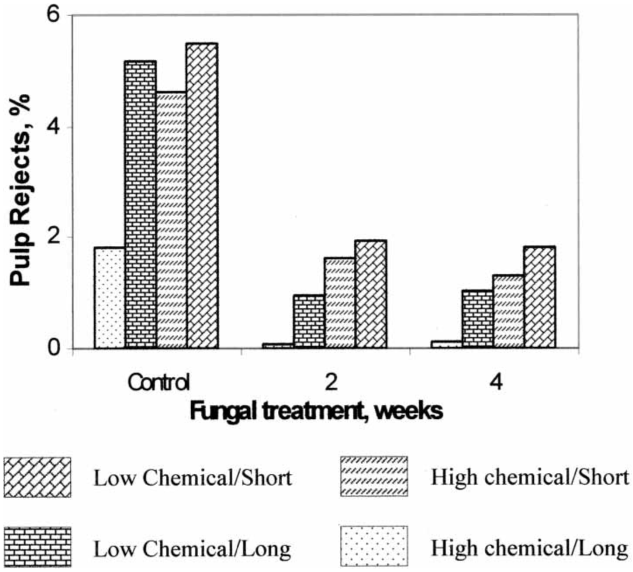

Figure 2. Effect of the chip fungal treatment time and kraft pulping conditions on pulping rejects.

the kraft liquor into the chips, thereby decreasing the proportion of screened rejects after pulping.

Delignification

The degree of delignification was followed by measuring the residual lignin content of the pulps. Kappa number and lignin content (both insoluble and soluble) were determined on both the control and fungally-treated pulps. Biological treatment time of the chips aided in reducing the lignin content of the kraft pulps. The kappa numbers of the biotreated pulps were significantly different than the control pulps for all the kraft pulping variations (Figure 3). An average reduction of 20% in the kappa number was observed after 2 weeks of fungal treatment for all the kraft pulping variations. The most drastic decrease in kappa number at 2 weeks of incubation was observed in kraft pulps produced at the extreme pulping conditions. The insoluble (Klason) lignins for the control and treated conditions which are shown in Figure 4 exhibit a similar beneficial effect of fungal treatment on delignification.

Pulping Selectivity

The progress of a pulping reaction is usually followed by two major factors: the lignin content of the pulp and the cellulose degree of polymerization. Usually

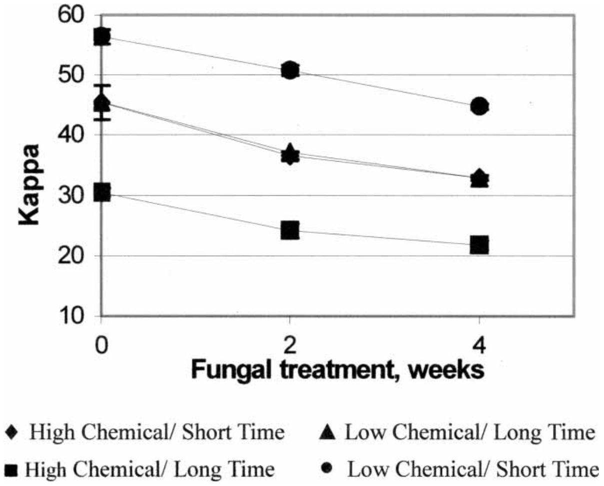

Figure 3. Effect of the chip fungal treatment time and kraft pulping conditions on the pulp kappa number.

the highest degree of delignification consistent with preservation of yield and pulp viscosity is desired. However, removal of the lignin in kraft pulping provides higher accessibility and thereby vulnerability of the wood polysaccharides. It is convenient to evaluate the benefits in lignin reduction accomplished by the fungal treatment against losses in yield. As illustrated in Figure 1, except for the mildest pulping conditions (low chemical/short time) and 2-weeks fungal treatment the pulp yields from the biotreated chips were

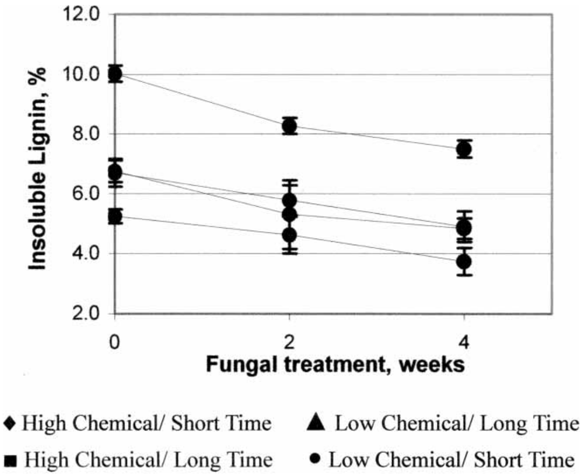

Figure 4. Effect of the chip fungal treatment time and kraft pulping conditions on the pulp Klason lignin.

lower than for the control chips. One interesting phenomenon was the fact that although there were no significant differences in wood component composition between untreated control chips and those treated with fungus for 2 weeks kraft pulps from these chips were significantly different. The most likely explanation for these findings is that the fungus causes structural changes to the fibers without significant material loss that enables the easier penetration of the cooking liquor, in turn enhancing delignification.

The lignin/carbohydrate ratios for control and treated samples for different combination of kraft pulping conditions are shown in Figure 5. It is evident that there is a significant decrease in the ratio of lignin to carbohydrate in the pulps with fungal pretreatment for all of the pulping conditions. Looking at the different kraft pulping combinations, pulping at a short time at maximum temperature (both low and high chemical charge), LS and HS, showed the maximum drop in the lignin/carbohydrate ratio after 2 weeks of fungal treatment of the pine chips. However, the maximum benefit was obtained with 4 weeks of fungal treatment of the chips followed by pulping with a high chemical charge and a short cooking time. This combination yielded a 32% drop in the lignin/carbohydrate ratio. An interesting feature of the combined fungal treatment and chemical pulping is that the harshest set of conditions (high chemical charge/long time) is not the best option to take full advantage of the fungal treatment.

Viscosity

The ability of fungi to remove lignin from wood selectively is one of the bases for their effectiveness in biopulping.[6] However, degradation of the wood

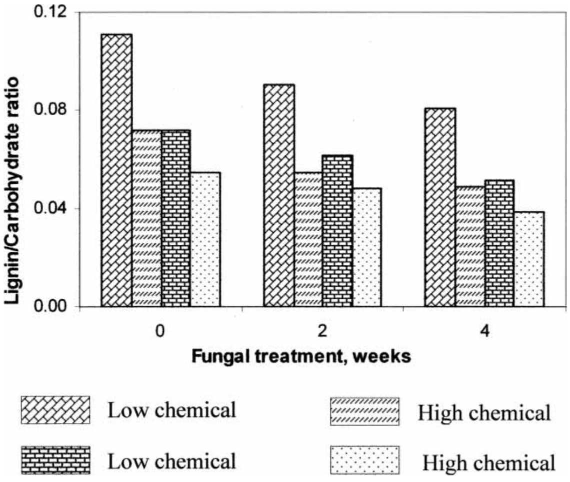

Figure 5. Effect of the chip fungal treatment time and kraft pulping conditions on the lignin/carbohydrate ratio in the pulp.

polysaccharides can also occur during the fungal delignification or subsequent chemical pulping. Pulp viscosity can be an indication of such deterioration since it can be related to the average degree of polymerization of the wood polysaccharides, primarily cellulose. Figure 6 shows the viscosity of pulps from control and treated chips corresponding to the different combinations of pulping conditions. The viscosities of pulps from the control chips ranged from 33.4 to 22.7 mPa.s for the mildest to the strongest pulping conditions, respectively. Similar viscosities were obtained by using either high chemical/short time (HS) or low chemical/long time (LL) pulping conditions. The HL conditions (high chemical charge/longest time at T_{max}), being the harshest set of conditions, yielded the lowest viscosities. For the mildest pulping conditions (LS), there was no significant difference in the viscosities of the pulps from the control chips and those treated with the fungus for 2 weeks. The same was true for the intermediate sets of conditions, HS and LL (high chemical charge/short time and low chemical charge/long time). However, for the harshest pulping conditions the viscosity of the pulp from the chips treated with fungus for two weeks was significantly lower than the viscosity of the control pulp. In all cases the viscosities of pulps from chips treated with fungus for four weeks were significantly lower than the viscosities of the respective control pulps.

The maximum viscosity losses for the shortest fungal treatment (2 weeks) were less than 10% for any of the kraft pulping conditions. This was also applicable for the mildest set of pulping conditions with chips treated with

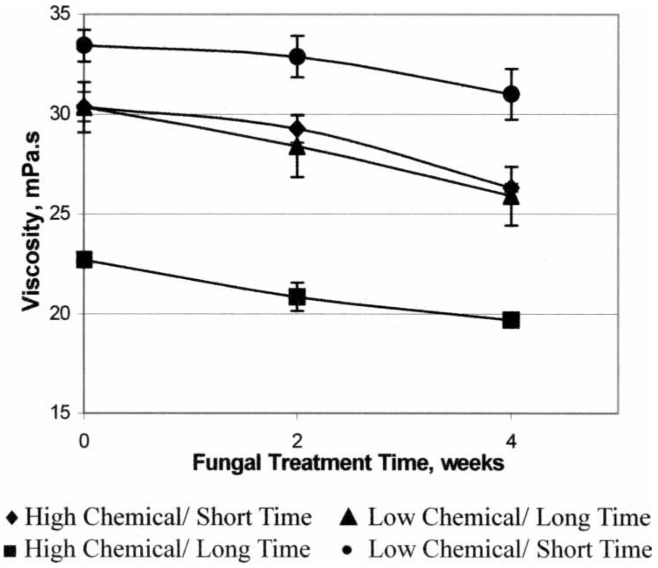

Figure 6. Effect of the chip fungal treatment time and kraft pulping conditions on the pulp viscosity.

fungus for four weeks. However, if the pulping conditions were more severe, viscosity losses could reach 15%.

The potential advantage provided by the fungal pretreatment can be seen in Figure 7 in which the relationship between Klason lignin and viscosity for the different pulping conditions and time of biotreatment are shown. As indicated in Figure 7, the control kraft pulp had the lowest selectivity at any lignin content. The differences in lignin content between the pulps from the control chips and those subjected to 2 weeks of fungal treatment are more evident at high viscosities (between 25 and 30), than at lower viscosities.

Viscosity and Delignification

Even though the longest fungal treatment (4 weeks) resulted in the lowest lignin content, it was associated with a decrease in viscosity. It seems clear that the mildest treatments can take the best advantage of the fungal treatment, in other words, high viscosities, (between 25 and 30) and significant lignin decreases can be achieved with just 2 weeks of fungal treatment. The best responses in terms of low delignification and low viscosity loss are reflected in the kraft pulps prepared at short cooking times (at low and high chemical charges, LS, HS) at 2 weeks pretreatment. The greatest advantage was obtained with the mildest pulping conditions (LS) that decreased the lignin content by 17% while reducing the viscosity by only 1.5%. Another interesting observation is that 4 weeks of fungal pretreatment in conjunction with relatively mild pulping conditions (LL or HS) gave pulps with better characteristics than those from control chips cooked at high chemical charge/long time (HL). This is one of the potential benefits of the biotreatment, i.e. savings in chemicals or decreasing the cooking time in kraft pulping. It can be established from these data that

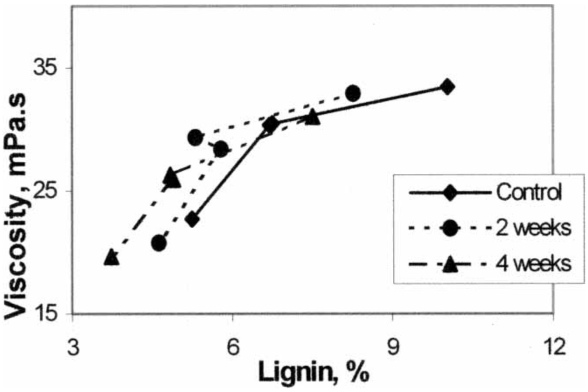

Figure 7. Viscosity *versus* lignin content for kraft pulps as a function of chip fungal treatment time.

the harshest set of pulping conditions involving a high chemical charge with long time (HL) overpower the potential benefits of the biotreatment. Based on these results, it appears that the most beneficial use of the fungal pretreatment might be in producing linerboard or other high kappa number products.

Refining

To obtain a better understanding of the benefits of chip fungal pretreatment on kraft pulps, refining studies were conducted on the pulps from untreated and treated chips. Fungal treatment of wood introduces alterations such as cell wall thinning, fragmentation, swelling, and relaxing of the normally rigid cell wall. It is expected then, that the modified fiber structure will respond more easily to refining than the untreated one.

Figure 8 shows the freeness as a function of the PFI mill revolutions for the control and biotreated kraft pulps. Although lower CSF values were found for the biotreated kraft pulps compared to the control, the differences were not statistically different for all four kraft pulping conditions. After four weeks of biological treatments the differences compared to both the control and 2 weeks treatment were statistically significant. The decreased freeness implies that less beating time (or energy) is required for a desirable freeness after fungal pretreatment.

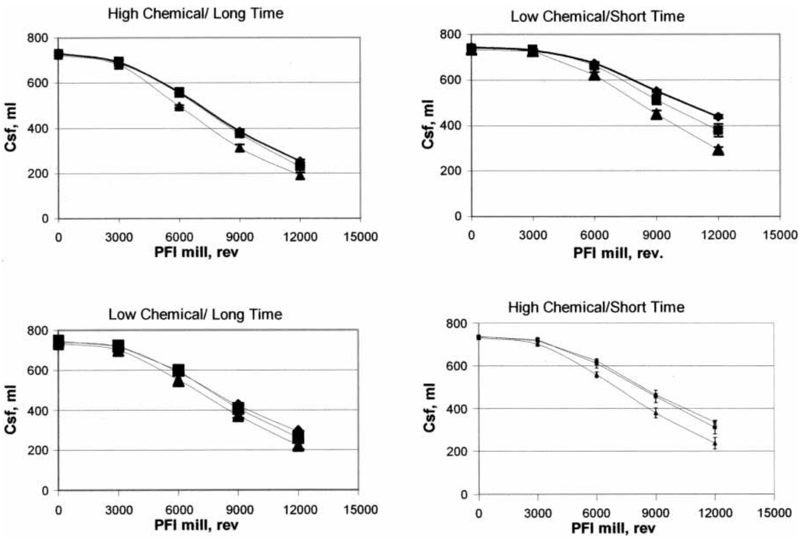

Figure 8. Canadian standard freeness (CSF) as a function of PFI mill revolutions for the combination of the different treatments (◆ Control, ■ 2 weeks incubation, ▲ 4 weeks incubation).

Sheet Properties

The tensile properties of a paper sheet are functions of bonding, fiber strength, and fiber length. Tensile strength is a direct indication of the durability and potential end-use performance of those papers that receive direct tensile stresses in use. Although a certain minimum tensile strength is required of any paper that undergoes a web converting operation, this property is particularly important for papers such as bags, wrapping, and printing papers. Figure 9 shows the effect of the different pulping conditions on the tensile properties of pulps from control and treated chips after the pulps have been refined to 12,000 revolutions in a PFI mill.

The tensile indices of kraft pulps from fungally-treated chips were greater than those of the control pulps, with the exception of the low chemical/short time pulping conditions. In this case the tensile index for the pulp from the chips treated for two weeks was not statistically different from the control pulp. The data indicates that the maximum benefit with respect to the tensile index is obtained from treated chips pulped under the low chemical/long time (LL) conditions.

The tearing strength of a paper sheet is a function of sheet density, fiber length, bonding, and fiber strength. Tear strength is particularly valued as a test for paper and paperboard which will be subjected to tearing type stresses during converting or in its end use. Bags, wrapping papers, tissue papers, books, magazines, newsprints, etc. are all types of papers where tear strength

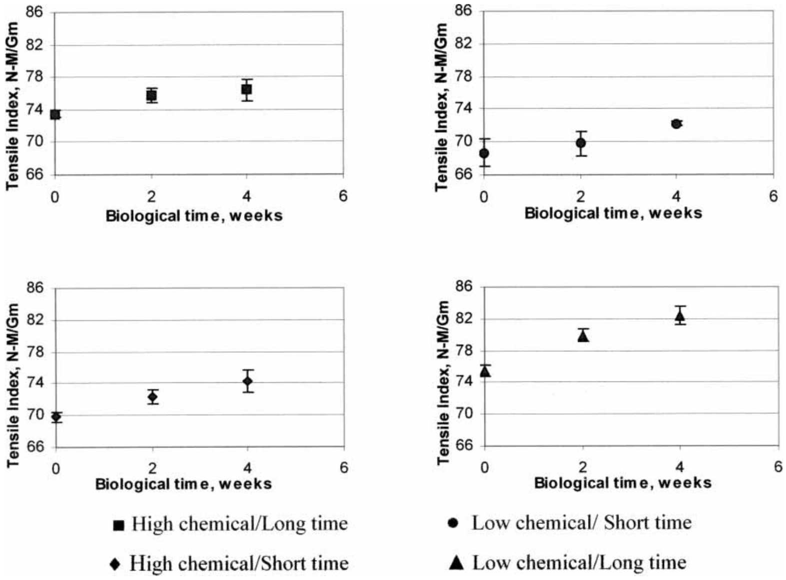

Figure 9. Effect of the chip fungal treatment time and kraft pulping conditions on pulp handsheet tensile indices.

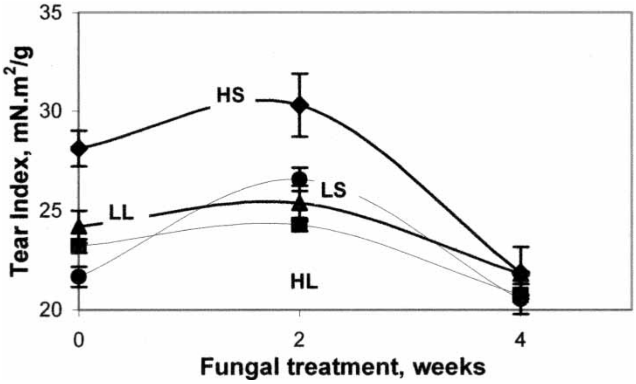

Figure 10. Effect of the chip fungal treatment time and kraft pulping conditions on the pulp handsheet tear indices.

is of critical importance. Figure 10 illustrates the tear index variation as a result of processing control and treated chips at different kraft pulping conditions. It all cases, the maximum tear is achieved with the 2-week treatment, although the actual increase depends on the pulping conditions.

CONCLUSIONS

All the effects of fungal treatment (extractives removal, lignin depolymerization, and increased porosity) appear to facilitate the kraft cooking process. Modification of the chips by the fungus left larger and/or additional pore structures capable of enhancing access of the pulping liquor to the cell wall components. The effectiveness of the kraft pulping process was enhanced, as demonstrated by the higher lignin removal in pulps from chips treated with the fungus. Although wood lignin losses were not statistically significant after 2 weeks of incubation with the fungus, the chemically modified lignin was more readily solubilized by the cooking liquor. The fungal treatment also helps to preserve pulp viscosity while achieving lignin degradation. This study also corroborates results reported by other authors,[6] that the milder the cooking conditions, the greater the benefits of the fungal pretreatment. Some changes observed in pulping and papermaking properties can also be considered as encouraging, such as the reduction in refining energy and the improvement in some mechanical properties (tear and tensile) in pulps produced from chips pretreated with the fungus.

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