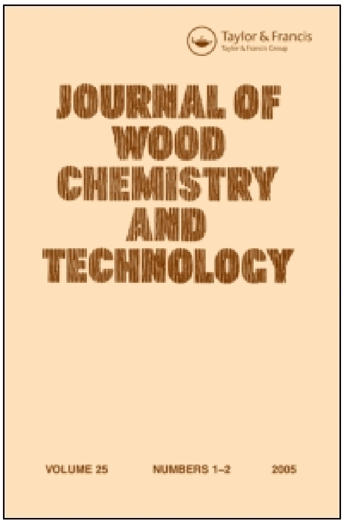

Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

Alkaline Pulping of Oxygen-Pretreated Pine Wood

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To cite this Article Hagström, Christine and Sjöström, Eero(1982) 'Alkaline Pulping of Oxygen-Pretreated Pine Wood', Journal of Wood Chemistry and Technology, 2: 4, 431 — 446
To link to this Article: DOI: 10.1080/02773818208085144
URL: http://dx.doi.org/10.1080/02773818208085144

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 2(4), 431-446 (1982)

ALKALINE PULPING OF OXYGEN-PRETREATED PINE WOOD

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KEYWORDS

Alkaline pulping, anthraquinone, delignification, ethanol, oxidation, oxygen.

ABSTRACT

Wood meal and chips of pine (Pinus sylvestris) were pretreated with oxygen in ethanol-water solutions of sodium hydroxide and then subjected to soda-anthraquinone pulping. It was found that the pretreated wood was delignified much faster than the untreated wood. Additional effects were the improved yield and higher brightness of the resulting pulp. The delignification could be extended nearly to the same kappa number as by kraft pulping and subsequent oxygen bleaching (about 15), although the viscosity of the pulp was comparatively low. The effect of pretreatment and pulping conditions on the delignification and carbohydrate yield is discussed.

INTRODUCTION

To avoid pollution problems much interest has been directed toward the possibilities of minimizing the use of sulfur and chlorine in pulping and bleaching processes. Production of unbleached kraft pulps having a low residual lignin content is one way to decrease the consumption of bleaching chemicals and to reduce the effect of bleaching effluents on the environment[1-7]. However, the nonselectivity of delignification, especially during the residual delignification phase, results in high carbohydrate losses and depolymerization of cellulose[8].

The resistance of polysaccharides toward peeling by hot alkali is increased by converting their reducing end groups to carboxylic acids[9] although earlier experiments on the use of oxygen for this purpose were not successful[10]. Vuorinen and Sjöström[11] recently found in experiments with hydrocellulose, that the selectivity of oxygen was greatly improved when the oxidations were carried out in solvents less polar than water, such as alcohol-water mixtures. They found that the delignification by soda anthraquinone was markedly accelerated when the chips (pine) had been pretreated with oxygen in alkaline ethanol-water solutions. This also resulted in a more extensive delignification. The purpose of the present work was to study this delignification system in greater detail.

RESULTS AND DISCUSSION

First, the effect of the ethanol concentration in the pretreatment on the delignification in soda-anthraquinone pulping of pine wood meal was studied. The liquor-to-wood ratio in the pulping stage was chosen high to maintain a nearly constant alkali concentration throughout the cook. The pretreated wood meal could be delignified to a lower lignin content than the reference sample without pretreatment even when the pretreatment was carried out in alkaline water solutions (in the absence of ethanol - see Table 1). However, as can be seen from Fig. 1, the delignification was markedly improved when ethanol-water was used for pretreatment. Almost a maximum effect was reached at a 50 % ethanol

TABLE 1

Results from the Soda-AQ Cooking of Pine Wood Meal Pretreated with O_2-NaOH at Various Ethanol Concentrations. Other Reaction Conditions as in Fig. 1.

Ethanol, weight-%	Kappa number	Total yield, %	Lignin-free yield, %
-[a]	27.0	42.1	40.4
0	23.6	42.3	40.8
20	19.2	43.1	41.8
50	15.5	41.8	40.8
80	15.0	41.0	40.1

[a] Soda-AQ pulping of untreated wood meal.

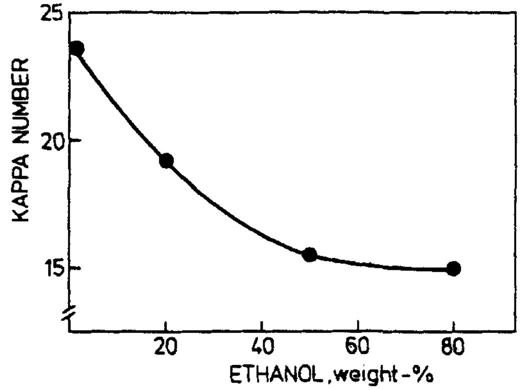

FIGURE 1. Delignification of pine wood meal pretreated with O_2-NaOH at various ethanol concentrations. Pretreatment conditions: 66.7 g wood meal/dm^3 0.25 M NaOH, 1 % $MgSO_4$ on dry wood, O_2 pressure 600 kPa, 20°C → 65°C 20 min, 120 min at 65°C. Cooking conditions: 10.0 g wood/ dm^3 0.5 M NaOH, AQ 1 % on wood, N_2 pressure 200 kPa, 20°C → 173°C 40 min, 150 min at 173°C.

TABLE 2

Yields of Various Wood Constituents (Calculated on Dry Wood) after Pretreatment with O_2-NaOH in Ethanol-Water Solution. Pretreatment Conditions: 100 g wood/dm^3 0.2 M NaOH, Ethanol 500 g/dm^3, 1 % $MgSO_4$ on Wood, O_2 Pressure 400 kPa, 20 → 65°C in 30 min, 120 min at 65°C.

Wood Constituents	Pine Wood	Pretreated Pine Wood
Cellulose, %	39.6	38.5
Glucomannan, %	16.8	15.3
Xylan, %	9.0	8.0
Other carbohydrates and various components, %	2.8	1.6
Lignin, %	27.6	23.8
Extractives, %	4.2	0.6
Sum of components (total yield), %	100.0	87.8

concentration. Although no significant increase in the carbohydrate yield was observed with a constant cooking time, it was about 2 % higher when compared at the same degree of delignification (Table 1).

Further pretreatment experiments were carried out with thin pine chips. The yields of the wood components after these pretreatments appear in Table 2. As can be seen, the extractives were almost completely dissolved during the pretreatment. The carbohydrate losses were about 5 %, which is attributable to the removal of acetyl groups and to peeling reaction which proceeds before the oxidative stabilization of the carbohydrates takes place through formation of aldonic acid end groups. The dissolution of lignin was about 4 %.

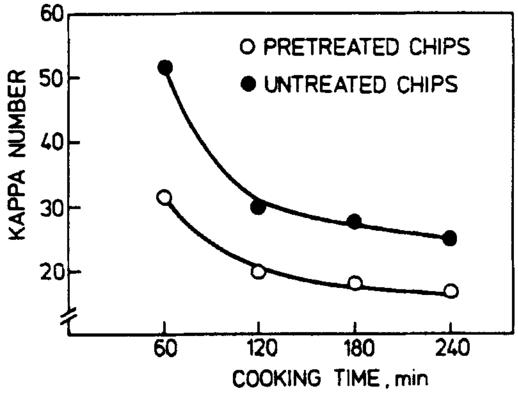

FIGURE 2. Effect of pretreatment on the rate of delignification in soda-AQ pulping of pine wood chips. Pretreatment conditions as in Table 2. Cooking conditions: 200 g wood/dm^3 1.0 M NaOH, AQ 0.2 % on wood, cooking temperature 170°C, time to 170°C 110 min.

The pretreated (as well as untreated) chips were delignified by soda-anthraquinone pulping at 170°C. As can be seen from Fig. 2, the pretreated chips could be delignified to a considerably lower lignin content (kappa number) than the untreated chips when the cooking time was kept constant. For example, to obtain a kappa number of 30 the cooking time for pretreated chips was only 60 minutes, whereas 120 minutes was required for untreated chips. The cooking time advantage is, however, lost if the alkali charge is reduced to avoid depolymerization of cellulose. The pretreated chips could also be delignified to a lower residual lignin content than the untreated chips.

The pretreatment of chips resulted in about 1 % higher pulp yield (compared at equal kappa numbers) (Fig. 3). As revealed by the carbohydrate analyses, the higher yield was caused by the increased proportion of glucomannan in the pulp (Table 3).

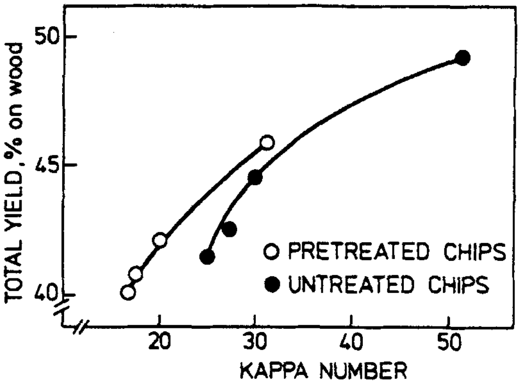

FIGURE 3. Effect of pretreatment on the total pulp yield in soda-AQ pulping of pine wood chips. Pretreatment conditions as in Table 2. Cooking conditions as in Fig. 2.

TABLE 3

Yields of Various Pulp Components (Calculated on Dry Untreated Wood) after Soda-AQ Cooking of Pretreated and Untreated Pine Chips. Pretreatment Conditions as in Table 2. Cooking Conditions as in Fig. 2.

Pulp Component	Yield, % Pretreated Chips	Yield, % Untreated Chips
Cellulose	35.8	36.4
Glucomannan	6.0	4.0
Xylan	2.2	2.2
Lignin-free yield	44.0	42.6
Lignin	1.9	1.9
Total pulp yield	45.9	44.5

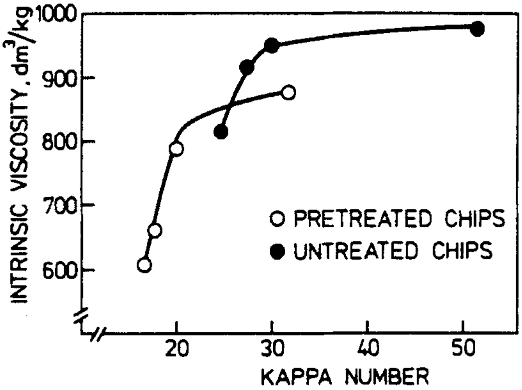

FIGURE 4. Effect of pretreatment on the intrinsic viscosity in soda-AQ pulping of pine wood chips. Pretreatment conditions as in Table 2. Cooking conditions as in Fig. 2.

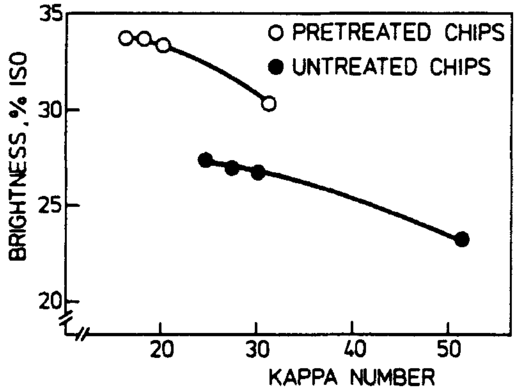

FIGURE 5. Effect of pretreatment on the pulp brightness in soda-AQ pulping of pine wood chips. Pretreatment conditions as in Table 2. Cooking conditions as in Fig. 2.

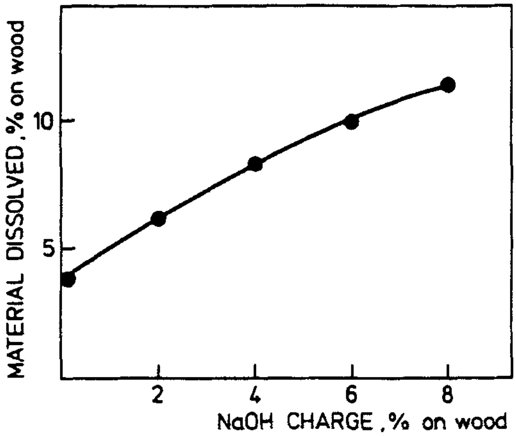

FIGURE 6. Effect of alkali charge on the material losses during pretreatment of pine wood chips. Other reaction conditions as in Table 2.

Delignification of pretreated chips resulted in a depolymerization of the polysaccharides during an early stage of the cook (Fig. 4). At delignification degrees corresponding to kappa numbers 25 and higher the pulp viscosities were about 100 units lower than obtained from the reference cooks, which resulted in a drastic depolymerization below this kappa number. For pretreated chips a sharp drop in viscosity was not obtained until the kappa number decreased below 20. At kappa numbers lower than 25 the viscosities of the pulps produced from the pretreated chips were thus higher compared with the reference pulps. The pulps obtained after cooking of pretreated chips were also significantly brighter than the reference pulps, as can be seen from Fig. 5.

To minimize the alkaline degradation of carbohydrates, additional experiments were done to optimize the alkali charge in both the pretreatment and cooking stages. Although an increased alkali charge in the pretreatment resulted in higher

TABLE 4

Results from Soda-AQ Cooking of Pine Wood Chips Pretreated with O_2-NaOH at Varying Alkali Charges. Pretreatment Conditions: 100 g Wood/dm^3, 1 % $MgSO_4$ on Wood, Ethanol 500 g/dm^3, O_2 Pressure 400 kPa, 20°C → 65°C in 30 min, 120 min at 65°C. Cooking Conditions: 200 g Wood/dm^3 1 M NaOH, AQ 0.2 % on Wood, N_2 Pressure 200 kPa, 20°C → 170°C in 110 min, 180 min at 170°C.

NaOH, % on Wood	Kappa number	Total yield, %	Lignin-free yield, %	Viscosity, dm^3/kg
-[a]	39.7	46.8	44.0	1023
0	37.1	46.3	43.7	1018
2	34.3	45.2	42.8	944
4	30.3	45.0	42.9	874
6	26.1	45.0	43.2	858
8	18.5	44.3	43.0	738

[a] Soda-AQ cooking of untreated chips.

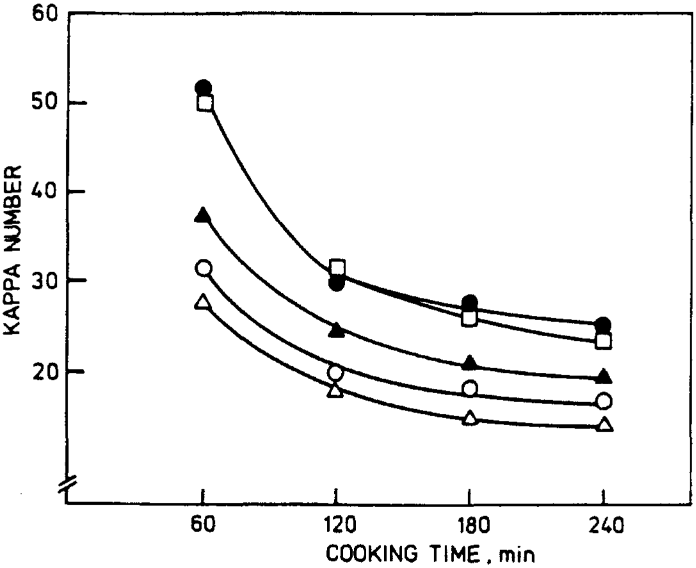

FIGURE 7. Effect of alkali charge (cooking stage) on the delignification of pretreated pine wood chips. ☐ 16 % NaOH, ○ 20 % NaOH, △ 25 % NaOH. Filled symbols: Untreated chips. Open symbols: Pretreated chips. Pretreatment conditions as in Table 2. Other cooking conditions as in Fig. 2.

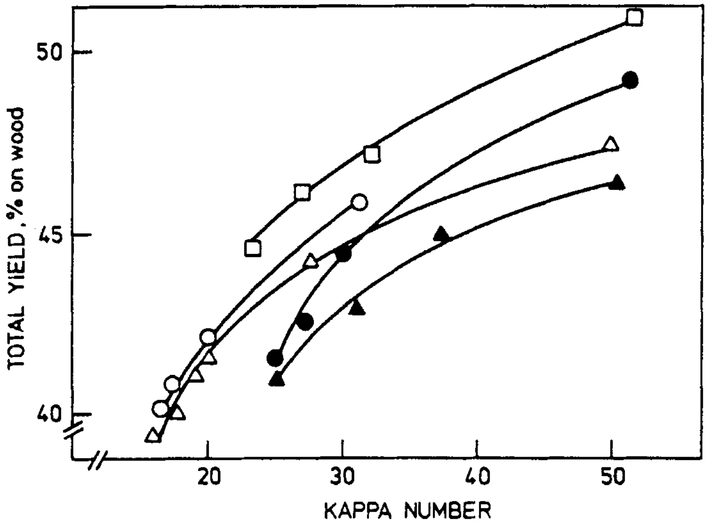

FIGURE 8. Relationship between yield of pulp (calculated on dry untreated wood) and kappa number for pulps cooked at different alkali charges. For explanation of symbols, see Fig. 7.

material losses in this stage (Fig. 6), it has no significant effect on the carbohydrate yield in the following soda-anthraquinone pulping stage (Table 4). On the other hand, higher alkali charges resulted in both reduced viscosity and lower kappa number.

Finally, the effect of the alkali charge in the cooking stage was studied (Fig. 7). Only 16 % alkali (calculated on pretreated wood or 14 % on wood) was needed to obtain the same rate of delignification as for the reference cook with 20 % alkali charge. Because in the pretreatment stage 8 % alkali was used, the total alkali charge was 22 % (based on wood). However, the actual alkali consumption was lower, since about 3 % of alkali remained unconsumed after the pretreatment. When the alkali charge in the cooking stage was decreased the pulp

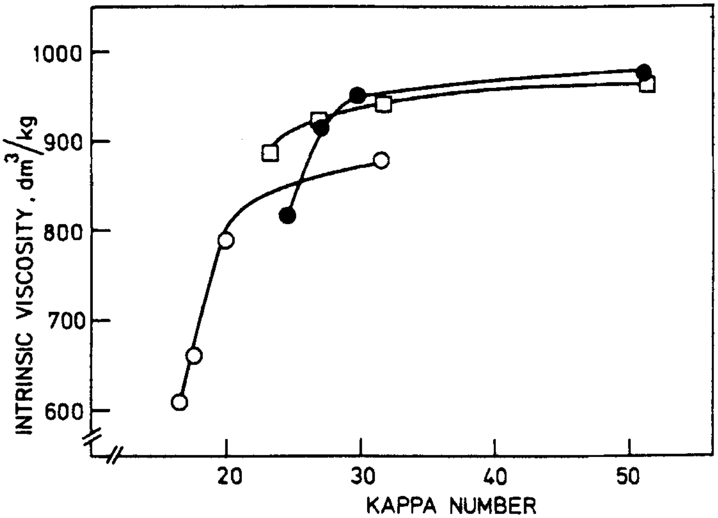

FIGURE 9. Relationship between pulp viscosity and kappa number for pulps cooked at different alkali charges. For explanation of symbols, see Fig. 7.

yield was markedly improved (Fig. 8). For example, with 16 % alkali for pretreated chips, the total pulp yield was 47.0 % (kappa number 30) compared to 44.5 % in the reference cook with 20 % alkali (the same kappa number). The pulp viscosities were also improved when the alkali charge was decreased (Fig. 9). When 16 % alkali was used the viscosity at higher kappa numbers almost reached the viscosity level of the reference pulp cooked with 20 % alkali.

CONCLUSIONS

When pine chips are pretreated with oxygen in alkaline ethanol-water solutions the delignification in the subsequent soda-anthraquinone cooking stage is accelerated significantly. The pretreated chips can also be delignified to a lower residual lignin content than untreated chips. The lowest kappa number obtained for pretreated chips is 15, which is nearly the same as obtained by sulfate pulping and subsequent oxygen bleaching.

Although extensive peeling of wood polysaccharides cannot be avoided, this pretreatment results in a 1-2 % higher pulp yield than the reference cooks without pretreatment (compared at the same degree of delignification). Additional yield increases can be obtained when the alkali charge in the cooking stage is decreased. However, delignification of pretreated chips results in a depolymerization of polysaccharides during an early stage of the cook, reflected by lower pulp viscosities than for the reference pulps at kappa numbers higher than 25. On the other hand, the sharp drop in viscosity, which occurs below this kappa number, is not obtained until the kappa number decreases below 20. The viscosity loss associated with the pretreatment can be avoided by lowering the alkali charge in the cook at the expense of delignification rate. The pulps produced from pretreated chips are also significantly brighter than the reference pulps.

Studies on the effect of this pretreatment on the lignin are now in progress and will be reported in another paper[12].

EXPERIMENTAL

The wood material consisted of pine chips (Pinus sylvestris) used either as such or after grinding in a Wiley mill. The wood meal was screened and the 0.25-0.50 mm fraction was used for the pretreatment experiments.

The pretreatments of wood meal were carried out in teflon-lined autoclaves (50 ml) equipped with magnetic stirring.

Air-dried wood meal corresponding to 2.00 g of dry wood and $MgSO_4$ (1 % on wood) were mixed in the autoclave with sodium hydroxide solutions (0.25 mol/l), containing various amounts of ethanol. The autoclaves were then closed and the air removed by introducing oxygen until a pressure of 600 kPa was reached after which the pressure was released. This procedure was repeated twice before adjustment of the final oxygen pressure (600 kPa). The pressurized autoclaves were placed in a preheated polyglycol bath (65°C). After a proper reaction time the autoclaves were cooled in cold water and opened. The pretreated wood meal was finally washed carefully with hot water and dried.

The pretreatment of pine chips was carried out in an electrically heated rotating autoclave (8000 ml) of stainless steel. Air-dried chips (1 x 20 mm) corresponding to 300 g dry wood were introduced to the autoclave. After addition of 3000 ml sodium hydroxide solution (0.20 mol/l), containing 1500 g ethanol and 3.0 g $MgSO_4$, the autoclave was closed and oxygen introduced until a pressure of 400 kPa was reached. The autoclave was heated to 65°C in 30 minutes and maintained at this temperature for 2 hours. The pressure was then released and the autoclave opened. After washing with hot water the chips were air-dried, and weighed for yield determination.

Wood meal (2.00 g) or pretreated wood meal (corresponding to 2.00 g untreated wood meal) were cooked under nitrogen atmosphere in a teflon-lined autoclave (500 ml) equipped with a magnetic stirrer in a polyglycol bath. The cooking conditions were as follows:

Wood:liquor	10 g/dm^3
Maximum temperature	173°C
Time to max. temp.	40 min

Time at max. temp.	150 min
NaOH concentration	0.5 mol/l
AQ charge	1 % on wood
N_2 pressure	200 kPa

After the cook the autoclave was cooled in cold water and opened. The resulting pulps were filtered off on a glass filter (G2) and washed with hot water, hot ethanol (to remove AQ) and finally with hot water. The pulps were then oven-dried (103°C) for 24 hours and the yields and kappa numbers determined.

Pine chips (20 g, or pretreated chips corresponding to 20 g untreated chips) were cooked in stainless steel autoclaves (150 ml) using 100 ml liquor with various sodium hydroxide concentrations. The AQ charge in all cooking experiments was 0.2 % based on dry wood. When pretreated chips were cooked the AQ and NaOH charges were calculated on dry pretreated wood. The autoclaves were heated in a polyglycol bath, in which 8 cooks could be carried out at the same time thus ensuring equal temperature conditions. The maximum temperature was 170°C and the heating up time 110 minutes. The time at maximum temperature was varied. After the cooks the autoclaves were cooled in cold water and the resulting pulps washed with hot water overnight. The pulps were fiberized in a disintegrator, centrifuged and weighed.

The pulp yield was determined as the weight of o.d. pulp on o.d. wood. When pretreated chips were cooked the yield was determined on o.d. untreated wood. For determination of the dry-matter content the pulps were oven-dried (24 h, 103°C), conditioned in a desiccator and weighed.

The lignin contents of wood, pretreated wood and pulps were calculated as sums of gravimetric lignin[13] and acid-soluble lignin, the latter measured by UV spectrophotometry at 203 nm, using an absorptivity value of 128 $l \cdot g^{-1} \cdot cm^{-1}$ [14].

The content of extractives of wood and pretreated wood was estimated from the material losses in the extraction (24 h) with methanol:benzene (1:1) made before the gravimetric lignin determination.

The lignin-free yield of the pulps was calculated as the difference between the total yield and the lignin yield.

Sugar analyses were carried out according to the method of Sjöström et al.[15] and polysaccharide composition was calculated after Janson[16].

The kappa number, viscosity and ISO brightness of the pulps were determined according to SCAN standards, SCAN-C 1:77, SCAN-C 15:62, and SCAN-C 11:75, respectively.

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