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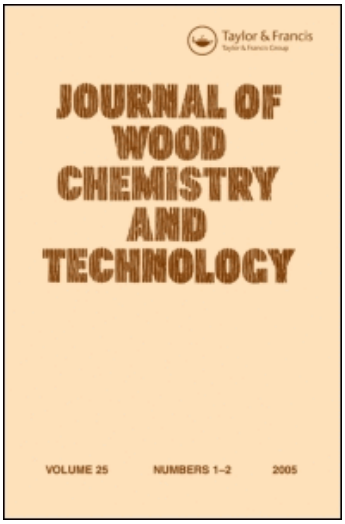

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Delignification and Bleaching Response of Earlywood and Latewood

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Abstract: The delignification response in cooking and the impact of bleaching on earlywood and latewood were studied. Spruce earlywood and latewood chips were pulped by the kraft process and subsequently treated with one bleaching chemical at a time. In cooking, latewood required a higher alkali charge to reach the same kappa number. No difference in the light absorption coefficient between the different fiber types was observed. After oxygen delignification the earlywood fibers had a higher light absorption coefficient at the same kappa number. The difference in light absorbing material was maintained when bleaching was performed with chlorine dioxide, ozone, and peracetic acid. Hydrogen peroxide decreased the light absorbing structures in the earlywood to the same level as for latewood. The earlywood pulp had a higher brightness at a given kappa number than the latewood. The higher brightness remained through all bleaching operations and was primarily due to a higher light scattering ability.

Keywords: Softwood, latewood, earlywood, delignification, bleaching response

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INTRODUCTION

The main cost in pulp production is the raw material, particularly in the northern hemisphere in which the wood species are not as fast-growing. The wood supplies in a pulp mill consist of pulpwood and sawmill chips. Pulpwood is generally the upper parts of the trees and thinnings with a large proportion of juvenile and earlywood in which the fibers are slender and thin-walled. The outer part of the stem has a higher proportion of latewood compared to the inner core of juvenile wood. Consequently, sawmill chips originating from the peripheral parts of the stem have a higher amount of latewood fibers characterized by thicker cell walls. It is common practice to control the type of chips fed to the digester as sawmill chips tend to give pulp with high tear strength, whereas juvenile wood enhances the tensile strength of pulp.

The purpose of chemical pulping and subsequent bleaching is to delignify the fibers. The highest concentration of lignin is found in the middle lamella but a significant part of the lignin is located in the S2 layer of the fiber wall. The S2 layer comprises 80–85% of the latewood fiber wall and contains 2/3 of its lignin. In the case of earlywood, the S2 layer is much thinner and contains less than half of the total amount of lignin.[1] The earlywood has a higher proportion of its lignin located in the middle lamella compared to the latewood fibers.

To use the full potential of the wood raw material, the differences in the morphology of latewood and earlywood fibers should be taken into account. At present there is no economically feasible method on an industrial scale to separate thin- and thick-walled fibers. However, developments in fractionation techniques are rapidly advancing, enabling separation of fibers by morphological features. This will make it possible to construct products demanding certain fiber properties.

The objective of this study was to see if earlywood and latewood, in addition to affecting the strength properties of pulps, respond differently to delignification and specific bleaching agents. Chips from veneer consisting of either earlywood or latewood were delignified by kraft cooking and subsequently treated with one bleaching chemical at a time. The increase in brightness and decrease in chromophoric groups was monitored.

MATERIAL AND METHODS

Starting Material

Air-dried veneer of spruce was cut along the annual rings, using a scalpel, to separate the earlywood and latewood. Three categories of chips were cooked; the original veneer sample, earlywood veneer, and latewood veneer.

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The dimensions of the veneer chips were very different from ordinary wood chips. Thus, the validity of pulping veneer chips was checked by comparison with technical chips. It was found that the veneer chips had the same relationship between pulp yield and degree of delignification as technical wood chips of typical chip dimensions.

Cooking

Chips (50 g) were placed in steel autoclaves, which were evacuated for 30 min. The cooking liquor was then sucked the autoclave and the chips were impregnated under N_2 pressure (5 atm) for 30 min. The liquor-to-wood ratio was 4:1, L/kg. The effective alkali charge was 18.5–21% (as NaOH on wood) and the sulfidity was 40%. After impregnation, the pressure was relieved and the autoclaves were placed in a glycol bath at 70°C. The temperature of the glycol bath was increased to 160°C at a rate of 1°C/min. and then maintained at 160°C to an H-factor of 1700. The cook was terminated by cooling the autoclaves rapidly in cold water. The chips were then washed with deionized water for 10 h. The pulp was fiberized in a NAF-water jet defibrator (2 mm hole) followed by a Wennberg screen (0.2 mm slit). The fiberized pulp was collected on a fine mesh wire (20 μm).

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Bleaching

To remove the fines prior to bleaching, the pulp was further screened on a wire (125 μm). The pulp was dewatered to approximately 25% solids. Steel autoclaves were used for oxygen delignification, a rotating glass reactor for ozone treatments, and sealed polyethylene bags in thermostatic water baths for complexing agent, chlorine dioxide, hydrogen peroxide, and peracetic acid stages. Deionized water was used in all bleaching experiments. The pulp samples were bleached using the sequences OQ, ODQ, OZQ, OQPQ, and OQPaaQ. The conditions in the bleaching stages are given in Table 1.

Analyses

Wood, dry content SCAN-CM 39:88; pulp, dry content ISO 638; residual alkali SCAN-N 33:94; kappa number SCAN-C 1:77R; viscosity ISO 5351; brightness ISO 2470; metal analysis ICP-AES; DKM-extract SCAN-C7:62; amount of fines, BDDJ (Britt Dynamic Drainage Jar), TAPPI T 261 cm-90; carbohydrate analysis per Reference.[2] The amount of earlywood and latewood fibers in the pulp was counted microscopically. A fibers was classified as latewood when

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Table 1. Bleaching conditions

Bleaching stage	Charge, kg/t	Additive, kg/t	Temp., °C	Pressure, MPa	Time, min	End pH	Conc., %
O-stage	12–25 (NaOH)	5 ($MgSO_4$)	100	0.7	30–90	10.5–11.2	12
Q-stage (1 and 2)	2.7 (DTPA)	3.3 (H_2SO_4)	90	—	60	ca 5,5	10
D-stage	13–28 (a. Cl)	0–2.6 (H_2SO_4)	50	—	45	2.5–2.8	8
Z-stage	2–9.1 (ozone)	7.8 (H_2SO_4)	20	—	3	2.9–3.4	40
P-stage	5–30 (peroxide)	10–19 (NaOH)	80	—	22 h	10.4–10.9	10
Paa-stage	5–30 (Paa)	4–23 (NaOH)	70	—	60	5.3	10

the lumen was less than or equal to two fiber wall thicknesses. Everything else was classified as earlywood fibers in the microscopic counting.

The fiber dimensions were analyzed with a FiberLab Dimensions Analyzer provided by Metso.

The total fiber charge was determined by conductometric titration. The surface charge was determined by electrolyte titration using polyDADMAC ($Mw > 920,000$ and charge density $5.8 \cdot 10^{-3}$ ekv/g).[3]

Light absorption coefficients were determined at 457 nm on single sheets towards two different backgrounds. The light-scattering coefficients were determined at 557 nm according to ISO 9416:1998.

RESULT AND DISCUSSION

In this study, the response of delignification and bleaching was studied for earlywood and latewood from spruce veneer. The technique to separate earlywood from latewood used in this study resulted in two chip fractions consisting of very thin irregularly shaped chips with a thicknesses of approximately 1 mm. The latewood chips were of darker color and more brittle compared to the earlywood chips.

The chemical compositions of the spruce veneer chips are reported in Table 2. As expected from literature reports, the earlywood had a higher amount of lignin, which is due to the middle lamella making up a greater proportion of the fiber wall. The latewood fibers had a larger proportion of glucomannan and less cellulose, as anticipated.[5]

Cooking

The results from pulping the earlywood and latewood are presented in Table 3. Although the latewood veneer had a lower lignin content, it required a higher alkali charge to reach a certain kappa number at the same cooking time and residual alkali. There was a large difference in pulp yield; the yield from the latewood veneer was 7% lower, the difference partly explained by the higher alkali charge. Also the selectivity, defined as viscosity at a given

Table 2. Carbohydrates (calculated according to Jansson[4]), lignin, and extractives in spruce veneer chips

	Lignin, %	Carbohydrate composition, %			DKM, %
		Xylan	Glucomannan	Cellulose	
Earlywood	29.1	6.7	17.6	45.8	0.68
Latewood	27.1	6.5	23.4	42.4	0.51

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Table 3. Characterization of pulp from earlywood and latewood fibers

	Earlywood	Latewood
EA, %	18.5	21.0
Kappa no.	25.7	25.8
Viscosity, mL/g	1160	1030
Total yield, % on wood	48.5	41.3
Rejects, % on wood	0.6	0.1
Fines, % on wood	0.76	0.46
Brightness, % ISO	36.7	28.6
Light abs. coeff., m^2/kg	18	18
Light scatt. coeff., m^2/kg	27	18

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kappa number, was lower for the latewood. The lignin in the thicker S2 layer of the latewood is less accessible for leaching than the lignin in the thin S2 layer of the earlywood fiber.[6] The higher alkali demand of the latewood may be partly dependent on less leaching but is probably due mainly to the fact that the latewood veneer had a substantially higher amount of glucomannan with alkali consuming acetyl groups (see Table 2).

The pulp from earlywood had much higher brightness than the latewood pulp. The light absorption coefficient was the same for latewood and earlywood fibers whereas the light scattering coefficient was higher for the earlywood fibers.

Chemical Composition of the Unbleached Pulps

The carbohydrate compositions of the unbleached pulps are presented in Table 4. Although the latewood and earlywood chips had very different chemical compositions (Table 2), the dissimilarities disappeared after delignification. However, the yield of latewood fibers was much lower so when calculating on wood, it can be concluded that the yield of glucomannan and cellulose was low in the latewood pulp compared to the earlywood. The amount of hexenuronic acids was determined as well. There was no significant

Table 4. Pulp carbohydrate composition (26 kappa no.)

	Pulp carbohydrate composition, %		
	Xylan	Glucomannan	Cellulose
Earlywood	7.0	7.4	82.2
Latewood	7.7	7.1	82.0

Table 5. Unbleached fiber metal content[a]

Metal content, mg/kg	Al	Ba	Ca	K	Mg	Mn
Earlywood	2.0	15.0	810	12	100	59
Latewood	3.6	8.1	330	16	170	31

[a]The primary fines were removed from the pulp samples.

difference between earlywood and latewood pulp, 43 and 44 μmole/g respectively.

The metal content in the pulp samples is shown in Table 5. Earlywood fibers had about twice as much barium, calcium, and manganese compared to latewood. The latewood had a higher magnesium content.

The earlywood fibers had a higher surface charge compared to latewood fibers (Table 6). Latewood fibers had a somewhat higher total charge, most likely due to the higher amount of xylan (Table 4).

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Oxygen Delignification

In Table 7 the amounts of earlywood and latewood fibers in the pulps from the veneer samples are shown. Primary fines have been shown to affect the bleachability as their lignin content is higher and the lignin structures are less reactive.[7,8] In order to eliminate the influence of fines, the pulps were screened prior to the bleaching study. Nevertheless, a minor fraction of the fines remained in the pulps.

The unbleached earlywood pulp had a higher brightness than the latewood pulp. After oxygen delignification, the difference in brightness became smaller, but the earlywood pulp still had a higher brightness than latewood pulp (Figure 1).

In Figure 2, the decrease in light absorption coefficient caused by oxygen delignification is shown. The unbleached pulps subjected to oxygen delignification had the same initial light absorption coefficient. However, after treatment with oxygen, the earlywood fibers had more light-absorbing structures at the same kappa number (same lignin content) than the latewood

Table 6. Pulp charge density

	Total charge, μmole/g	Surface charge, μmole/g
Earlywood	75.2	3.5
Latewood	82.2	2.7

Table 7. Fiber and fines analyses of screened pulps from the chips

	Earlywood fibers, %	Latewood fibers, %	Fines, % in pulp
Earlywood	98	2	0.8
Latewood	23	77	0.5
Original veneer	71	29	0.6

fibers. Oxygen has been shown to favor the S2 layer of the fiber wall in delignification.[9] A thicker cell wall has been shown to be favored in oxygen delignification; the thicker the cell wall, the larger the reduction in kappa number.[10] Thick-walled fibers have a higher proportion of phenolic hydroxyl groups than thin-walled fibers[8] and it can be assumed that oxygen finds more reactive sites in the S2 layer of the latewood fibers than in earlywood fibers with more middle lamella lignin.

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Treatment with Bleaching Chemicals

Hydrogen peroxide, chlorine dioxide, peracetic acid, or ozone was used one at a time on oxygen-bleached pulp. A Q-stage was placed after treatment with the bleaching chemical so that the pH would be the same when the pulps

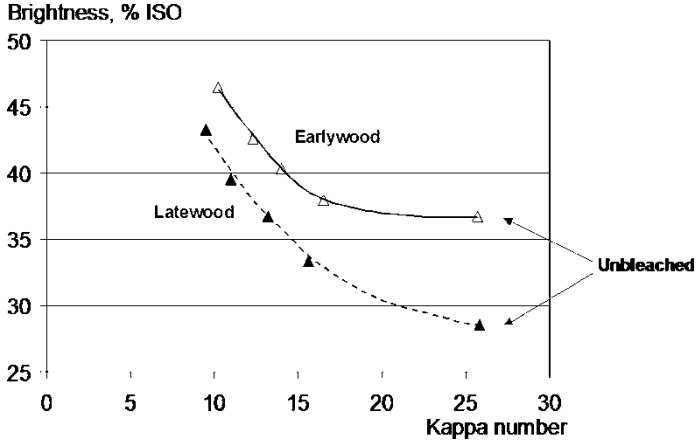

Figure 1. Brightness versus kappa number for oxygen delignification of spruce earlywood and latewood kraft pulps.

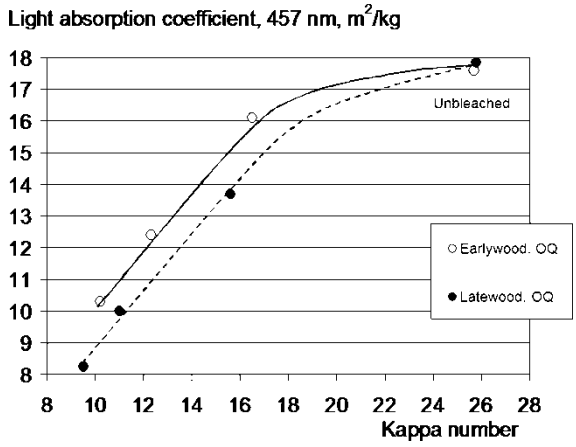

Figure 2. Light absorption coefficient versus kappa number for oxygen delignification of spruce earlywood and latewood kraft pulps.

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were subsequently analyzed. The characteristics of the pulps used for bleaching are given in Table 8.

When the oxygen-delignified pulps were treated with bleaching agents the difference in the amount of light absorbing structures between the earlywood and latewood fibers no longer remained, with one exception; ozone, Figure 3. In this case the earlywood showed a higher light absorption coefficient at a given kappa number. Different bleaching chemicals led to different levels of chromophoric groups. At the same kappa number, chlorine dioxide had the highest light absorption coefficient and hydrogen peroxide the lowest.

When monitoring the brightness increase on the basis of chemical charge (or chemical consumption) the latewood fibers consumed slightly more bleaching chemicals. However, the brightness of the latewood pulp was already lower in the unbleached state and this difference was maintained after treatment with a bleaching chemical.

The higher brightness of the earlywood fibers can be attributed to their higher light scattering ability (Figure 4). There was no change in light scattering ability of the pulps through the bleaching procedure. The bleachability can

Table 8. Oxygen-bleached pulps used in the bleaching response study

Pulp for bleaching after O-stage	Kappa no.	Viscosity, mL/g	Light abs. coeff., m^2/kg	Light scatt. coeff., m^2/kg	Brightness, % ISO
Earlywood	14	1000	14	25	40
Latewood	13	920	12	19	37

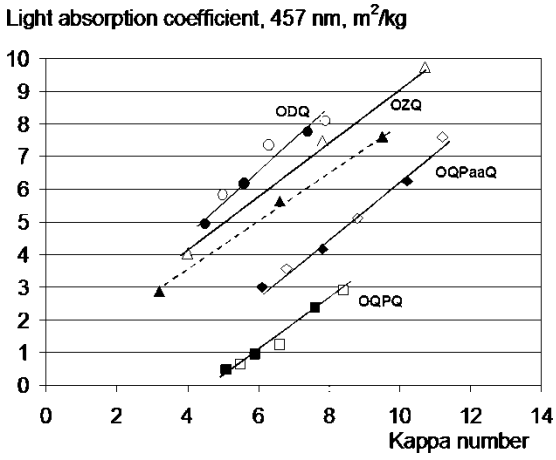

Figure 3. Light absorption coefficient versus kappa number for bleached, oxygen-delignified spruce earlywood and latewood kraft pulps. Unfilled symbols represent earlywood fibers, filled symbols latewood fibers.

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also be evaluated as the decrease of light absorbing structures achieved by a given amount of OXE (Figures 5 and 6). Hydrogen peroxide managed to decrease the higher light absorption ability of the earlywood fibers down to the same level as of the latewood fibers. All other bleaching agents removed light absorbing structures from earlywood and latewood fibers at the same rate, thus maintaining the higher amount in earlywood.

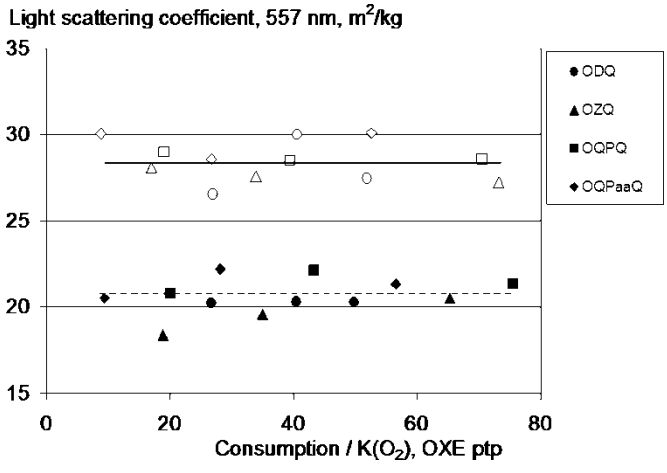

Figure 4. Light scattering coefficient versus OXE for bleached, oxygen-delignified spruce earlywood and latewood kraft pulps. Unfilled symbols represent earlywood fibers, filled symbols latewood fibers.

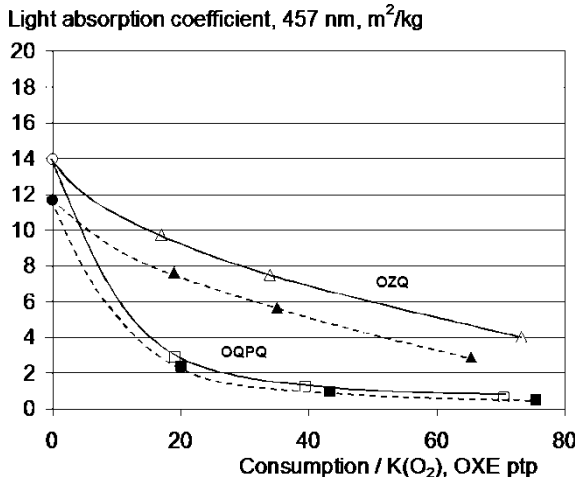

Figure 5. Light absorption coefficient versus OXE for ozone and peroxide bleached, oxygen-delignified spruce earlywood and latewood kraft pulps. Unfilled symbols represent earlywood fibers, filled symbols latewood fibers.

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Fiber Dimensions and Optical Properties

The length of unbleached latewood and earlywood fibers was 3.33 mm and 2.71 mm, respectively. Their lengths were unaffected by the bleaching. The

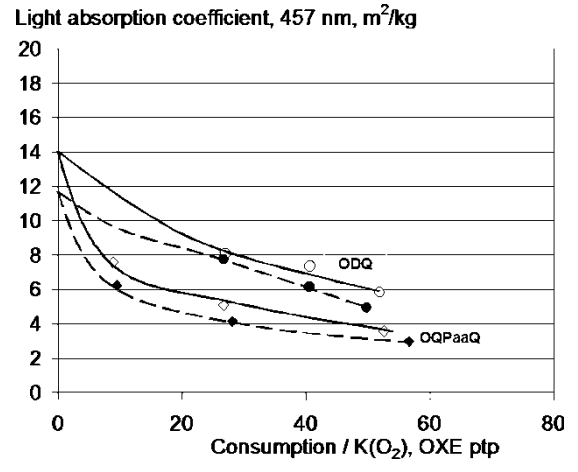

Figure 6. Light absorption coefficient versus OXE for chlorine dioxide and peracetic acid bleached, oxygen-delignified spruce earlywood and latewood kraft pulps. Unfilled symbols represent earlywood fibers, filled symbols latewood fibers.

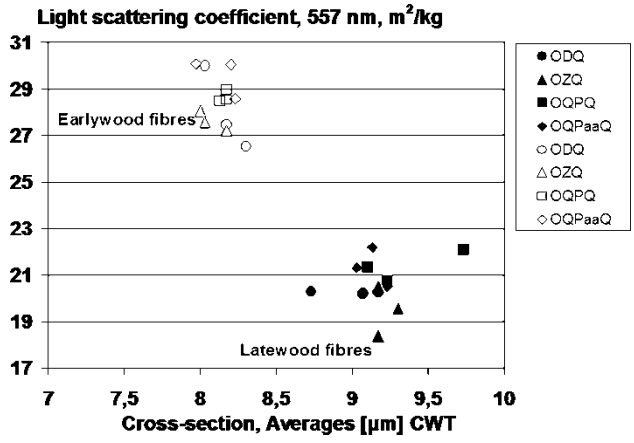

Figure 7. Light scattering coefficient as a function of fiber cross-section. Unfilled symbols represent earlywood fibers, filled symbols latewood fibers.

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cell wall thickness was not significantly affected by removal of lignin. As seen from Figure 7, the cell wall thickness index was approximately 9 μm for the latewood fibers and 8 μm for earlywood fibers. As coarseness, that is, fiber wall material per unit length, determines the number of fibers in a sheet of certain grammage, a sheet with earlywood fibers will have a larger amount of fibers than a sheet made from latewood fibers. A sheet made of earlywood fibers will consequently have more fiber surfaces available for light scattering.

CONCLUSIONS

The results from this study show that latewood and earlywood fibers respond differently to delignification and, to some extent, bleaching. However, from an industrial point of view the main difference between these two types of fibers is their large difference in light scattering ability, which influences the brightness of the pulp or the produced paper.

A general conclusion is that it is important to consider the fiber morphology when studying the bleachability of fibers with different structural features. Sheets from earlywood fibers provide more surfaces for the light to scatter on, due to a larger number of fibers in a sheet made of earlywood fibers compared to latewood fibers. Earlywood fibers result thereby in a sheet of higher brightness even though the colored material in the pulp, measured as light absorption coefficient, is higher.

Latewood fibers required a higher alkali charge to reach a certain kappa number at the same residual alkali and cooking time compared to earlywood fibers. This means that in industrial kraft cooking the latewood fibers attain a higher kappa number than that of earlywood fibers. Latewood

pulp had considerably lower yield and viscosity, partly explained by the higher alkali charge.

The brightness of the earlywood pulp was higher after cooking as well as after oxygen delignification and treatment with different bleaching agents. The higher brightness is conclusively attributed to the higher light scattering ability of the earlywood pulp.

The light absorbing structures, as measured by the light absorption coefficient, were the same for earlywood and latewood after cooking. In the oxygen delignification, the light absorbing structures were more efficiently removed from the latewood pulp, so when subjected to treatment with bleaching chemicals, the latewood pulp entered with a lower light absorption coefficient. The lower light absorption coefficient remained after treatment with ozone, chlorine dioxide, and peracetic acid. Bleaching with hydrogen peroxide, however, reduced the light absorbing structures more rapidly in the earlywood pulp. As a consequence, the light absorption coefficient at a certain consumption of hydrogen peroxide was equal for latewood and earlywood pulp.

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