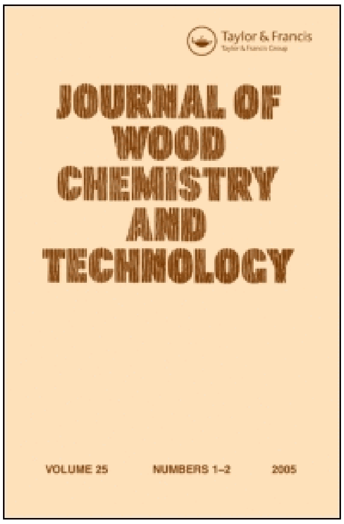

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A NOVEL OZONE BLEACHING TECHNOLOGY FOR THE ALCELL® PROCESS

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ABSTRACT

The ALCELL ® process is an ethanol-based autocatalyzed solvent pulping technology which is being developed by Repap Enterprises Inc. The paper will present a novel ozone bleaching process (Zn), which is compatible with the present ALCELL ® technology. It is based on that an acidified ethanol-water mixture is used as the pulp impregnation liquor during ozone bleaching. It was found that the presence of ethanol dramatically reduces that carbohydrate degradation while delignification is not affected. Process parameters in the Zn stage, including the ethanol concentration and pH, on the delignification efficiency and carbohydrate degradation were studied. The underlying mechanism of this novel bleaching technology will also be discussed.

INTRODUCTION

The ALCELL ® process is an ethanol based auto-catalyzed solvent pulping technology, which has been successfully operated by Repap Enterprises Inc. in a demonstration plant located in Newcastle, N.B. Canada. The advantages of this novel ethanol based solvent pulping, as compared to the conventional kraft pulping include that neither Na_2S nor NaOH is required. This eliminates the generation of malodorous sulfur compounds and the requirement for a complex and expensive recovery boiler and lime kiln. The production of lignin and hemicellulose derived products enhances the economical viability of the ALCELL ® process . Also, it has been recognized that the pulp produced from the ethanol based solvent process is easy to be bleached, which certainly represents another important feature in the present more environmentally conscious time. Therefore, it has been concluded [1] that the ethanol based solvent process will become an increasingly important alternative pulping process in the near future.

Chlorine is a traditional delignifying chemical used in pulp bleach plants. However, because of the growing public concern about the environmental impact of chlorinated organic compounds, chlorine is being rapidly phased out of the pulp and paper mills. Oxygen delignification becomes more and more important in efforts to reduce the use of chlorine containing chemicals in the bleach plant. However, since there is no caustic recovery system in the ethanol/solvent process, it might not be as practical to incorporate the oxygen delignification technology into the ALCELL ® process although it was reported [2] that the brownstock pulp cooked from the ethanol based solvent process responds extremely well to oxygen delignification.

Ozone has been known as a good delignification chemical for a long time. It is now generally accepted that ozone is one of the most promising non-chlorine bleaching agents. The drawbacks which delayed the industrial adoption of ozone bleaching include the cost of ozone, and more severe carbohydrate degradation, especially when more than 1% ozone charge is applied, in comparison with chlorine based conventional bleaching processes. Presently, because of advances in ozone generation technology the first problem appears less important. However, the poor lignin-carbohydrate selectivity, during ozone bleaching, compared to that during chlorine and/or chlorine dioxide bleaching is still unresolved.

It is known that the lignin to carbohydrate selectivity can be improved by the addition of carbohydrate protectors during ozone bleaching. For example, Mbachu and Manley [3], Brolin et al. [4] reported that the presence of acetic acid in the pulp slurry reduces the carbohydrate degradation during ozone bleaching. Kamishima et al. [5] found that the use of methanol leads to a positive result of about 3 to 4 mPa.s improvement in viscosity when ozone bleaching is performed at neutral pH and the pulp is suspended in the organic solvent medium. However, in the same publication [5] Kamishama et al. showed that ethanol is not effective in improving the viscosity of ozone delignified pulp.

In this paper, we will report that the presence of ethanol in the impregnation liquor during ozone bleaching of the ALCELL ® cooked pulp significantly improves the ozone to lignin(carbohydrate) selectivity compared to the conventional ozone bleaching. This improved ozone bleaching technique (Zn) uniquely fits into the present ALCELL ® technology and provides a great potential for a successful ECF and TCF bleach plant excluding the use of oxygen delignification for the ethanol based solvent process. In addition, further study was undertaken to elucidate the underlying mechanisms of the cellulose protection during the so-called Zn process.

RESULTS AND DISCUSSION

A brownstock pulp produced from the ethanol based solvent cooking process (kappa no. 51.3, viscosity 27.5 mPa.s) was washed with ethanol-water (50:50 v/v) at a consistency of 10% for 1 hour at 60°C. The washed pulp (kappa no. of 38.5 and viscosity of 27.3 mPa.s) was subsequently treated with ozone in accordance with the conventional ozone bleaching procedure, i.e. ozonation of pulp in pH 2 water solution at about 40% consistency. Three consecutive ozonation stages were used (see Experimental Procedure). The kappa no. and viscosity of the resulting pulp after each ozonation stage were determined and the results are listed in Table 1. It shows that at the consumption of 2.34% O_3, equivalent to 31.3

TABLE 1
Ozone Bleaching with pH 2 100% Water Solution as the Impregnation Liquor (Initial kappa no: 38.5, Initial viscosity: 27.3 cP)

Stage no.	O_3 (% on o.d. pulp)		Kappa no.	Viscosity mPa.s
	Supplied	Consumed		
1st	1.08	0.86	22.2	16.1
2nd	1.08	0.80	13.3	10.4
3rd	1.08	0.68	7.2	7.2

TABLE 2
Ozone Bleaching with pH 2 70% Ethanol Solution as the Impregnation Liquor (Initial kappa no: 38.5, Initial viscosity: 27.3 cP)

Stage no.	O_3 (% on o.d. pulp)		Kappa no.	Viscosity mPa.s
	Supplied	Consumed		
1st	1.08	0.89	23.0	23.7
2nd	1.08	0.86	13.0	20.3
3rd	1.08	0.82	8.9	18.7

kappa units of lignin is removed, i.e. 0.07% ozone is consumed per kappa unit. This confirms that ozone is a very efficient delignifying chemical. However, at the same time the pulp viscosity of the ozonated pulp decreases from 27.5 cP to 7.2 cP. Therefore, one can conclude that carbohydrates were subjected to severe degradation during the above ozone treatment.

In the second set of experiments, the same washed pulp (38.5 kappa no., 27.3 mPa.s viscosity) was impregnated with pH 2 ethanol-water mixture (70 weight % ethanol) and subsequently subjected to an ozone treatment following otherwise

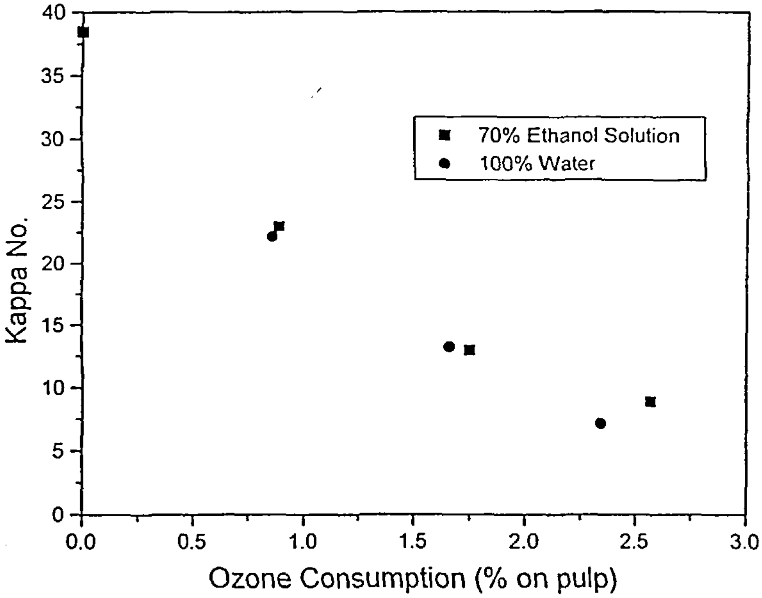

FIGURE 1. Influence of the Presence of Ethanol in the Impregnation Solution on the Ozone Delignification Efficiency of ALCELL® Pulp (Initial kappa no: 38.5, Initial viscosity: 27.3 cP)

the same procedure as the previous set. The development of kappa number and viscosity is recorded in Table 2. Comparison of Table 2 with Table 1 shows that at a similar ozone consumption, ozone bleaching in 70% ethanol solution results in much less pulp viscosity loss than that in 100% water (0% ethanol) solution.

The difference from ozone bleaching in 70% ethanol solution and 100% water can be better visualized in Figures 1 and 2 as respectively the kappa number versus ozone consumption and the viscosity versus kappa number. Figure 1 shows that the delignification of the 70% ethanol impregnated pulps is similar to that of the water impregnated pulps. More important, however, is the substantially lower viscosity loss at the same kappa shown in Figure 2 for the 70% ethanol impregnated pulps after ozonation as compared to the water impregnated pulps. In other words, the presence of ethanol in the pulp during ozone bleaching leads to a substantial improvement in the lignin to carbohydrate selectivity.

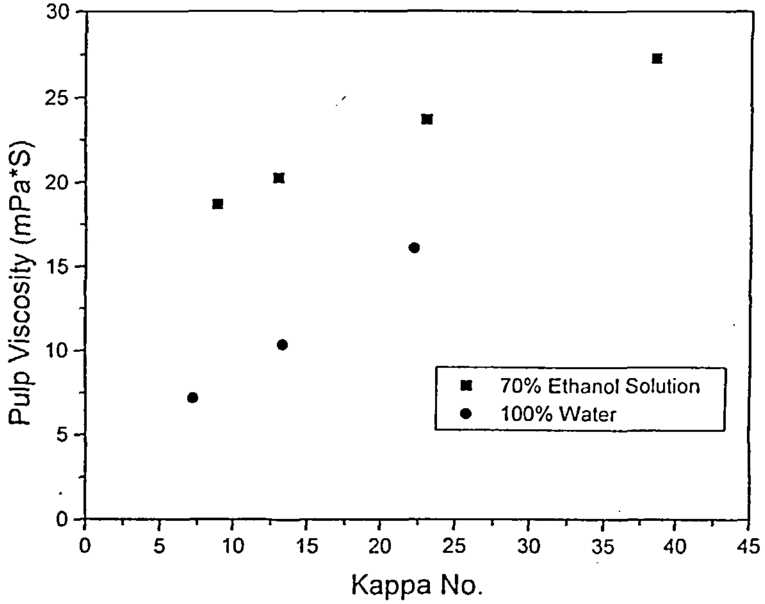

FIGURE 2. Influence of the Presence of Ethanol in the Impregnation Solution on the Lignin to Carbohydrate Selectivity of ALCELL® Pulp (Initial kappa no: 38.5, Initial viscosity: 27.3 cP)

Effect of the Ethanol Concentration

Table 2 shows that ozone bleaching in 75% ethanol as the impregnation liquor improves the lignin to carbohydrate selectivity. The question arises as to what is the effect of the ethanol concentration in the impregnation liquor on the lignin to carbohydrate selectivity during ozone bleaching. The aqueous ethanol solutions were acidified to 1.8 pH. Five solutions containing ethanol concentration of respectively 0, 10%, 30%, 55%, and 70% were used. After impregnation, the pulp was squeezed to remove excess of the impregnation liquor, fluffed, transferred at a consistency of about 40% to the flask of the rotovap equipment, and treated with three consecutive stages of ozone treatment. See the Experimental section for more detailed conditions. We found that the delignification efficiency, i.e. the kappa number reduction at a given ozone consumption, is almost independent of the ethanol concentration. Therefore, we concluded that the ozone consumption due to the reaction between ozone and ethanol is very small. With about 2.5% ozone consumption, the original pulp with an initial kappa number of 38.5 was delignified to a kappa number of about 8.8 (± 0.4) in all cases. The effect of the ethanol concentration on the lignin to carbohydrate selectivity is shown in Figure 3. We can observe that the presence of ethanol increases the viscosity of the ozone delignified pulp dramatically and that a higher ethanol concentration in the impregnation liquor leads to a better lignin to carbohydrate selectivity. For example, when ozone bleaching was performed with 100% water (0% ethanol) as the impregnation liquor, the pulp viscosity decreases from 27.3 mPa.s to 8.3 mPa.s, while a pulp viscosity of 18.7 mPa.s was obtained when 70% ethanol solution was used as the impregnation liquor during ozone bleaching. Further experiments with 95% ethanol solution as the impregnation liquor showed that the delignification was negatively affected, indicating that the amount of water in the impregnation liquor must be sufficient to achieve a good delignification during ozone/solvent bleaching.

Effect of pH

The effect of the pH of the impregnation liquor on the performance of the ozone/solvent bleaching was also investigated. The pulp used was obtained after a different washing procedure which consists of four consecutive batch washing stages with ethanol-water (50:50 v/v) at 1.1% consistency and room temperature (See reference [6] for more detailed conditions). The kappa no. and viscosity of the resulting pulp are 21.5 and 27.6 mPa.s respectively. The pH of the impregnation solution in three separate series of tests was adjusted to 1.8, 2.5 and 3.0. The ozone/solvent bleaching was performed at 25°C and about 40% pulp consistency. The results are listed in Table 3. Comparison of the results shows that the delignification efficiency appears to be slightly better at a lower pH. This is maybe

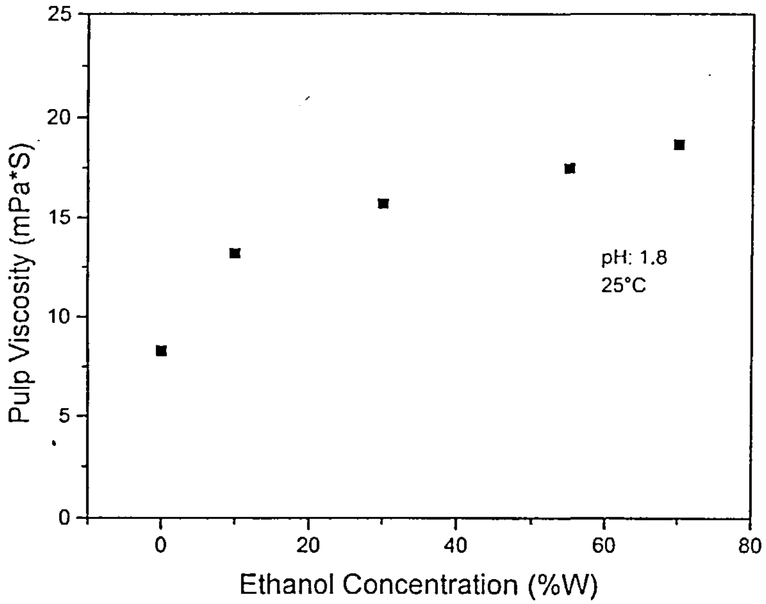

FIGURE 3. The Influence of the Ethanol Concentration in the Impregnation Liquor on the Pulp Viscosity during Ozone Bleaching (Initial kappa no: 38.5, Initial viscosity: 27.3 cP)

due to that a lower pH may stabilize ozone so that the ozone consumption due to its decomposition becomes less. On the other hand, Table 3 shows that the pulp viscosities obtained at three pH levels are approximately the same, indicating that the pulp viscosity is not affected by the pH during ozone treatment. This is in agreement with our earlier findings [7]. Therefore, we conclude that within the present investigated range of acidity the performance of the ozone/solvent bleaching is not sensitive to the change in pH and that the ozone/solvent bleaching can be performed at a pH as high as 3.

Possible Mechanisms of Cellulose Protection in the Ozone/Solvent Process

Two possible mechanisms may account for the much improved lignin to carbohydrate selectivity when ethanol is present in the impregnation liquor during

TABLE 3
Influence of the pH of the Impregnation Liquor
on the ozonation response of ALCELL ® pulp (Initial kappa no: 21.5,
Initial viscosity: 27.6 cP).

Stage No.	pH = 1.8				pH = 2.5				pH = 3.0			
	O_3 (% on pulp)		Kappa No.	Visc. mPa.s	O_3 (% on pulp)		Kappa No.	Visc. mPa.s	O_3 (% on pulp)		Kappa No.	Visc. mPa.s
	Supp.	Cons.			Supp.	Cons.			Supp.	Cons.		
1st	1.08	0.88	14.4	23.1	1.08	0.88	14.7	22.9	1.08	0.86	15.3	23.2
2nd	1.08	0.89	9.0	19.0	1.08	0.89	9.9	19.8	1.08	0.88	10.0	18.6
3rd	1.08	0.90	6.4	16.8	1.08	0.91	7.4	17.7	1.08	0.92	7.6	16.7

ozone bleaching. Since there seems to be a consensus that hydroxyl radicals are mainly responsible for the carbohydrate degradation during ozone bleaching, it might be that ethanol scavenges these highly reactive radical species, which can be formed by ozone decomposition and by ozone-lignin reactions. Alternatively, the protective effect of ethanol may be the result of reduced accessibility of ozone in cellulose-rich regions, and of enhanced accessibility of ozone in lignin-rich regions of the fiber.

In an earlier paper on the effect of ozone treatment of cellulose and lignin model compounds in homogeneous aqueous systems [8], it was found that the consumption of the cellulose model compound increased when phenolic lignin model compounds, such as creosol, were present during the ozone treatment. The increase was explained by the generation of reactive radical species by the ozone-lignin model reactions. Therefore, it is logical to propose that the reactive radical species are also produced during ozone bleaching of ALCELL ® derived pulp through the ozone to lignin reactions. It is well known that the highly reactive radical species are unselective and degrade both lignin and cellulose. On the other hand, many of the organic solvents are good radical scavengers. Therefore, with ethanol present in the fiber wall during ozone bleaching, the generated radical species could be scavenged in-situ, and thus protecting cellulose from degradation.

We have found that a small fraction of ethanol is converted to acetic acid during the ozone/ethanol bleaching. It is expected that acetic acid, in turn, has also radical scavenging potential, which contributes to the observed improved lignin to carbohydrate selectivity. The details of a kinetic study of ozonation of an aqueous ethanol solution will be presented in a future publication.

It is well accepted[9] that the fiber wall consists of cellulose and lignin gels, which are separated by polyoses. Since cellulose gels swell extremely well in water, it is possible that the observed severe carbohydrate degradation during ozone bleaching is due to the earlier accessibility of cellulose by ozone. However, the presence of ethanol in the impregnation liquor may deswell the cellulose gels (relative to that in water) that the cellulose portion of the fiber is less accessible by ozone when the pulp fibers are impregnated with an ethanol containing solution. Consequently, the decreased carbohydrate degradation observed during the ozone/solvent process might be attributed to the decreased swelling of the cellulose gel.

Further experiments were undertaken to determine the degree of fiber swelling of the pulp produced from the ethanol/solvent process as a function of the ethanol concentration. The centrifugation technique[10] was used. The fiber swelling was determined at a centrifugal force of 900 g and 30 minutes, and expressed as the volume (ml) of liquid retained per gram of moisture-free fiber after centrifugation. The results are shown in Figure 4. The maximum pulp fiber swelling of 1.89 ml/g fiber is obtained in pure water. Figure 4 also shows that as the ethanol concentration increases, the fiber swelling continues to decrease. Therefore, it is confirmed that the swelling of pulp fibers is reduced in the presence of ethanol as compared to that in pure water. In addition, it is known[11] that the lignin gels swell much more in the presence of organic solvents such as ethanol, than in pure water. Therefore, it is expected that lignin gels are much more accessible towards ozone when an ethanol containing solution is used as impregnation liquor during ozone bleaching. Since ethanol is a much better solvent

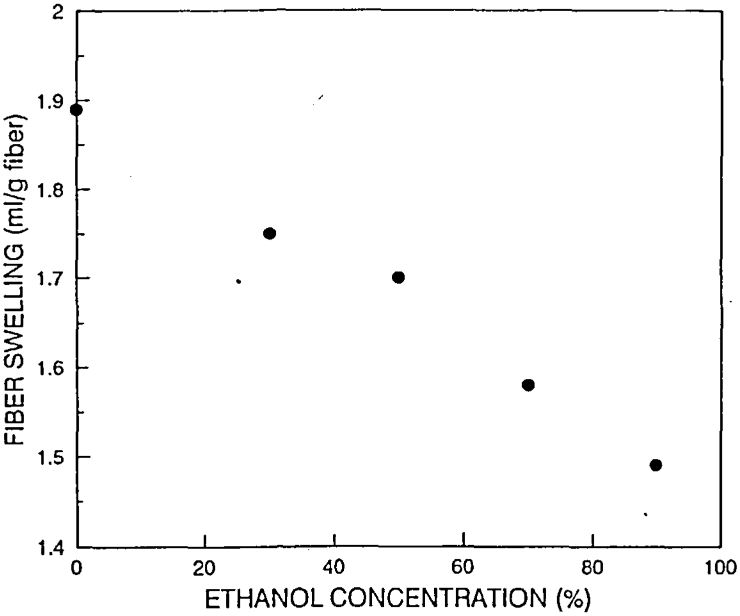

FIGURE 4. **Effect of Ethanol Concentration on the Fiber Swelling Determined by Centrifugation Technique**

for lignin than water, the degree of lignin degradation needed for its dissolution in an ethanol containing solution may not be as high as that in pure water. This may also contribute to the observed improved lignin to cellulose selectivity when ozone bleaching takes place in the presence of ethanol rather than in water.

CONCLUSIONS

A novel ozone/solvent bleaching technology was developed for the ALCELL ® process in this study. It was found that severe carbohydrate degradation occurred when pH 2 100% water was used as the impregnation liquor during ozone bleaching. However, when an acidified ethanol solution was used as the impregnation liquor, the carbohydrate degradation was greatly reduced during ozone bleaching. It was shown that the ethanol concentration in the impregnation liquor influences the lignin to carbohydrate selectivity. At 25°C, the viscosity of the resulting pulp continues to increase until about 70% ethanol concentration. At the pH range of 1.8 to 3.0, the effectiveness of this ozone/solvent bleaching technology is not affected by the pH of the impregnation liquor. The underling mechanisms explaining the cellulose protection was examined. It was proposed that ethanol may scavenge the reactive radical species generated by the ozone-lignin reactions. Alternatively, the protective effect of ethanol in the impregnation liquor may be the result of the reduced accessibility of ozone in the cellulose-rich regions and of enhanced accessibility of ozone in the lignin-rich regions of the fiber. In addition, the better solubility of lignin in an ethanol containing solution may contribute to the better selectivity of this novel ozone bleaching technology.

EXPERIMENTAL

The brownstock of the ethanol/solvent pulp samples used in this study were received from ALCELL Developments Inc. in Miramichi, N.B. Ozone was produced in a PCI ozone generator model GL-1.

The Brownstock pulp samples were first subjected to a washing stage either with 50% (v/v) ethanol solution in a batch system or 70% (by weight) ethanol solution in a displacement system. Subsequently the washed pulp was impregnated with acidified ethanol solutions containing appropriate amounts of ethanol. The wet pulp mass was then pressed to a consistency of about 40%, before being fluffed at room temperature for about 10 seconds. The fluffed pulp was then transferred to a 1l round bottom flask which was ready for the ozone bleaching.

The ozone bleaching experiments were performed in a standard rotovap equipment modified with a fritted glass gas dispersion tube inserted in the rotating round bottom flask. About 10 grams of fluffed unbleached pulp at approximately 40% consistency was contacted in the flask with a 3.83% (by weight) ozone in air mixture introduced through the gas dispersion tube at a flow rate of 1.04 l/min.

The unreacted ozone leaving the flask was captured in a wash bottle filled with a KI solution. The ozone captured in this manner was determined by the iodometric titration method. The ozone charge can be varied by changing the time that the ozone-air mixture flows through the pulp. The rotational speed of the flask was kept at a low level of 4-5 rpm. The ozonation of pulp is performed at about 25°C.

The total amount of ozone was added in more than one stage. Between the stages the pulp was first washed, then reimpregnated with the acidified ethanol-water mixture and pressed to the desired consistency and finally fluffed. This practice was purely due to the restriction of the experimental set-up. It was found that continuous rotation of the reaction flask for more than 2 minutes resulted in agglomeration of the fluffed pulp into ball-shaped clumps. Therefore, refluffing became necessary to keep the good contacting between ozone and fibers when the ozone charge was more than 1%. We have found that in larger set-up, where fiber agglomeration is unlikely to occur, refluffing may not be necessary even at an ozone charge as high as 4%, and that the results obtained in the 1 l flask with interstage fluffing were reproduced in a 20 l reaction vessel without interstage fluffing [12]. After ozone treatment, the pulp samples were washed, then made into handsheets and air-dried for analysis. Kappa no. and pulp viscosity were determined in accordance with Tappi standard methods: T236 cm - 85 and T230 om - 89 respectively.

REFERENCES

1. Pye, E.K. and Lora, J.H., Tappi, 74, 113 (1991)

2. Cronlund, M. and Powers, J., 1991 Tappi Pulping Conference, P. 547, Orlando, U.S.A.

3. Mbachu, R.A.D. and Manley, R. St. John, Tappi, 64: 67 (1981)

4. Brolin, A., Gierer, J. and Zhang, Y., Wood Sci. Technol., 27:115 (1977)

5. Kamishima, K., Fujii, T. and Akkatsu, I., Japan Tappi, 31:699 (1977)

6. Ni, Y. and van Heiningen, A.R.P., Tappi, 79, (1996)

7. Ni, Y. Kang, G.J. and van Heiningen, A.R.P., J. Pulp and Paper Science, 22 (1996)

8. Kang, G.J., Zhang, Y., Ni, Y. and van Heiningen, A.R.P., J. Wood Chemistry and Technology, 15 (1995)

9. Kerr, A.J. and Goring, D.A.I., Cellulose Chemistry and Technology, 9, 563 (1975)

10. Scallan, A.M. and Carles, J.L., Svensk Papperstidning, 75, 699 (1972)

11. Schuerch, C., J. Amer. Chem. Soc., 74, 501 (1953)

12. Zhang, X., Ni, Y. and van Heiningen, A.R.P., to be presented in the 1996 International Bleaching Conf., Washington, DC, April 1996