

INFLUENCE OF ALKALINE AND ALKALINE/OXIDATION PRETREATMENTS OF HORNBEAM WOOD ON THE PROPERTIES OF KRAFT PULP

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A series of comparable specimens of hornbeam wood were pretreated with diluted sodium hydroxide, sodium hydroxide and hydrogen peroxide, or peracetic acid sequences. Under identical conditions of kraft cooking, all pretreatments improved the digestibility of hornbeam wood. Pulps from pretreated wood differed much from that obtained from untreated wood. Pretreatments reduced the yield of the pulps, diminished their Kappa number noticeably, reduced the degree of polymerisation and increased extremely their brightness. One-step peroxide bleaching of pulps from pretreated wood gave a much higher brightness, compared to that of bleached pulp from sound wood. Bleached, unrefined pulps from sound and pretreated wood evidenced different fibre dimensions, as well as a different distribution according to length and width. Unexpected, however, was the higher consumption of energy for refining bleached pulps from pretreated wood. Pretreatments increased the rate of pulp interactions with water in the initial phase of wetting, but markedly reduced the final value of their swelling. Pretreatments also improved the breaking length and tear index of the sheets from bleached, refined pulps. From the viewpoint of improved pulp properties, the most efficient pretreatments were the sodium hydroxide/peracetic acid and sodium hydroxide/activated H_2O_2 sequences.

Keywords: hornbeam wood, pretreatment, kraft pulp, kappa, interactions, fibre distribution, mechanical strength, optical properties, UV/VIS and ATR FTIR spectra difference

INTRODUCTION

The production of chemical pulps is expensive, if considering the consumption of raw materials, energy, water, chemicals and the cost of the inevitable technology. Possible ways to improve the economy of pulp production involve the modification of the pulping methods and technology. Another option might be the treatment of the chips before processing, for reducing the expenses related to pulp production and to its further processing. Comparatively with the biotic ones, the mechanical and chemical pretreatments of wood offer the advantage of a

shorter duration and a more uniform effect on the chip properties. An efficient chip impregnation, prior to cooking, results in a lower Kappa number of the pulps and in a narrower fibre distribution, in higher average fibre contents in the pulp, as well as in a diminished consumption of bleaching chemicals and a higher pulp quality.¹

The principle of mechanical pretreatments involves the formation of ruptures and cracks in the chips, allowing the release of the entrapped air from their capillary system during the impregnation step. A similar effect is provided by

pre-steaming and hydrothermal pre-hydrolysis of the chips.²

The alkaline treatment of the chips prior to mechanical pulping or alkaline cooking may improve the pulp properties. For example, a single pretreatment of birch wood with diluted sodium hydroxide modified substantially its mechanical properties and apparently improved the papermaking strength of the chemo-mechanical pulp.³ Kraft cooking of hornbeam wood pretreated with diluted sodium hydroxide and its combinations with oxidation agents yielded pulps with noticeably increased brightness and reduced the content of residual lignin.⁴

The alkali influence on the chemical and physical properties of wood either during or prior to alkaline pulping was studied by several researchers.^{1,4-9} The obtained data might be summarised as follows: the alkaline solutions cause extreme swelling and deacetylation of wood, increase its accessibility to water and improve its impregnation and digestibility. The neutralisation of uronic and acetic acids split off from hemicelluloses in the course of alkaline pretreatment results in reduced consumption of alkali during alkaline cookings.^{5,10}

The present paper, estimating the basic properties of kraft pulps from sound and pretreated hornbeam wood with sodium hydroxide, sodium hydroxide and hydrogen-peroxide, or peracetic acid solution, resumes the study on the alteration of hornbeam wood properties during alkaline and alkaline/ oxidation pretreatments.^{4,9}

EXPERIMENTAL

Wood species

Model specimens of hornbeam wood (*Carpinus betulus* L.) were prepared from two 35 cm long sections taken from the middle part of the tree trunk, at approximately 1m height. The age of the tree was between 85 and 90 years. The sections were used for the preparation of 2.5×2.5×1.0 cm specimens. The larger dimensions were in radial and tangential directions, the shortest one was parallel to the grain.

Pretreatments

Prior to chemical pretreatments, a series of specimens were immersed for 48 h into a 0.0155 M solution of Chelaton III in deionised water. The

penetration depth of the solution was enhanced by a vacuum (10 min at a pressure of 10 kPa), after which the following pretreatments were applied to the specimens: **1**/ a 48 h treatment of comparable series of specimens with 2.5% NaOH; **2**/ their 48 h treatment with 2.5% NaOH, with a subsequent 72 h oxidation treatment with 7.5% H₂O₂; **3**/ the same pretreatment as in **2**, however with the addition of dicyandiamide (DCDA) activator (0.028 g/g o. d. wood.); **4**/ a 48 h treatment with 2.5% NaOH, and a subsequent 24 h oxidation with 7.5% H₂O₂ with the addition of dicyandiamide (DCDA) activator (0.028 g/g o. d. wood.) at 55 °C; **5**/ the same alkaline treatment followed by a 72 h oxidation with 8% peracetic acid. The wood to alkali solution or oxidation agent ratio was constant, of 1:5 w/w. All pretreatment sequences were carried out at 20 °C, with the exception of pretreatment **4**, in which the oxidation step was carried out at a higher temperature (55 °C).

A review of all pretreatment sequences is given in Table 1, where P denotes hydrogen peroxide, PAA – peracetic acid and DCDA – dicyandiamide as activator.

Kraft pulping

Model chips, with 2.5×0.3×1 cm dimensions, (first dimension in radial direction and the last one parallel to the grain) were used for cookings. After the assessment of their physical properties, the chips were cut from the test specimens. Pulping was performed in rotating 1000 mL stainless autoclaves, with a liquor of 28.5% sulphidity and 16.0% active alkali on the absolutely dry mass of chips. The chips-to-liquor ratio was 1:4.2. The air-dried chips were used for pulping. Kraft cooking involved a 120 min heating step from 80 to 170 °C and a 60 min delignification at the same temperature. The initial temperature of both chips and liquor in the stainless steel autoclaves, prior to their immersion into the pre-heated oil bath, was of 22 °C.

Bleaching

Hydrogen peroxide activated by dicyandiamide (DCDA) was used for pulp bleaching.¹¹ The consistency of the defibred pulp was of 7%. The amounts of chemicals in the bleaching solution, based on the oven dry mass of pulp, were as follows: H₂O₂ – 10%; NaOH – 3%; Chelaton III – 0.7% and DCDA – 1.5%. Time and temperature of bleaching: 120 min to reach the temperature of 72 °C and 90 min bleaching at this temperature. Further on, the pulps were washed with 5% acetic acid, deionised water to neutral pH and finally with acetone, and dried at ambient temperature.

Table 1
Pretreatment sequences

Pretreatment sequence	Agent/time, h/temp., °C
1	NaOH/48/20
2	NaOH/48/20 + P/72/20
3	NaOH/48/20 + P/72/20 + DCDA
4	NaOH/48/20 + P/24/55 + DCDA
5	NaOH/48/20 + PAA/72/20

Chemical analyses and assessment of pulp physical properties

- The mass loss of the specimens resulting from pretreatments was calculated from the mass of both sound and pretreated series of specimens, in absolutely dry state. Drying of 3 specimens for determining the mass of the dry residue was carried out at room temperature, in a desiccator. The drying media were 98% H₂SO₄ and then P₂O₅.
- The yield of the pulp, including rejects, was determined according to the standards in force.¹²
- Pulps were defibred by the STN EN 5263 (50 022):1999 method.¹³
- Estimation of the dimensional characteristics of bleached, non-refined pulps was performed at MONDI SCP Ružomberok, Ltd. pulp mill, using a Lorentzen & Wette FIBER TESTER instrument. Minimum 20 000 fibres per sample were analysed. Pulp mass in 100 mL of water suspension = 1 g.
- The kappa number of pulps was determined by the STN ISO 302 (50 0258) method.¹⁴
- The average degree of polymerisation (DP) of the bleached pulps was calculated¹⁵ from the intrinsic viscosity of their solutions, in the EWNN_{NaCl} complex (ISO 5351/2.1981). The pulp samples for DP determination were bleached with activated H₂O₂ and then with a buffered NaClO₂ solution, according to the method used by Tirtowidjojo *et al.*¹⁶
- The bleached pulps were refined to 38° Schopper-Riegler, according to the standard STN ISO 5267-1 (50 0219):1993 method.¹⁷
- The assessment of water retention, expressed in °SR, was carried out¹⁸ according to STN ISO 5267-1 (50 0219):1993.
- The brightness of both unbleached and bleached kraft pulp sheets was measured¹⁹ by the standard STN ISO 3688 (50 0240):1994 method.
- α-cellulose in the bleached refined pulps was determined²⁰ according to STN 50 0260:1984 method.
- Pulp breaking length was determined²¹ according the STN ISO method 1924-1 (50 0340):1996.

- The tear index was determined by the STN ISO (50 0348):1997 method.²²
- The kinetics of pulp interactions with water was estimated indirectly, by monitoring the swelling kinetics of the sheets made of bleached refined pulps, by the modified method.²³ The change in sheets dimension, in a perpendicular direction to their plane, was monitored at 0.2 s intervals within the first 10 min, and then at 1.0 s intervals during the next 40 min. The initial moisture content of the sheets was of 4.2%.
- The colour of the unbleached and bleached pulp sheets was estimated²⁴ on a Konica Minolta CM-2600 D spectrometer, over the 360-740 nm range, with a resolution of 10 nm. Band width = 10 nm, at a 0.01% precision of the reflex registration. Of each sample, comprising 13 sheets, 52 scans were taken. A random choice of the measured spot was used. The spectra were evaluated in a*, b* and L* coordinates, over the "CIELAB" colour space, and differential spectra were constructed as the difference between the spectra of both pretreated and sound wood pulps. The moisture content of the pulps was of 3.5%.
- The ATR FTIR spectra of the sheets made of bleached refined pulps from both pretreated and sound wood were obtained on a NICOLET Magna 750 spectrometer, on using a variable horizontal angle ATR Max II accessory with ZnSe crystal; the sheets were analysed in an absolutely dry state (pulps stored over P₂O₅ in a desiccator).

Note: symbols w_{init.}, w_{abs.} in the legends denote the initial moisture content or the moisture content of the sheets in an absolute mode, while n expresses the number of specimens or measurements of any pulp property observed.

RESULTS AND DISCUSSION

General data on the basic properties of the pretreated hornbeam wood and of the corresponding kraft pulps are presented in Tables 2, 3 and Figure 1.

All pretreatments applied to hornbeam wood resulted in its mass loss, as depending on the agent used. A relatively deep mass loss, in the case of a single 48-h pretreatment with a sodium hydroxide solution (9.94%), can be attributed to the partial dissolution of hemicelluloses, to wood deacetylation and to the slight removal of lignin from wood. The effect of the oxidation agents used after the NaOH pretreatment depended on the nature of the applied agent and on the experimental conditions. When 8% peracetic acid was used in the second step, a significant mass loss (20%) of the pretreated wood was observed.

The data in Table 2 evidence a strong impact of the pretreatments on the pulp properties. The unscreened yield of the kraft pulp from pretreated hornbeam wood samples was reduced by 5.2 to 6.5%, according to the mode of hydrogen peroxide application. In the case of the pretreatment with peracetic acid in the second step, the pulp yield relatively increased (by 0.8%), due to the enrichment of the pretreated material with cellulose.⁴ However, the total unscreened yield of the unbleached pulps from pretreated hornbeam wood, when calculated based on the mass of the wood prior to the pretreatment, was markedly reduced, corresponding to that of "low yield" pulps for further chemical processing. On the other hand, the applied pretreatments considerably reduced the amount of screen rejects (Table 2). The Kappa number and brightness of the examined kraft pulps are presented in Table 3.

The chemical pretreatments of hornbeam wood reduced the Kappa number of the unbleached kraft pulps by 47.86–51.59 units. The most effective in this respect was the pretreatment with NaOH/peracetic acid. The effect of the remaining pretreatments on the pulp Kappa number was almost equal to and moderately less significant than that of the above-mentioned sequence (Table 3). One-step peroxide bleaching in the presence of a DCDA activator was accompanied by a mass loss of the pulps varying from 1.92 to 3.63%, whereas a higher value corresponds to the pulp from sound hornbeam wood (Table 3). Compared to unbleached pulps, the brightness of bleached pulps from the pretreated samples was higher (by 22.7 to 30.1% ISO) while, for the bleached pulp from sound wood, the increase was only 10.4%.

A higher difference between the brightness of pulps from pretreated and sound hornbeam wood was noticed for bleached pulps. The variability of the obtained data was very low, the variation coefficients ranging from 0.12 to 0.64% for unbleached pulps, and from 0.14 to 0.90% for the bleached ones, respectively.

The reduction in Kappa number and the increase in crude pulp brightness due to bleaching are illustrated in Figure 1. According to Figure 1, one-step peroxide bleaching of pretreated hornbeam wood pulps resulted in a more significant reduction in their Kappa number and in a markedly high brightness, compared to that of the pulp from the sound material. From the viewpoint of effective Kappa number reduction and brightness gain due to bleaching, the best results were exhibited by the pulps from wood pretreated in sequences 2 and 5.

The apparently improved properties of the kraft pulps from the pretreated hornbeam wood (Table 3, Fig. 1) resulted most probably from its altered physical and chemical properties. The physical properties firstly evidenced an increased wood accessibility to water,²⁵ expressed by a higher swelling and water uptake, as compared to sound wood. An extreme swelling of the wood pretreated with alkali limits essentially its axial permeability. This phenomenon, however, might have been over-compensated by an increased rate of the diffusion processes in the pretreated wood, due to its enhanced water uptake⁹ and also, possibly, by the higher uptake of pulping chemicals dissolved in water. An improved digestibility of the pretreated wood can be explained by its more complete, faster and even impregnation. However, the efficiency of alkaline cooking may also significantly promote the deacetylation of wood^{4–8} and the dissolution of a certain portion of hemicelluloses²⁶ during the alkaline pretreatments.

The dimensions, shape, fine contents, number of kinks and fibre distribution in the defibred bleached pulps were estimated on a FIBER TESTER instrument. The basic characteristics concerning the examined kraft pulps are given in Table 4 and Figures 2 to 5.

As illustrated in Table 4, the pulps from the sound and pretreated samples of hornbeam wood had different dimensions. The fibres in the pulps

of all pretreated samples of hornbeam wood were approximately by 5.5% shorter and by 15% narrower, compared to those in the pulp from sound wood. The mean shape of the fibres in the examined pulps differed only slightly in all length classes. All pretreated wood pulps contained fibres of less regular shape (approximately by 1%), compared to the fibres in untreated wood pulp.

Figure 2 points out approximately 5 µm wider fibres in the pulp from sound wood in the length classes from 0.2 to 2.0 mm. In the length classes

from 2.0 to 3.0, and from 3.0 to 7.5 mm, the fibres were wider by 17.5 and 28 µm, respectively.

The mean width of the fibres in the pretreated wood pulps slightly varied within an interval of approximately 3 µm, in all fibres length classes under consideration.

Figure 3 presents the ratio of fibres in pulps, in each length class estimated.

Table 2
Final pH of the agents used for pretreatments, mass loss of hornbeam wood
due to pretreatment, pulp yield and amount of rejects

Pretreatment sequence	Final pH of agent	Weight loss (%)	Unscreened yield (%)	Total unscreened yield ^a (%)	Screen rejects (%)
0	-	-	56.42	56.42	1.290
1	12.80	9.94	51.03	45.96	0.008
2	9.47	11.18	50.48	44.84	0.020
3	9.26	10.96	51.22	45.61	0.006
4	8.98	11.92	49.92	43.99	0.000
5	2.88	20.20	57.22	45.66	0.005

Note: Initial pH of the fresh sodium hydroxide solution: 13.16. The pH of all agents after pretreatments was reduced, due to the neutralisation of the acids, the dilution of sodium hydroxide with water in saturated wood, the water present in H₂O₂ and the neutralisation by peracetic acid

^a The total unscreened yield expresses the yield of pulp recalculated to the wood mass prior to pretreatments, considering its mass loss due to pretreatment

Table 3
Kappa number and brightness
of unbleached and bleached pulps from sound and pretreated hornbeam wood

Pretreatment sequence	Kappa of unbleached pulp	Brightness of unbleached pulp (% ISO)	Pulp mass loss in bleaching (%)	Kappa of bleached pulp	Brightness of bleached pulp (% ISO)
0	61.42	19.7	3.63	41.30	30.1
1	12.84	44.7	2.13	8.81	67.4
2	13.56	43.2	2.35	7.53	70.3
3	12.54	45.2	2.26	7.04	72.3
4	12.51	44.1	2.31	7.05	69.6
5	9.83	44.8	1.92	4.59	74.9

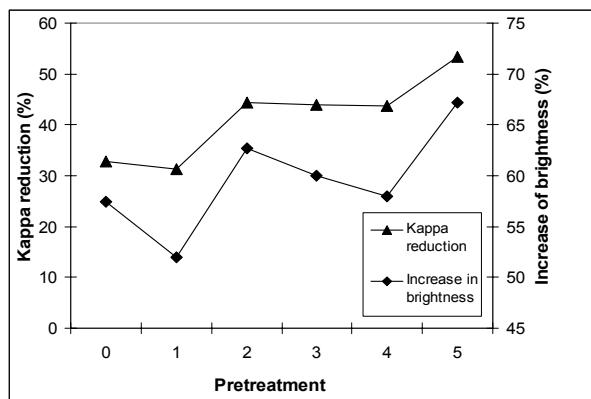


Figure 1: Reduction of Kappa number and increase in the brightness of pulps from sound (0) and pretreated hornbeam wood (sequences 1-5, see Table 1 for pretreatment sequences) resulting from one-step hydrogen peroxide bleaching

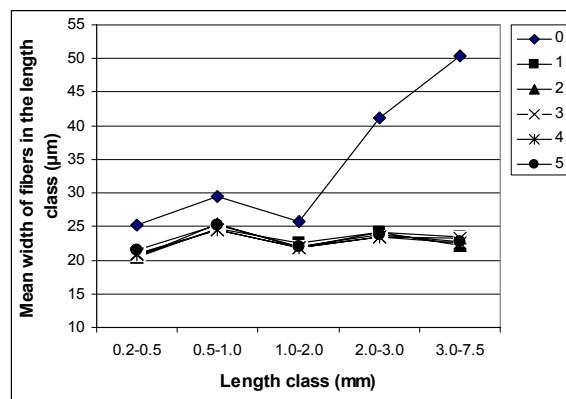


Figure 2: Mean width of fibres in length classes; 0 – sound wood pulp, 1-5 – pulps from wood pretreated by the sequences described in Table 1

Table 4
Dimensions, fibre shape, mean kink angle and number of kinks per fibre in sound and pretreated hornbeam wood pulps

Pretreatment sequence	Mean length (mm)	Mean width (µm)	Mean shape (%)	Mean kinks angle (°)	Number of kinks per fibre	Number of large kinks per fibre
0	1.28	26.6	92.86	44.91	0.2495	0.0434
Std.	0.027	0.89	0.29	0.30	0.035	0.006
1	1.21	22.94	92.01	49.04	0.4227	0.1078
Std.	0.044	3.02	0.50	0.84	0.043	0.015
2	1.20	22.62	92.26	49.12	0.3978	0.1016
Std.	0.033	5.23	0.49	0.70	0.051	0.013
3	1.21	22.31	91.71	48.71	0.4667	0.1117
Std.	0.023	0.99	0.30	0.31	0.024	0.008
4	1.21	22.28	92.13	47.75	0.4382	0.1016
Std.	0.026	1.17	0.38	0.43	0.0434	0.011
5	1.21	22.62	91.47	50.51	0.4614	0.1284
Std.	0.009	1.32	0.34	0.47	0.032	0.009

The distribution plots in Figure 3 evidence a more symmetric distribution of fibre proportions according to their length classes in the pulps prepared from pretreated hornbeam wood samples. The maxima in these plots are assigned in the 1.2-1.3 mm region of fibre length. An essential difference between the plots of pretreated and sound wood pulps appears in the position of this maximum which, in the case of the sound wood pulp, is shifted towards the fibre length class of 1.4 mm. This distribution plot is also less symmetric, with two lowest maxima in the length classes of 0.6 and 2.2 mm. All pulps contained a certain portion of short fibres or fines with length values between 0.1 and 0.2 mm. The smallest portion of fines was present in the pulp from sound wood and the highest one was exhibited by the pulp from wood pretreated only with NaOH.

The fibres in the pretreated wood pulps exhibited a markedly increased number of kinks (varying between 60 and 80%), compared to those in the untreated wood pulp, a possible explanation being the softer and less rigid character of the fibres in the pulps from pretreated hornbeam wood, characterized by deeply reduced residual lignin contents and, generally, lower width in all examined length classes (Figs. 2 and 4).

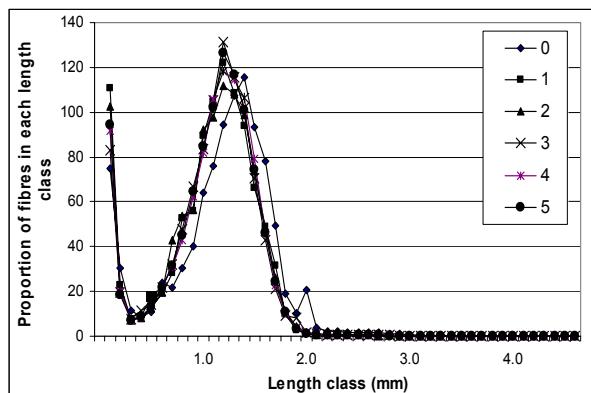


Figure 3: Distributional plot of fibre proportion (number of fibres) in each length class of the kraft pulps compared: 0 – sound wood pulp, 1-5 – pulps from wood pretreated by the sequences described in Table 1

Fibre proportion in the pulps, according to their width, is illustrated in Figure 4.

The distribution curve of the pulp from untreated hornbeam wood is less symmetric, broader and shifted towards a region of the higher fibre width classes. The curves of the pulps from pretreated wood are more symmetric, almost of the shape of a Gauss distribution, pointing out a narrower fibre distribution in all width classes of these pulps.

The contents of α -cellulose and DP were determined in the bleached pulps, followed by the refining of the pulps to approximately 38 °SR. The pretreatments on wood increased unexpectedly the number of revolutions necessary to achieve the given freeness (Table 5). As shown in Table 5, pretreatments of hornbeam wood resulted in the reduction of pulps DP by 15 to 27%, which could hardly result from a single alkaline pretreatment of wood, especially in the absence of oxygen. In the case of combined alkali/hydrogen peroxide pretreatments, however, depolymerisation of cellulose by the hydroperoxide anion might occur, influencing the DP value of the pulps. A statistically random cleavage of the 1-4 β -glucosidic bonds in the pulps by the hydroperoxide anion was reported by Mattor²⁷ and Kleinert²⁸ during alkali-cellulose ageing in the presence of oxygen.

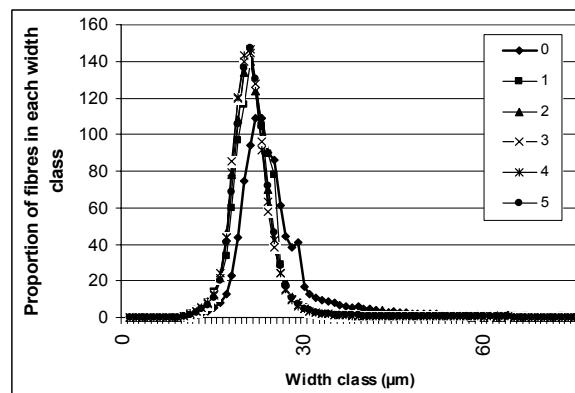


Figure 4: Fibre distribution (number of fibres) in pulp, according to fibre width in each width class: 0 – sound wood pulp, 1-5 – pulps from wood pretreated by the sequences described in Table 1

Table 5
Degree of polymerisation of bleached, unrefined pulps, number of revolutions to achieve a freeness of about 38 °SR and content of α -cellulose in bleached, refined pulps

Pretreatment sequence	DP	Initial freeness (°SR)	Number of revolutions	Final freeness (°SR)	α -cellulose content (%)
0	1305	13.0	5600	37.5	80.20
1	978	15.0	9900	38.0	82.62
2	955	14.0	8200	39.0	82.53
3	990	14.0	7900	39.0	83.16
4	986	13.5	7700	39.0	83.49
5	1142	11.5	12000	37.5	79.01

As the differences in the DP of the pulps from the wood after alkaline and alkaline-hydrogen peroxide pretreatments, were negligible, the reduction in pulp DP could be more likely attributed to a higher concentration of active alkali in the liquors, in the later stages of the pretreated wood cookings. A negative influence of the increased alkali concentration on pulp DP in the later stages of kraft cookings was reported by Fengel and Wegener.²⁹ A less pronounced decrease in the DP of pulp from the wood pretreated with a NaOH/peracetic acid sequence possibly results from the acid hydrolysis of hemicelluloses accompanying the cellulose in wood and causing the enrichment of pulp in cellulose. The absence of hydroperoxide anions degrading the polysaccharides including cellulose cannot be excluded in this case, either. Also, a slightly higher consumption of active alkali by the free carboxylic groups in the chips pretreated in this way might be assumed. The influence of mechanical degradation of cellulose in cutting the chips can be neglected, as all samples of hornbeam wood specimens were cut under identical conditions, in a wet state, using a sharp blade.

The refining of pretreated hornbeam wood pulps to a freeness value of about 38 °SR requested apparently a higher number of revolutions, compared to the sound wood pulp, while the pulps from wood pretreated by NaOH and especially by NaOH/peracetic acid were the most difficult ones to refine (Table 5). Based on the FIBER TESTER analysis and the assessment

of α -cellulose in the pulps, at least a partial explanation of this phenomenon could be provided. The difference between the refining energy consumed by the sound wood pulp and pretreated wood pulps may involve different dimensions and fibre distribution according to fiber length and width classes. All pulps from the pretreated wood samples were characterized by shorter and narrower fibres with symmetric distribution, according to their dimensions within the sample, as compared to the sound wood pulp.

The pulps from hornbeam wood pretreated by NaOH or NaOH/H₂O₂ sequences contained higher portions of α -cellulose, the increase ranging from 2.3 to 3.3%, compared to the sound wood pulp. On the contrary, the content of α -cellulose in the pulp from NaOH/peracetic acid-pretreated wood was diminished by 1.2%, which may indicate a partial oxidation of cellulose in acidic medium (conversion of $-\text{CH}=\text{O}$ and $-\text{CH}_2-\text{OH}$ to $-\text{COOH}$), resulting in its enhanced dissolution during α -cellulose assessment. As evidenced by the comparison of the α -cellulose content in the pulps and their refining energy, no correlation occurs between these two properties, regardless of the pH of the agent used in the pretreatment (Table 5). Similarly with the pulps from the hornbeam wood pretreated by alkaline or alkaline/oxidation solutions, an increase in the refining energy was also reported for eucalyptus kraft pulp, with hemicelluloses contents diminished by a preliminary counter current extraction with hot water.²⁶

A higher consumption of refining energy and reduction in the viscosity of eucalyptus kraft pulp due to chlorine dioxide bleaching at elevated temperatures were also reported.³⁰

The sheets were prepared from bleached and refined kraft pulps, and their breaking length and tear index were determined (Fig. 5).

According to Figure 5, pretreatments of hornbeam wood increased the breaking length of

bleached and refined pulp sheets. The exception was the pretreatment with a single NaOH, resulting in a moderately reduced strength of the kraft pulp. The best breaking length (higher by 10-14%) was recorded in the pulps from the wood pretreated with NaOH/H₂O₂ sequences, either activated with DCDA or not.

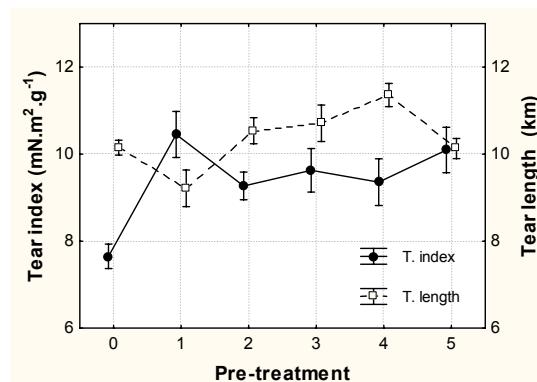


Figure 5: Breaking length and tear index of bleached kraft pulps from sound and pretreated hornbeam wood (w_{abs} 3.8%, n – tear index 9, n – breaking length 13); 0 – sound wood pulp, 1-5 – pretreated wood pulp, see Table 1 for pretreatment sequences (vertical bars denote 0.95 confidence intervals)

Table 6
ANOVA tests for breaking length and tear index

Breaking length					
-	SS	Degree of freedom	MS	F	p
Intercept	8455.50	1	8455.50	30734.61	0.000
Pretreatment	34.28	5	6.86	24.92	0.000
Tear index					
-	SS	Degree of freedom	MS	F	p
Intercept	4780.00	1	4780.00	13332.00	0.000
Pretreatment	42.50	5	8.50	23.70	0.000

Abbreviations: SS – sum of squares, MS – mean square, F – value of F test, p – level

Table 7
Results of Duncan test for breaking length and tear index
(Statistical significance of the differences between sampling averages)

Pretreatment sequence	0	1	2	3	4	5
	Breaking length (km)					
Average	10.148	9.215	10.538	10.709	11.358	10.129
0	–	0.000	0.060	0.010	0.000	0.927
1	0.000	–	0.000	0.000	0.000	0.000

2	0.060	0.000	–	0.406	0.000	0.061
3	0.010	0.000	0.406	–	0.002	0.010
4	0.000	0.000	0.000	0.002	–	0.000
5	0.927	0.000	0.061	0.010	0.000	–
Tear index ($\text{mN m}^2 \text{ g}^{-1}$)						
Average	7.651	10.451	9.268	9.628	9.357	10.096
0	–	0.000	0.000	0.000	0.000	0.000
1	0.000	–	0.000	0.007	0.001	0.214
2	0.000	0.000	–	0.237	0.756	0.009
3	0.000	0.007	0.237	–	0.342	0.104
4	0.000	0.001	0.756	0.342	–	0.016
5	0.000	0.214	0.009	0.104	0.016	–

All pretreatments applied increased the tear index of the bleached pulp sheets by 20-30%, as depending on the agent used, which indicates improved papermaking properties of fibres in the pulps made from pretreated samples of hornbeam wood. The confidence intervals calculated at a 95% level and the statistical significance of the differences among the average values of the obtained analytical data on the pulp mechanical strength were assessed by ANOVA and Duncan test (Tables 6 and 7).

The ANOVA test confirmed the high significance of the hornbeam wood pretreatments on both breaking length and tear index of the compared pulps.

In Table 7, the results of Duncan test for breaking length and tear index are presented. Statistically, all sampling average values of breaking length for the pretreated wood pulps differed significantly from the average breaking length of the sound wood one. The exception was the average breaking length of the pulp from the wood pretreated with NaOH/peracetic acid, exhibiting no difference, compared to the sound wood pulp. Furthermore, the difference between the sampling breaking length average values of NaOH/H₂O₂-pretreated wood pulps, with and without addition of DCDA activator, was statistically insignificant (Table 7).

The Duncan test confirmed the very significant difference between the sampling average values of the tear index for pulp from sound wood and pulps from all pretreated wood samples.

A high significance was also evidenced for the differences between the sampling averages of the tear index for the pulps from wood submitted to

the following pretreatment sequences: 1-4; 4-5; 1-3 and 2-5. The differences between the remaining 7 combinations of sampling averages for the pretreated wood pulps were insignificant.

The interactions of bleached, refined kraft pulp sheets with water have been estimated indirectly by monitoring their swelling kinetics. Each kinetic plot illustrated in Figure 6 represents a mean of five individual plots for each sample (the plot for the pulp from the wood pretreated by sequence 3 is absent from the figure, due to the lack of sufficient amounts of this sample). The relative rate constants of the initial swelling phase of pretreated wood pulps indicate their slightly higher rate of interaction with water in the first few seconds of the contact with water. On the other hand, the final swelling of the pretreated wood pulp sheets after a 40-min contact with water was by 15 to 20% lower, as compared to the sheets made of sound wood pulp (Fig. 6). This different behaviour of the pulps compared might be partly attributed to their different contents of residual lignin and α -cellulose. The cohesion (binding) forces among the fibres in the sheet, reflected also in breaking length and tear index, probably play an important part in this phenomenon.

The colour of the sheets from defibred unbleached and bleached refined pulps was examined spectrometrically, over the 360-740 nm range. Axis a* in the CIELAB colour space comprises the surface colour, ranging from green (-100 to 0%) to red (0 to 100%), while axis b* expresses the colour range from blue (-100 to 0%) to yellow (0 to 100%).

Coordinate L* represents the lightness of the monitored surface expressed as percent of a standard (lightness of 100%).

The chemical pretreatments of hornbeam wood changed not only the brightness, but also the colour of the kraft pulps examined (Figs. 7 and 8). The differential reflection spectra revealed striking differences between the optical properties of the pulps from sound and pretreated hornbeam wood (Fig. 9).

As illustrated in Figure 7, the colour of the unbleached pulps from pretreated hornbeam wood

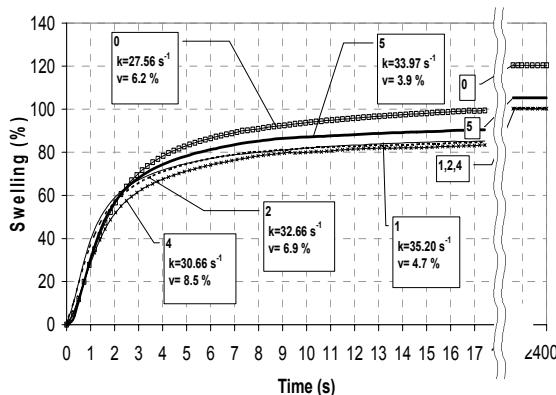


Figure 6: Swelling kinetics and relative rate constants of the fast initial swelling phase of bleached, refined kraft pulp sheets, in a perpendicular direction to the sheets (w_{init} 4.5%, n 5); 0 – sound wood pulp, 1, 2, 4 and 5 – pretreated wood pulps, see Table 1 for pretreatment sequences

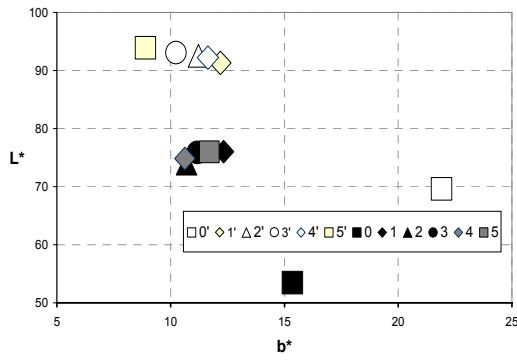


Figure 8: Changes in lightness (L^*) and colour of unbleached and bleached sheets of pulps in coordinate b^* ; Unbleached pulps: 1 – from sound wood, 1-5 – from wood pretreated by the sequences described in detail in Table 1; number with apostrophe denotes bleached pulp (w_{abs} 3.5%, n 52)

was shifted from a red shade towards the region of green colour by 6 to 8.5% in coordinate a^* , compared to the unbleached pulp from sound wood. The increase in pulp lightness varied within 15 to 30% of the scale, according to the pretreatment applied.

Bleaching of pretreated wood pulps resulted in an additional 3 to 6% shift in their colour towards green, on raising their lightness by approximately 20%.

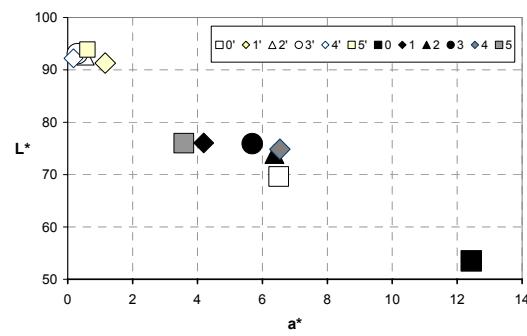


Figure 7: Changes in lightness (L^*) and colour of unbleached and bleached sheets of pulps in coordinate a^* ; Unbleached pulps: 1 – from sound wood, 1-5 – from wood pretreated by the sequences detailed in Table 1; number with apostrophe denotes bleached pulp (w_{abs} 3.5%, n 52)

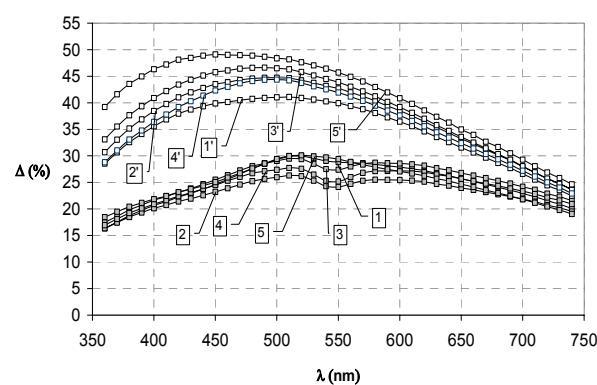


Figure 9: Differential reflection spectra of kraft pulps from pretreated hornbeam wood; 1-5 – spectra of unbleached pulps from the wood pretreated by the sequences described in detail in Table 1; number with apostrophe denotes the spectrum of bleached pulp (w_{abs} 3.5%, n 52)

The comparison of colour shifts in coordinate a^* and the increase in the lightness, L^* , of the pulps from sound and pretreated hornbeam wood, due to peroxide bleaching, results in a lower bleaching efficiency in the untreated sound wood pulps.

Figure 8 points out very small differences in the colour of the compared sheets of the bleached and unbleached pulps from pretreated hornbeam wood. The only exception is represented by the bleached pulp from the wood pretreated by a NaOH/peracetic acid sequence. In this case, a small, but well-distinguished shift in coordinate b^* towards the blue region of the spectrum was recorded.

The unbleached kraft pulp from sound wood behaved differently. Its colour shade, due to peroxide bleaching, was markedly shifted by 6.5% towards the yellow colour region.

The differences in the colour shade and lightness of the unbleached pulps from sound and pretreated wood and the extent of their alterations due to bleaching hint at different contents of residual lignin in them. Most probably, the amount and values of the absorption coefficients of chromophores in the residual lignin of these pulps are also different.

Differential reflection spectra of unbleached and bleached pulps from pretreated hornbeam wood are illustrated in Figure 9.

The differential spectra of the unbleached pulps from pretreated wood exhibit an increase in light reflection from the sheets surface over the whole region of the applied wavelengths. The spectra of the unbleached pulps from the wood pretreated with NaOH (1) and all NaOH/H₂O₂ sequences (2, 3 and 4) show a mild minimum at λ_{\min} 540 nm, which might result from the formation of new, relatively stable chromophoric structures in lignin during alkaline pretreatments, also persisting in the residual lignin of unbleached pulps. The maxima in the differential spectra of all unbleached pulps from pretreated wood are allocated approximately at 520 nm. The unbleached pulps from pretreated wood also evidenced more or less distinguished maxima at 590-600 nm (Fig. 9).

Apparently, bleaching increased the intensity of light reflection of the sheets of pretreated hornbeam wood pulps. At the same time, the

maxima in the difference spectra shifted to the region of shorter wavelengths (λ_{\max} 450-490 nm) and the reflection intensity in the maxima increased by 41-49%, compared to the reflection from the sheets of sound wood bleached pulp (not illustrated in Fig. 9). The highest shift of the maximum to the region of shorter wavelengths (λ_{\max} 450 nm) and the highest reflection within the whole range of applied wavelengths were exhibited by the bleached pulp from wood pretreated with a NaOH/peracetic acid sequence. The shift in the pulps maxima of light reflection and, generally, the increased reflection in the 360-550 nm region, due to bleaching, indicate the preferential decomposition of chromophores as absorbtion medium and shorter wavelengths of the applied light (Fig. 9). The chromophores possibly present in the residual kraft lignin are α -carbonyl and C _{α} -C _{β} π bond systems conjugated with phenolic aromatic nuclei, then methoxy-, hydroxy-substituted stilbene structures with absorption maxima at 350-368 nm (in alkaline pH). Other possible chromophores are chalkones, providing, in neutral pH, an absorption maximum at 368 nm, which is shifted in an alkaline environment to a region over 400 nm. The extremely high absorption with a maximum at 480 nm ($\epsilon = 40300$) is characteristic of stilbene chinones that might occur in kraft lignin in trace amounts.³¹

The ATR FTIR spectra of the sheets of bleached refined pulps from pretreated hornbeam wood apparently differ in the 1480-1730 cm⁻¹ region from the spectrum of bleached refined pulp from sound wood (Figs. 10 and 11). Only tiny differences among the spectra present in the region from 800 to 1200 cm⁻¹ were observed. The strong and well-distinguished absorption bands in this part of the spectra can be assigned to various modes of -C-O-, C-O-C and C=O stretching vibrations in cellulose³²⁻³⁴ (Fig. 12). The spectra of all pulps in the 2000-4000 cm⁻¹ region were almost identical. For this reason, the bands comprising the bending and stretching modes of C-H in -CH₂- and -CH₃ (2830-2950 cm⁻¹) and the stretching mode of the associated -O-H groups (3000-3700 cm⁻¹) in the spectra were not evaluated.^{29,35}

The enlarged FTIR spectra of the pretreated wood pulps (Figs. 10 and 11) differ from that of

the pulp from untreated wood by the appearance of a new band at 1540 cm^{-1} and by the suppressed band absorbance at $1555\text{-}1558\text{ cm}^{-1}$. These absorption bands in the spectra are difficult to assign unanimously either to lignin or to cellulose, due to the lack of relevant data. A marked reduction in the absorbance of peaks at wavenumbers 1514 and 1590 cm^{-1} (skeletal vibrations of aromatic nuclei)^{29,34,35} corresponds well with the diminished contents of residual lignin in pulps from pretreated wood samples. A drop in the absorbance of the band at 1682 cm^{-1} in these spectra shows a diminished concentration of the conjugated α -carbonyl in the *p*-substituted arylketone structures^{33,34} of lignin, compared to the spectrum of pulp from sound wood (Figs. 10 and 11). A small maximum at 1710 cm^{-1} (overlapped in the spectrum of sound wood pulp) in the spectra of the pulps from sound and pretreated wood with NaOH, NaOH/H₂O₂ and with NaOH/H₂O₂+activator at $20\text{ }^{\circ}\text{C}$ indicates

trace amounts of β -carbonyl groups in the phenyl-propane units of their residual lignin (Figs. 10 and 11).³²⁻³⁴ However, this maximum may be a composed structure, representing the β -carbonyl groups in the phenyl-propane units of lignin and the reducing end groups of polysaccharides in their oxo-form.

The spectrum of the pulp from NaOH/peracetic acid-pretreated wood (spectrum 5 in Fig. 12) is not presented in Figures 10 and 11, because of the high level of noise in the enlarged record.

A weak, yet satisfactorily distinguished peak with a maximum at 1750 cm^{-1} (C=O stretching in carboxylic groups, esters in polysaccharides and unconjugated ke-tones)^{29,32,35} in the spectra of pulp from sound and pretreated hornbeam wood with NaOH/peracetic acid (Fig. 12) indicates the presence of tiny amounts of carboxyl groups in these preparations.

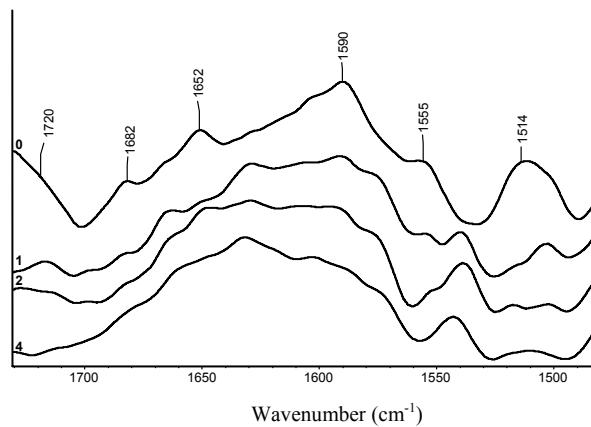


Figure 10: ATR FTIR spectra of bleached pulp sheets made of: 0 – sound wood; 1, 2, 4 and 5 – wood pretreated by the sequences given in Table 1 (region $1480\text{-}1730\text{ cm}^{-1}$)

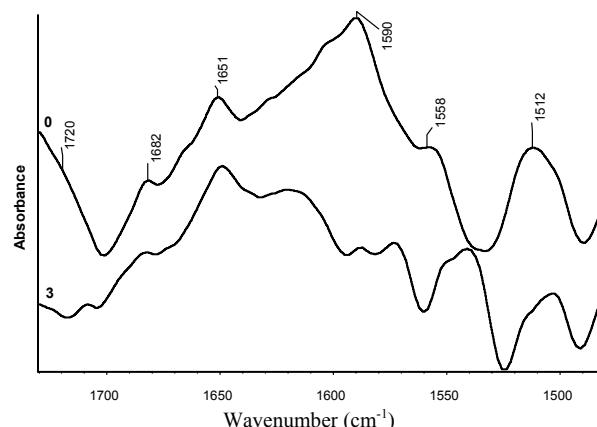


Figure 11: ATR FTIR spectra of bleached pulp sheets made of: 0 – sound wood; 3 – wood pretreated by sequence 3 (region $1480\text{-}1730\text{ cm}^{-1}$)

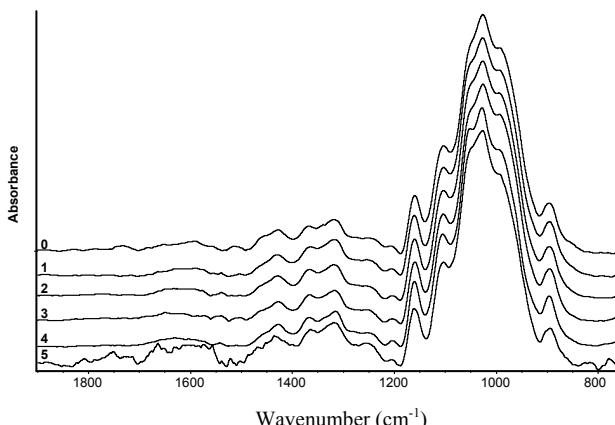


Figure 12: ATR FTIR spectra of bleached kraft pulp sheets made of: 0 – sound wood, 1-5 – pretreated wood,
see Table 1 for pretreatment sequences

CONCLUSIONS

The experimental data describing the properties of pulps from sound and pretreated hornbeam wood allowed the formulation of the following conclusions:

- Significant differences between the unscreened yield of both sound and pretreated wood kraft pulps, prepared under identical conditions and calculated based on the mass of the wood prior to pretreatments, indicate an improved digestibility of pretreated hornbeam wood chips.

- All pretreatments led to extremely reduced Kappa numbers of the pulps.

- The pretreatments contributed to an unexpectedly high gain in the brightness of the corresponding pulps, representing 120-138%, compared to the brightness of the untreated wood pulp.

- Apparently, the pretreatments influenced fibre dimensions and distribution in the bleached, non-refined pulps, whereas the sound wood pulp fibres were moderately larger and coarser, while their distribution according to length and width was less symmetric.

- To achieve a freeness of 38 °SR, the refining energy of the bleached pulps from pretreated wood samples had to be increased from 37 to 114%, compared to that consumed by the pulp from sound hornbeam wood.

- Despite a slightly slower rate of the initial phase swelling, the final swelling of the bleached, refined sheets of sound wood pulp in water was

by 15-20% higher, compared to pretreated hornbeam wood pulps.

- All pretreatments markedly improved the breaking length and tear length of the sheets made of bleached and refined kraft pulps, with the exception of a single pretreatment with NaOH, which moderately diminished the breaking length of the corresponding pulp.

- The Kappa number reduction and the gain in brightness of the pretreated wood pulps resulting from peroxide bleaching, expressed as percent values, were apparently more significant, compared to those of the sheets made of sound wood pulp.

- Pretreatments of hornbeam wood improved the optical properties of both unbleached and bleached pulps. The positive effect of bleaching on the shift of colour to shorter wavelength and lightness of the pulp was much more expressive in the case of the pretreated wood pulps.

- ATR, FTIR and differential UV/VIS spectra confirmed the reduced content of residual lignin and the negligible amounts of chromophore structures in the pretreated hornbeam wood pulps.

Finally, it can be stated that all agents and sequences used in the pretreatment improved noticeably the digestibility of hornbeam wood, as well as the properties of the resulting kraft pulps. Despite the moderately better properties of the pulps from the wood pretreated by NaOH/oxidation agent sequences, a single application of a NaOH step seems to be a more feasible way, due to its simplicity, low cost and

shorter pretreatment time. A certain disadvantage of the tested pretreatments might be the drop in the pulp DP.

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