Proceedings of the 6th international Conference on Biotechnology in the
Pulp and Paper Industry: Advances in Applied and Fundamental Research

# Biosulfite Pulping using *Ceriporiopsis subvermispora*

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**SUMMARY**
In this study, we examined the effect of fungal pretreatment of wood chips prior to sodium bisulfite and calcium acid sulfite pulping. The pretreatment involved a 2-week incubation of loblolly pine chips with two strains (CZ-3 and L-14807 SS-3) of the white-rot fungus *Ceriporiopsis subvermispora.* Focus was on the kappa number and yield and liquor consumption. Effluent quality was discussed in a previous publication (l). During sodium bisulfite pulping, the fungal pretreatment reduced the kappa number by 27% with slightly lower pulp yield compared to the control. The two strains produced about the same results. However, during calcium acid sulfite pulping, strains CZ-3 and SS-3 reduced the kappa number by 48% and 21%, respectively, compared to the control, but had the same pulp yield as that of the control. Liquor consumption was not appreciably affected by the fungal pretreatment. Thus, fungal pretreatment is advantageous for sulfite pulping.

## INTRODUCTION

Biopulping, defined as the fungal treatment of wood chips prior to pulping, may solve some of the problems associated with the traditional sulfite pulping processes. To date in our laboratory, we have focused only on the effect of fungal pretreatment of chips prior to refiner mechanical pulping. The 2-week process saved at least 30% electrical energy during refining, improved paper strength properties, and reduced the environmental impact of pulping (2-6) However, a study (7) done in collaboration with the Technical University, Vienna, Austria, and a recent review (8) indicate that fungal pretreatment also offers a great advantage for magnesium-based sulfite pulping. We have further explored this approach, and extended the use of fungal pretreatment for sodium bisulfite and calcium acid sulfite pulping.

We hypothesized that the fungal pretreatment can be beneficial in several ways. The treatment cart reduce the amount of cooking time, hence the energy that is required for pulping. The chemical demand can also be lessened due to prior degradation of the lignin by the fungus. The amount of bleaching can be reduced by selectively removing lignin from the wood by the fungus. Using these criteria, the effect of the best biopulping fungus for mechanical pulping, *Ceriporiopsis subvermispora* (2), was studied on kappa number and pulp yield, effluent properties, and pulp bleaching characteristics after sulfite pulping. Previous work (1) emphasized reducing the environmental impact of the traditional sulfite pulping processes and pulp bleaching characteristics.

## MATERIALS AND METHODS

Freshly cut loblolly pine logs were debarked and chipped to a size averaging 16 mm and frozen. The chips were then thawed, inoculated with two strains of *Ceriporiopsis subvermispora.* and incubated for 2 weeks at 27°C. and aerated with a specific aeration rate of 0.0227 L/L/min. At harvest, the fungus-treated chips and control chips were made into pin chips by processing the chips in a lab-scale atmospheric refiner equipped with "devil's teeth" plates. The chips were screened on an 3.2-mm mesh screen to remove fine material. The resulting chips averaged approximately 4 by 4 by 20-mm in size. Details regarding the experimental procedure can be found in a previous publication (1).

We pulped the chips in 90-ml bombs that were indirectly heated in an oil bath. The temperature was ramped from 70°C to the final temperature over a period given in Table 1. which also details the typical liquor conditions used. For the calcium-based cooks, the liquor was obtained from a commercial source and titrated according to Tappi test method T 604. The sodium-based liquor was prepared as needed from reagent grade sodium hydrogen sulfite ($NaHSO_3$). No gas relief (as is commonly done in the industry) was performed during the cook.

At the conclusion of the cook, the contents of the bombs were cooled to 90°C and then disintegrated in a Waring blender for 5 minutes. The resulting pulp was washed over filter paper, dried, and the yield and kappa number determined. The kappa number was determined using Tappi test method T 236. The spent liquor was analyzed using Tappi test method T 604 for residual pulping chemicals.

## RESULTS AND DISCUSSION

We performed 28 sets of 4 cooks, varying the chemistry, temperature, cooking time, chemical charge, and ramp speed. Table 1 details the conditions for the cooks. Cooks under other conditions were performed but are not discussed in this paper.

*Kappa and Yield:* The objective of sulfite pulping is to remove the lignin from the wood while leaving the cellulose and hemicelluloses unreacted. We speculated that the fungal pretreatment either consumes some of the lignin or modifies the lignin in such a way that it is easier to remove in the subsequent pulping process. The efficiency of the pulping is measured by the yield (dry weight of pulp per dry weight of wood charged) and the kappa number, a relative measurement of the residual lignin in the pulp. The goal of these cooks was to sufficiently reduce the lignin to produce a more bleachable pulp.

Table 2 summarizes the results for the sodium bisulfite cook at a cooking time of 5.12 to 5.25 h. The fungally treated chips resulted in a slightly lower yield and a 27% reduction in kappa number. During the cook, both the yield and the kappa decreased with time. The yield decrease is due both to the dissolution of lignin as well as the concurrent attack on the carbohydrates. The fungal pretreatment in this case seemed to accelerate the pulping process but did not seem to change the selectivity between lignin and carbohydrates. Figure 1 shows the kappa numbers for each of the pulping treatments at two different times. An additional 30 minutes of cooking reduced the kappa number of the control to the same level as that of the fungally treated chips. As the reaction continued, the differences between the control and the treated chips decreased. This could be due to the difficulty in removing the residual lignin in this pulping process. Finally, no differences were seen between the two fungal strains: both CZ-3 and SS-3 gave comparable yields and reduced kappa numbers.

Table 3 summarizes the results for the calcium acid sulfite cooks at a cooking time of 9.50 h. Again, the fungal treatment resulted in a significant reduction in the kappa number. For strain CZ-3, the kappa number was reduced by 48%, from 27 to 14. The SS-3 strain reduced the kappa number by 21%. In contrast to the sodium-based cooks. there were no differences in the yields between the control and the fungally treated chips. This indicates that calcium-based sulfite pulping is more selective towards lignin degradation. Figure 3 shows the kappa number for each treatment at 9.5 h and 10.0 h. Again, an additional 30 minutes of cooking was required for the control to reach the same kappa number as the biotreated chips (SS-3). Also, as in the case of the sodium-based cooking, the difference between the control and the treatments was reduced to approximately 20% in kappa.

*Consumption of cooking liquor:* In addition to reductions in the kappa number of the pulp, the possibility existed that the fungal treatment would reduce the consumption of pulping chemicals. Figure 3 summarizes the amount of liquor charged and consumed for the control and the CZ-3 treated chips with the calcium-based cooking. Each data bar represents the average of two cooks. The same amount of cooking chemicals was consumed in each case: Approximately 0.24 g $SO_2$/g ovendried (O.D.) pulp. Thus, the fungal pretreatment did not increase the amount of pulping chemicals needed for this process. Remember that the treatment resulted in a 48% reduction in the kappa number that will presumably make the pulp easier to bleach. This supports the theory that the fungal treatment modifies the lignin in the pulp, making it easier to remove in the subsequent pulping step.

**CONCLUDING REMARKS**

Results show that the fungal pretreatment of the wood had several beneficial effects on the pulping process. The fungal pretreatment significantly reduced the kappa number of the resulting pulp in both the sodium bisulfite and calcium acid sulfite cooks. In the we of the calcium acid sulfite cooks, this was done without adversely affecting the yield. For the same cooking time, the pulp can be cooked to a lower kappa number. Alternatively, shorter cooking times can be used to reach the same kappa number as the control, thus increasing throughput and reducing energy consumption. We also noted that the amount of shives in the pulp was qualitatively reduced compared to the control. This results in a higher screened yield for the biosulfite process. The consumption of pulping liquor was not significantly affected. Previous work has showed that the fungal pretreatment has several other beneficial aspects including color improvement, lower effluent toxicity, and improved bleaching response (1). More details can be found in a longer paper to be published in *The Proceedings of the 1995 Tappi Pulping Conference* (9).

Future work needs to be directed at further assessing the effects of the biotreatment on the pulp and optimization of the process. Brightness and color stability of the resulting pulp need to be investigated. It is expected that the significantly decreased lignin content will produce a pulp that is more resistant to color reversion. Strength and mechanical properties of the pulp also need to be explored. The fungus used, *C. subvermispora,* is the best mechanical biopulping fungus for mechanical pulping discovered to date. However, it may not necessarily be the best fungus to use for biochemical processes. Thus, additional fungi need to be screened for their biochemical pulping efficacy. Finally, the biopulping process needs to be extended to additional species as well as different pulping chemistries. including neutral sulfite and kraft.

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Table 1: Nominal cooking conditions

| | Sodium Bisulfite | Calcium Sulfite |
|---|---|---|
| O.D. charge of wood | 10 g | 10 g |
| Total $SO_2$ on wood | 20.0% | 32.0% |
| Combined $SO_2$ on wood | 10.0% | 9.7-10.9% |
| Liquor-to-wood ratio | 4.0:1 | 5.9-6.8:1 |
| Maximum temperature | 161°C | 140°C |
| Time to temperature | 1.5 h | 5 h |
| Total cooking time | 5-6 h | 9-10 h |

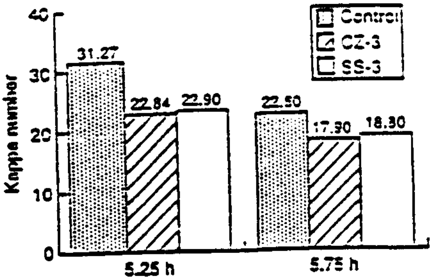


Fig. 1. Pulp kappa numbers for sodium bisulfite cooking.

Table 2: Summary of sodium bisulfite cooks

| Treatment | Yield | Kappa |
|---|---|---|
| Control | 49.93± 0.39% | 31.27±0.28 |
| CZ-3 | 48.16± 0.21% | 22.84±0.98 |
| SS-3 | 48.20% | 22.90 |

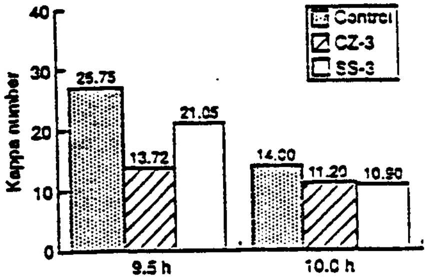


Fig. 2. Pulp kappa numbers for calcium acid sulfite cooking.

Table 3: Summary of calcium acid sulfite cooks

| Treatment | Yield | Kappa |
|---|---|---|
| Control | 47.63± 0.15% | 26.75±0.70 |
| CZ-3 | 47.70± 0.12% | 13.72±1.78 |
| SS-3 | 47.80± 0.69% | 21.05±0.84 |

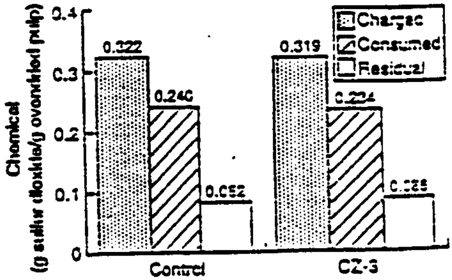


Fig. 3. Comparison of the consumption of pulping liquor by cooks.

# Biotechnology in the Pulp and Paper Industry

## Recent Advances in Applied and Fundamental Research

*Proceedings of the Sixth International Conference on Biotechnology in the Pulp and Paper Industry*

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Facultas-Universitätsverlag
*Vienna, Austria*

Die Deutsche Bibliothek - CIP-Einheitsaufnahme

Biotechnology in the pulp and paper industry : recent advances in applied and fundamental research ; proceedings of the Sixth International Conference on Biotechnology in the Pulp and Paper Industry / ed. by Ewald Srebotnik ; Kurt Messner. - Vienna, Austria : Facultas-Univ.-Verl., 1996
ISBN 3-85076-405-2
NE: Srebotnik, Ewald [Hrsg.]; International Conference on Biotechnology in the Pulp and Paper Industry <6, 1995, Wien>


Druck: WUV-Universitätsverlag
Printed in Austria
ISBN 3-85076-405-2