

**ALKALINE AND ALKALINE/OXIDATION PRE-
TREATMENTS OF SPRUCE WOOD****PART 1: CHEMICAL ALTERATIONS OF WOOD AND ITS
DIGESTIBILITY UNDER CONDITIONS OF KRAFT COOK**

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ABSTRACT

A series of comparable specimens of spruce wood were submitted to chemical pre-treatments. Chemical pre-treatments were carried out with diluted sodium hydroxide, or sodium hydroxide and then by hydrogen peroxide, or per-acetic acid. All pre-treatments modified the chemical composition of wood and led to its weight loss. The pre-treatments resulted in a complete deacetylation, and partial delignification of wood and did not cause apparent loss of cellulose. Chemical alterations of the pre-treated spruce wood were markedly reflected in its improved digestibility under conditions of kraft cook. The obtained pulps were characterized with apparently reduced content of residual lignin, lower yield, moderate drop in DP, higher brightness and better optical properties (colour and lightness) of both unbleached and bleached pulps.

KEY WORDS: spruce, pre-treatments, kraft pulp, brightness, colour, differential UV/VIS spectra

INTRODUCTION

Production of pulp is connected with a high consumption of energies, raw materials and chemicals. From the economic reasons, various modifications of the properties of raw materials were tested in laboratory and pilot plant scale to improve them from the viewpoint of pulping and the properties of the resulting pulp.

In principle, the digestibility of raw materials may be improved by mechanical, biotic (mostly fungal) and chemical pre-treatments.

The principle of mechanical pre-treatments dwells in the formation of ruptures and cracks inside chips allowing the release of the entrapped air from their capillary system during the impregnation step. Similarly, a uniform impregnation of chips can be often achieved by their pre-steaming or by application of vacuum (Malkov 2002, Malkov et al. 2003, Rydholm 1965).

Pre-treatments of chips with white-rot fungi resulting in their modified physical properties and partial delignification were performed in laboratory and pilot plant scale. As a result, reduction

in defibration (mechanical pulps) or refining energy consumption (chemical pulps) was reported (Bar-Lev et al. 1982, Sachs et al. 1990, Messner and Srebotnik 1994). At the same time a significant improvement in mechanical strength of pulps, due to minimal mechanical damage of softened and swelled fibres in defibration, was observed (Sachs et al. 1989, Settliif et al. 1990).

An alternative to mechanical and biotic pre-treatments might be the chemical pre-treatments, especially those leading to deacetylation, partial delignification and relaxation of sub-microscopic structure of wood. The advantage of the chemical pre-treatments might be shorter time of pre-treatment, more uniform effect on chips and absence of their sterilisation before inoculation by fungi.

The pre-treatments of chips based on the application of alkali or alkali followed by oxidation agents such as hydrogen-peroxide or per-acetic acid have recently been tested (Solár et al. 2008a, 2008b, 2009). The pre-treatments noticeably improved digestibility of hornbeam wood (*Carpinus betulus* L.) and mechanical and optical properties of the resulting kraft pulp.

A stepwise treatment of hard and soft wood with NaOH and acidified peroxy-monosulphate followed by the subsequent alkaline extraction of lignin from the processed chips provided pulps of high quality (Minor and Springer 1993, 1995).

The course of impregnation of softwoods and hardwoods with alkaline solutions, diffusion of alkali through the specimens of wood under different experimental conditions, kinetics of deacetylation, and neutralisation of polyuronides with alkali were studied by a number of authors (Zanuttini and Marzocchi 1997, Zanuttini et al. 1999, Constanca and Constanca 2002, Malkov 2002, Zanuttini et. al 2005, Constanca and Zanuttini 2004, Zanuttini et. al 2005). The obtained information, kinetic equations, mathematical models for diffusion of pulping chemicals and deacetylation products in wood may serve for optimising alkaline semi-chemical and chemical pulping.

The aim of this presentation was to estimate the influence of alkaline and alkaline/oxidation pre-treatments on the chemical composition of spruce wood and yield, degree of polymerisation, brightness and colour of bleached and unbleached kraft pulps.

MATERIAL AND METHODS

Material

From a 75-year old spruce tree trunk were taken three 28 cm long sections in 1.5 m distance from each other. From each section a 12 cm thick board in radial plane was sawn. Positions of boards in the sections were mutually swivelled through a 60 ° angle. From the boards the test specimens with dimensions of 2.5×2.5×1.0 cm were prepared. The longest dimensions were in radial and tangential directions and the shortest one was parallel with grain. From the specimens a comparable series with proportional representation of mature and juvenile wood were selected.

Pretreatments

Prior to pre-treatments a series of specimens were immersed for 48 h into 0.0155 M solution of Chelaton III in deionised water. Penetration of the solution was enhanced by vacuum (two 10 min cycles at a pressure of 10 kPa).

A review of the applied pre-treatment sequences is given in the Tab. 1, where NaOH denotes its 2.5% solution in deionised water, P denotes 7.5% hydrogen peroxide, PAA is 8% per-acetic acid in deionised water, and DCDA dicyandiamide activator added to oxidation agent (P) in amount of 0.028g per 1g o.d. wood. All the pre-treatment sequences were carried out at 20 °C, the exception

was pre-treatment No 4, where the oxidation step was carried out at elevated temperature (60 °C) and shorter time. The ratio of wood to alkali or oxidation agent solution equalled to 1:5 w/w.

Tab. 1: Pre-treatment sequence

Pre-treatment sequences	Agent/Time (h)/Temperature (°C)
Sound wood	-
1	NaOH/48/20
2	NaOH/48/20 + P/72/20
3	NaOH/48/20 + P/24/60 + DCDA
4	NaOH/48/20 + PAA/72/20

Note: the time of alkaline pre-treatment of wet specimens was determined visually examining the core of split specimens and by measuring its pH. The time for complete alkaline impregnation of the specimens saturated preliminarily with water varied within 36-40 h.

Kraft pulping

The model chips with dimensions of 1×0.3×1cm (first dimension in radial direction and the last one in axial direction) in their air-dry state were used for cooks. Chips were cut from the test specimens after determination of their physical properties. Pulping was carried out in 60ml stainless steel autoclaves with a liquor of 25.07% sulphidity and 18.0% of active alkali on the absolutely dry weight of chips. For pulping, the air-dry chips were used with chips to liquor ratio 1: 4.2. The cook comprised a 120-min heating period from 80 to 170 °C and a 120-min delignification at the same temperature. Pulping was done using stainless autoclaves immersed in an oil bath without rotation or agitation. The initial temperature of chips and liquor in the autoclaves prior to their immersion into the pre-heated oil bath was 22°C.

Bleaching

A hydrogen peroxide activated by dicyandiamide (DCDA) was used for bleaching the pulps (Chen 1996). Consistency of the defibred pulp was 10%. The amounts of chemicals in the bleaching solution, based on the oven dry weight of pulp, were: H₂O₂ – 10%; NaOH – 3%; Chelaton III – 0.5% and DCDA – 1.6%. The time and the temperature of bleaching: 120 min at a temperature of 80 °C. Then the pulps were washed with 3% acetic acid (50 ml), deionised water to neutral pH, and finally with 50ml of acetone. Pulps were dried at the ambient temperature.

Chemical analyses of wood and determination of pulp physical properties

- Weight loss of the specimens resulting from the pre-treatments was calculated from weight of both the sound and pre-treated series of the specimens in their oven dry state. The drying of specimens for determination of their dry residue was carried out at room temperature in a desiccator. The drying media were 98% H₂SO₄ and then P₂O₅.
- Part of chips from sound and pre-treated spruce wood comprising proportional representation of juvenile and mature wood in the stem was disintegrated, sieved and a fraction with dimensions ranging from 0.5 – 1.0mm was used for chemical analyses.
- Content of extractives in the wood meal was determined according to D 1107 – 96 method “Standard Test Method for Ethanol-Toluene Solubility of Wood”
- Acetyl groups in wood meal were determined by a method of Solár et al. (1987)

- Lignin in extractive-free wood sawdust and unbleached pulps was determined by the TAPPI T-13m method (ASTM Standard D 1106-96). For the bleached pulps, a modified spectroscopic method of Iiyama and Wallis (1988) was used. The temperature of the sample dissolution was 55 °C and time of digestion equalled to 90 min.
- Cellulose in extractive-free wood meal was determined by the method of Seifert (1956).
- Yield of pulp, including rejects, was determined according to standards (Laurová et al. 2006).
- Pulps were defibred following the method STN EN 5263 (50 022):1999.
- Average degree of polymerisation (DP) of bleached pulps was calculated from intrinsic viscosity of their solutions in EWNN_{NaCl} complex (ISO 5351/2.1981). The samples of bleached pulps for DP determination were additionally bleached with buffered solution of NaClO₂ according to the method used by Tirtowidjojo et al. (1988).
- Brightness of unbleached and bleached sheets of kraft pulp was measured by using the standard method STN 50 0241.
- Colour and lightness of sheets of both unbleached and bleached pulps were estimated with the spectrometer Konica Minolta CM-2600 D in the range of 360–740 nm with a resolution of 10 nm. From each sample comprising 3 sheets of unbleached and bleached kraft pulp were taken 18 scans. A random choice of the measured area was used. The spectra were evaluated in a*, b* and L* co-ordinates in the colour space „CIELAB“, also differential spectra were constructed as a difference between the spectra of pulps from the pre-treated and sound wood. Moisture content of the examined pulps was 3.5%.

RESULTS AND DISCUSSION

In Tab. 2 the basic analytical data concerning mass loss, contents of extractives, klasson lignin and cellulose in sound and pre-treated spruce wood are presented.

Tab. 2: Basic analyses of the sound and pre-treated series of spruce wood (%)

Pre-treatment	Mass loss	T/A extract	Acetyl	TAPPI lignin	Cellulose *
Sound wood	-	2.20	1.41	28.96 (28.32)	43.60 (42.64)
1	3.47	0.60	0.03	27.80 (26.67)	46.50 (44.62)
2	3.94	0.35	0.02	27.61 (26.43)	47.01 (45.00)
3	5.35	0.45	0.03	27.51 (25.92)	47.89 (45.12)
4	10.02	1.35	0.04	19.25 (17.09)	49.67 (44.10)

* cellulose contents corrected for residual lignin (amounts of residual Tappi lignin in the cellulose preparations isolated according to the method of Seifert were as follows: 0 - 2.38; 1 - 2.51; 2 - 2.49; 3 - 2.31 and 4 - 1.20%
 Note: figures in parentheses express the amounts of lignin and cellulose expressed to weight of wood before its pre-treatment (mass loss of wood due to pre-treatment and contents of extractives were taken into the consideration)

As seen in Tab. 2, the mass loss of spruce wood depends on the pre-treatment sequence applied (Tab. 1). The deepest loss of wood substance caused the sequence NaOH/per-acetic acid. The reduction in the contents of the extractives in wood, mostly due to their dissolution in the pre-treatment media, was characteristic for all pre-treatments. The combined influence of alkaline medium and acidic oxidation agent (sequence 4) resulted in moderately increased amount of

extractives probably due to deeper oxidative and acidic degradation of the wood components.

All the applied pre-treatments removed almost totally the acetyl groups from spruce wood due to their splitting off from hemicelluloses (glucomannans) in alkaline environment.

The pre-treatments also altered apparently also the contents of lignin and cellulose in the spruce wood (Tabs. 2 and 3).

Tab. 3: Removal of lignin and increase in the cellulose contents in spruce wood due to pre- treatments (%)

Pre-treatment sequence	Loss of lignin	Increase in cellulose
1	5.83	4.64
2	6.67	5.53
3	8.47	5.82
4	36.65	3.43

As it follows from Tabs. 2 and 3, the most efficient delignification agent, removing more than 36% of lignin from spruce, was the NaOH/per-acetic acid - sequence 4. The least effective from this point of view was the pre-treatment with a single NaOH solution (sequence No 1). Extremely high delignification efficacy of the sequence with use of per- acetic acid at low pH dwells in progressive oxidative degradation of lignin including its aromatic nuclei (Chang and Allan 1971).

On the other hand, all pre-treatments led to an increase in the contents of cellulose in the pre-treated spruce wood. This increase was not only a relative, but also an absolute one when the amount of cellulose was expressed in relation to initial weight of wood before the pre-treatments (Tab. 2 and 3). This phenomenon might result from sorption of glucomannan on cellulose in the alkaline step of the pre-treatments. Similar results were reported for hornbeam wood pre-treated with ammonia and NaOH solutions at ambient temperature. The sorption of deacetylated hemicelluloses (xylans in this case) onto cellulose was confirmed by determination of pentosans (Solár and Melcer 1980) and chromatography of aldnitrile-acetates in the cellulose hydrolysates (Solár et al. 2008 b).

Chips cut from the specimens of sound and pre-treated wood were submitted to kraft cooks. The corresponding data concerning yield, residual lignin, brightness and DP of the prepared pulps are presented in Tab. 4.

Tab. 4: Yield, residual lignin content, brightness and average degree of polymerisation (DP) of kraft pulp from spruce wood samples

Pre-treatment	Yield of pulp*	TAPPI lignin in crude pulp	DP	Brightness of unbleached pulp (% MgO)	Brightness of bleached pulp (% MgO)	Increase in brightness (% MgO)	UV lignin in bleached pulp
Sound wood	53.76 (53.76)	9.28	1108	31.0	45,9	14.9	7.30
1	51.55 (49.76)	5.81	1029	36.1	54.0	17.9	4.63
2	51.13 (49.14)	4.62	875	39.4	56.6	17.2	3.65
3	49.59 (46.84)	4.03	858	41.1	58.4	17.3	3.44
4	52.49 (47.24)	0.89	919	44.7	67.4	22.7	1.12

* figures in parentheses represent the yield of pulp expressed to weight of chips before pre-treatment (mass loss of wood in the pre-treatment was taken into consideration)

The applied chemical pre-treatments resulted in a moderately reduced yield of the corresponding kraft pulps. The deepest - 8.9% reduction in the pulp yield caused the pre-treatment sequence No. 3 (NaOH/H₂O₂ + DKDA activator), and the smallest one corresponded to pulp from wood pre-treated with a NaOH/per-acetic acid (sequence 4). This may be explained by deep degradation of lignin and hemicelluloses causing the mass loss of wood pre-treated this way. Reduction in the yield of pulp from the pre-treated spruce wood partly results from diminished contents of residual lignin in them (Table 4).

In contrast to these data, the yields of pulp when expressed to weight of wood prior to pre-treatments were moderately reduced (sequences 1 and 2), and in the case of pulps from wood pre-treated with the sequences 3 and 4, the yields almost corresponded to "low yield" chemical pulps.

The pre-treatments markedly diminished the contents of residual Tappi lignin in the kraft pulps (Tab. 4). Extremely low content of residual lignin (representing a 90% reduction of lignin in pulp from sound wood) was determined in the unbleached pulp from spruce wood pre-treated with a NaOH/per-acetic acid sequence. The other pre-treatments reduced the content of residual lignin in the unbleached pulps to a lesser extent (37 to 56%) (Tab. 4).

The improved digestibility of spruce wood pre-treated with alkali and by alkali/oxidation sequences (Tab. 4) most probably results from its altered physical properties and chemical composition. From among the physical ones it might be the increased accessibility of de-acetylated wood to water (Sjöstrom and Haglund 1961, Sumi et al. 1964) increasing its uptake by the pre-treated wood. In connection with increased uptake of water by deacetylated wood it may be hypothesized that this phenomenon promotes the transport processes in wood based on diffusion. Increase in the diffusion coefficient for hornbeam wood pre-treated under identical conditions was reported by Solár et al. (2008 a).

Deacetylation and neutralisation of uronic acids in wood may also contribute to better digestibility of the pre-treated spruce wood under conditions of alkaline cooks. These reactions may lead to diminished consumption of alkali during the alkaline cook (Zanuttini and Marcocchi 1997, Constanca and Constanca 2002, Zanuttini et al. 2005). The influence of deacetylation on the consumption of alkali, however, may be less impressive as in the case of hardwoods due to lower contents of acetyl groups in the softwood species.

Chemical pre-treatments based on the use of NaOH solutions as an agent reduced to a different degree DP of the corresponding pulps. Explanation of this phenomenon is in a hydroperoxide anion formation in alkaline solution in the presence of oxygen (sequence 1) or in the presence of H₂O₂ (sequences 2 and 3). Hydro-peroxide anion is a potent agent cleaving randomly the glucosidic bonds in polysaccharides, including those in cellulose (Kleinert 1956, Mattor 1963).

Reduced DP of pulp from wood pre-treated with sequence 4 may result from hydrolysis of cellulose by hydro-peroxide anion in alkaline step of the pre-treatment and from acid hydrolysis and oxidation of cellulose with per-acetic acid in its second step.

Brightness of unbleached pulps from the pre-treated wood was higher by 6 to 14% MgO, according to the pre-treatment sequence used. One-step peroxide bleaching of the compared pulps resulted in increase in their brightness by 14.9 to 22.7% MgO. The data in Table 4 indicate easier bleaching of all pulps from the pre-treated samples of spruce wood under the same bleaching conditions. The highest brightness from all compared bleached and unbleached pulps exhibited the pulps from wood pre-treated with a sequence 4.

Peroxide bleaching reduced the contents of residual lignin in the compared kraft pulps by approximately 20 – 22%. The exception, however, represented the pulp from wood pre-

treated with NaOH/per-acetic acid sequence. In this case the content of residual lignin in the bleached pulp (determined by UV spectroscopy) was higher than that determined by the Tappi method in the corresponding unbleached pulp. We are of the opinion, that the cause of this discrepancy may dwell in increased portion of acid soluble fraction of residual lignin in the unbleached pulp from wood pre-treated by NaOH and per-acetic acid.

The colour of sheets from unbleached and bleached pulps was examined by Konica Minolta spectrometer in the range of 360–740 nm. Axis a^* in the CIELAB colour space comprises the colour of the surface ranging from green (-100 to 0%) to red colour (0 to 100%), and axis b^* expresses the colour range from blue (-100 to 0%) to yellow (0 to 100%). Co-ordinate L^* represents lightness of the monitored surface L expressed in per cent of inner standard of the instrument representing 100% of this value.

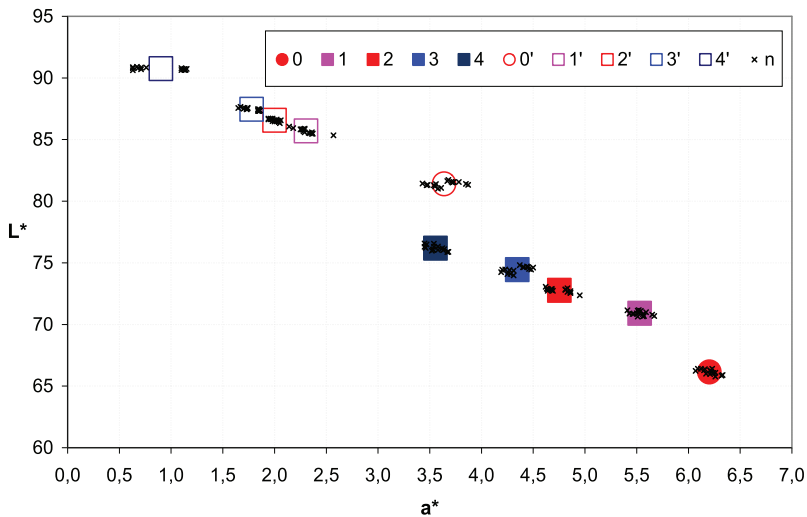


Fig.1: Lightness L^* and colour of unbleached and bleached kraft pulps from sound and pre-treated spruce wood in coordinate a^* ; Legend: empty mark with apostrophe over the number of pre-treatment denotes optical properties of bleached pulp, *n = 18

As it follows from Fig. 1, bleaching of pulps from spruce wood caused a marked shift in the shade of colour from red colour towards green region of the CIELAB space (axis a^*). The shift was approximately the same for all compared sheets of pulp, and equalled 2.5%. A similar effect on the shift in colour of unbleached pulps towards green colour had all pre-treatments, and the most effective in this regard was the sequence 4.

All sheets of bleached pulps were characteristic with for 13 to 16% higher lightness in colour shade as compared to those of unbleached ones. The highest increase of this property was observed in pulp sheets from sound spruce wood.

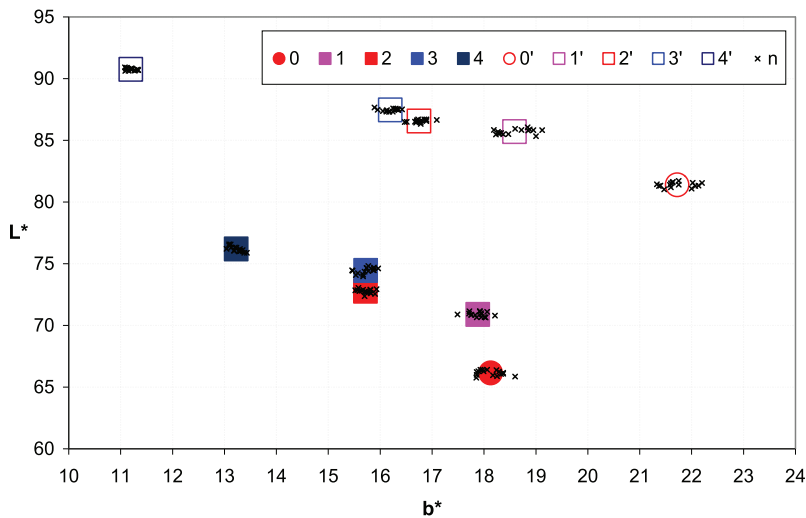


Fig. 2: Lightness L^* and colour of unbleached and bleached kraft pulps from sound and pre-treated spruce wood in coordinate b^* ; Legend: empty mark with apostrophe over the number of pre-treatment denotes optical properties of bleached pulp, *n = 18

Fig. 2 illustrates the influence of pre-treatments and bleaching on the colour and lightness of kraft pulp. Chemical pre-treatments of wood caused a more or less apparent shift in the colour of unbleached pulps towards blue region of colour. The most effective in this respect was the pre-treatment sequence No. 4.

Bleaching increased the lightness of all pulps markedly as already described in connection with Fig.1 and caused a more or less intensive shift in their colour along the coordinate b^* . The most striking shifts were observed for pulp from sound wood (shift for 3.8% of the scale towards yellow colour) and for pulp from wood pre-treated with the sequence 4 (shift of -2% in direction to blue colour).

In Fig. 3, the differential spectra of unbleached and bleached kraft pulps in the region of 360 – 740 nm are illustrated.

Increased reflection of light within the whole region of the applied wavelength, seen in the differential spectra of unbleached kraft pulps from the pre-treated spruce wood, point out their reduced contents of residual lignin and chromophores, as well. The best results in this respect provided the pulp from wood pre-treated with a sequence No. 4.

One-step peroxide bleaching of kraft pulps from the pre-treated samples of spruce wood increased the intensity of light reflection from the sheets apparently. At the same time, the maxima in the difference spectra were shifted to a region of shorter wavelengths (λ_{max} 410 – 460 nm) and the intensity of reflection in the maxima increased by 41 – 49%, compared to that from sheets of bleached pulp from the sound wood (not illustrated in Fig. 3). The most apparent shift of the maximum to the region of shorter wavelengths (λ_{max} 410 nm) and the highest reflection within the whole range of the applied wavelengths exhibited the bleached pulp from wood pre-treated with a NaOH/per-acetic acid sequence. The shift in the pulps maxima of light reflection and the generally increased reflection in the region of 360–460 nm due to bleaching indicate the preferential decomposition of chromophores absorbing medium and shorter wavelengths of the applied spectrum of light. The possible chromophores in the residual kraft lignin are α -carbonyl and

C_{α} - C_{β} π bond systems conjugated with phenolic aromatic nuclei and methoxy-, hydroxy- substituted stilbene structures with the absorption maxima at 350 – 368 nm (in alkaline pH). Other possible chromophores are chalcones providing in neutral pH the absorption maximum at 368 nm. This maximum is shifted in alkaline environment to a region above 400 nm. Extremely high absorption with a maximum at 480 nm ($\epsilon = 40300$) may be assigned to stilbenequinones present in kraft lignin in the trace amounts (Falkehag and Marton 1966).

The comparison of differential spectra of bleached and unbleached pulps above 625 nm points out a slightly reduced reflection of light from the surface of all bleached pulps. In this region, except dyes, absorb the catechol and catechol-methyl derivative structures complexed with Fe^{2+} (a broad peak with λ_{max} at 560-590 nm with ϵ 1100 in the spectrum). Such structures are present in softwood kraft lignin in amount of approximately 0.06 per C6-C3 constitutional unit of lignin (Falkehag and Marton 1966). In our opinion, however, the hydrogen peroxide alkaline bleaching of kraft pulp most probably converted the catechol structures to intermediate o-chinones which were apt to further oxidation.

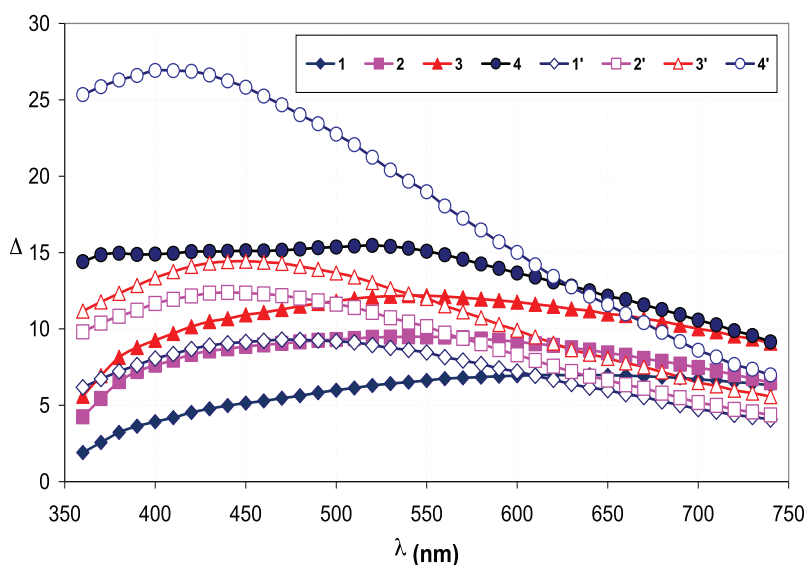


Fig. 3: Differential reflection spectra of unbleached and bleached kraft pulps from the pre-treated spruce wood ($w_{abs.}$ 3.5%, $n = 18$) Legend: empty mark with apostrophe over the number of the pre-treatment sequence denotes spectrum of bleached pulps

CONCLUSIONS

The obtained experimental data concerning the chemical composition of the pre-treated spruce wood and analyses of the examined properties of both unbleached and bleached kraft pulps allowed to derive the following conclusions:

- Pre-treatment of spruce with sodium hydroxide, sodium hydroxide followed by hydrogen peroxide or per-acetic acid oxidation improved noticeably its digestibility.

- The most efficient pre-treatment, considering the yield, contents of the residual lignin and brightness of the compared pulps was the sodium hydroxide/per-acetic acid sequence.
- All pre-treatments increased apparently the brightness and lightness in the shade of colour of kraft pulp, regardless the fact whether it was bleached or unbleached. The most efficient in this respect was the sodium hydroxide/per-acetic acid sequence.
- The pre-treatments resulted in more or less apparent drop in the pulp DP, the least reduction in this property caused the single pre-treatment of wood with solution of sodium hydroxide.
- The applied pre-treatments caused complete deacetylation of spruce wood, diminished the contents of extractives in wood and resulted in its partial delignification.

Improved digestibility of the pre-treated spruce wood results partly from its chemical alterations, e.g. complete deacetylation, partial delignification and degradation of hemicelluloses. These changes may result in reduced consumption of pulping chemicals (e.g. NaOH and Na₂S) during the cook and thus contribute to its increased delignification efficacy.

The preliminary data concerning physical properties of the pre-treated spruce wood, however, indicate their essential influence on the course of alkaline cooks and pulp properties. This problem will be dealt with in Part 2 of this article.

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REFERENCES

1. Bar-Lev, S.S., Chang, H.M., Kirk, T.K., 1982: Evidence that fungal treatment can reduce the energy requirement for secondary refining of thermomechanical pulp. *Tappi J*, 65(10), 111-113
2. Chang, H.M., Allan, G.G. 1971: Chapter 11. Oxidation. In: *Lignins Occurrence, Formation, Structure and Reactions*. Pp. 433-481. Eds. Sarkanen, K.V. and Ludwig, C.H. Wiley-Interscience, New York-London-Sydney-Toronto
3. Chen, J., 1996: Process for delignification and bleaching of chemical pulps. Canadian Patent. 2202150(1996) (http://patents.ic.gc.ca/claims?patent_number=2202150&language=X)
4. Constanza, V., and Constanza, P., 2002: Estimating pure contributions alkaline pulping processes Latin American Applied Research 32, 151-159
5. Constanza, V., and Zanuttini, M., 2004: Optimal operating conditions in alkaline Pulping *Lat. Am. Appl. Res.* 34(3), 22 pp.
6. Falkehag, S., Marton, J., 1966: Chromophores in Kraft Lignin, p. 75-89. In: *Lignin structure and Reactions – Advances in Chemistry Series 59*. American Chemical Society, Washington D.C., 267 pp.
7. Kleinert, T.N., 1956: Cellulosates and Alkali-Celluloses, 483-485. *Pulp Pap. Mag. Can.* 57, 102 In: D. Fengel and G. Wegener, 1984: *WOOD, Chemistry, Ultrastructure, Reactions*. Walter de Gruyter. Berlin-New York, 613 pp.
8. M. Laurová, J. Geffertová, T. Bubeníková, V. Kučerová, G. Kalmárová, 2006: Manual for practicals. Textbook. Technical University in Zvolen, 306 pp.

9. Malkov, S., 2002: Studies on liquid penetration into softwood chips – Experiments, models, and applications. Dissertation Thesis for the DrSc. degree, Helsinki University of Technology. Laboratory of Pulping Technology Reports. Series A29, Espoo, 67 pp.
10. Malkov, S., Tikka, P., Gustafson, R., Nuopponen, M., Vuorinen, T., 2003: Towards complete impregnation of wood with aqueous solutions. Part 5: Improving uniformity of kraft displacement batch pulping. *Paperi Puu* 85(4): 215-220
11. Mattor, J.A., 1963: *Tappi*, 46, 586: Cellulosates and Alkali-Celluloses, 483-485. In: D. Fengel and G. Wegener, Wood, Chemistry, Ultrastructure, Reactions. Walter de Gruyter. Berlin- New York, 613 pp.
12. Messner, K., and Srebotnik, E., 1994: Biopulping – An overview of developments in an environmentally safe paper making technology. *FEMS Microbiol. Reviews*, 13th Ed. Elsevier, 351-364
13. Minor, J.L., and Springer, E.L., 1993: Improved penetration of pulping reagents into wood. *Paperi ja Puu* 75(4): 241-246
14. Minor, J.L., and Springer, E.L., 1995: Method for pulping wood chips separately with peroximonosulfate treatments. United States Patent 5433825 <http://www.freepatentsonline.com/5433825.html>
15. Rydholm, S.A., 1965: *Pulping Processes*. Interscience Publishers, New York, 1269 pp.
16. Sachs, I.B., Letham, G.F., Mayers, G.C., 1990: Biomechanical pulping of aspen chips by *Phanerochaete chrysosporium*. Fungal growth pattern and effects on wood cell walls. *Wood and Fiber Science*, 21 (4), 331-342
17. Sachs, I. B., Letham, G. F., Mayers, G. C., Wegner, T. H. (1990): Distinguishing characteristics of biomechanical pulps. *Tappi J.*, 734(9): 249-254
18. Setliff, E.C., Marton, R., Grancow, S.G., Eriksson, K.L., 1990: Biomechanical pulping with white-rot fungi. *Tappi J.* 73(8): 141-147
19. Seifert, V. K., 1956: Über ein neues Verfahren zur Schnellbestimmung der Rein-Cellulose. *Das Papier*. Pp. 301-306
20. Sjöström, E., Haglund, P., 1961: Studies on factors affecting the determination of carboxyl groups in cellulose. *Svensk Papperstidn.* 64(11): 438-446
21. Solár, R., Kačík, F., Melcer, I., 1987: Simple semimicro method for determination of O-acetyl groups in wood and related materials. *Nordic Pulp and Paper Research Journal*, 2(4): 139-141
22. Solár, R., Melcer, I., 1980: Physico-chemical and chemical changes in the carbohydrate part of hornbeam wood in the process of wood plasticization with aqueous ammonia solution. *Cell. Chem. Tech.* 14(2): 197-202
23. Solár, R., Mamoň, M., Dibdiaková, J., Reinprecht, L., Pánek M., Hudec, J., 2008a: Effect of biotic and abiotic pretreatments of hornbeam wood on its properties interesting from viewpoint of pulping in alkaline media. Part 1: Physical properties. *BioResources – On line*, 3(4): 1278-1290
24. Solár, R., Kačík, F., Reinprecht, L., Laurova, M., Geffertová, J., Dibdiaková, J., 2008b: Effect of biotic and abiotic pretreatments of hornbeam wood on its properties interesting from viewpoint of pulping in alkaline media. Part. 2: Chemical alterations. *BioResources – Online*, 3(4): 1291-1302
25. Solár, R., Geffertová, J., Mamoň, M., Geffert, A., Košíková, B., 2009: Influence of alkaline and alkaline /oxidation pre-treatments of hornbeam wood on the properties of kraft pulp. *Cell. Chem. Tech.*, 3 (4): 20 pp. (accepted, in print)
26. STN EN ISO 5263: 1999 Pulps. Defiberation of pulps in wet state

27. STN EN ISO 5351: 1999 Pulps. Determination of DP of pulp
28. STN 50 0241, 1977: Pulps. Determination of diffuse reflectance in blue region of spectrum
29. Sumi, Y., Hale, R.R., Meyer, J.A., Leopold, A.B., Ranby, B.G., 1964: Accessibility of wood and wood carbohydrates measured with tritiated water. *Tappi J.* 47(10): 621-624
30. Tirtowidjojo, S., Sarkanen, Pla, F., McCarthy, J.L., 1988: Kinetics of delignification in butch and flow through reactors. *Holzforschung* 42 (3): 117-121
31. Iiyama, K., and Wallis, A.F.A., 1988: An improved acetyl bromide procedure for determining lignin in woods and wood pulps. *Wood Sci. Technol.* 22: 271-280
32. Zanuttini, M., Citroni, M., Marzocchi, V., Inalbon, Chr., 2005: Alkali impregnation of hardwood chips. *Tappi J.* 4 (2): 28-30
33. Zanuttini, M., and Marzocchi, V., 1997: Kinetics of alkaline deacetylation of poplar Wood. *Holzforschung* 51(3): 251-256
34. Zanuttini, M., Marzocchi, V., Citroni, M., 1999: Alkaline treatment of poplar Wood. *Holz als Roh und Werkstoff*, 57: 185-190
35. Zanuttini, M., Marzocchi, V., Citroni, M., Mocchiutti, P., 2003: Alkali impregnation of hardwoods. Part I: Moderate treatment of poplar wood. *J. of Pulp and Paper Sci.* 29(9): 313-317
36. Zanuttini, M., Marzocchi, V., Mocchiutti, P., Inalbon, Chr., 2005: Deacetylation consequences in pulping processes. *Holz als Roh- und Werkstoff* 63: 149-153

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