EFFECT OF BIOTIC AND ABIOTIC PRETREATMENTS OF HORNBEAM WOOD ON ITS PROPERTIES INTERESTING FROM VIEWPOINT OF PULPING IN ALKALINE MEDIA.
PART 1: PHYSICAL PROPERTIES

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A series of comparable specimens of hornbeam wood were submitted to pretreatments by white-rot fungi, by alkali alone, or by alkali and oxidizing agents. The pretreatments caused weight loss of wood and modified its physical properties and chemical composition. All pretreatments reduced markedly axial permeability of the test specimens in the wet state (w > FSP). The chemical pretreatments of the test specimens, however, increased the rate of diffusion in the direction parallel to the grain. All pretreatments made the kinetics of wood/water interactions in the initial phase much higher, especially when white-rot fungi were used. The chemical pretreatments caused extreme swelling of wood, and on the other hand, drying of the pretreated specimens to their initial moisture content resulted in extremely deep reduction of their dimensions. An increased rate of wood/water interactions, high uptake of water, and higher diffusion coefficients of wood pretreated by alkali may positively influence the pulping processes.

Keywords: Hornbeam wood; Pretreatment; White-rot fungi; Sodium hydroxide; Hydrogen peroxide; Facial swelling; Swelling kinetics; Permeability; Diffusion

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INTRODUCTION

In the past decades many experiments have been done to modify the properties of wood from the viewpoint of its easier mechanical and chemical pulping. Pretreatments of wood by various strains of white-rot fungi and ascomycete *Ophiostoma piliferum* have been tested to achieve this aim. The pretreatments caused a release in the ultra-structure of wood (bio-pulping effect), not always increased its permeability, and partially delignified the material. Despite the benefits of fungal pretreatment of wood, e.g. increased delignification kinetics, diminished pulp Kappa number, reduced consumption of refining energy, and improved mechanical properties of the pulp (Setliff et al. 1990; Sachs et al. 1990; Messner and Srebotnik 1994; Solár 2001), the method has not widely been used in practice.

Another approach to modify the properties of wood consists of chemical pretreatments, resulting in similar changes of wood as a result of the application of fungi. Advantages of this approach may be a shorter time, a uniform effect on wood, and more reproducible results. As reported by Vilkström and Nelson (1980), a single pretreatment of birch wood with 0.5 to 1.0 % sodium hydroxide solution modified its dynamic mechanical properties so substantially that the fibre length and the papermaking strength of the chemi-mechanical pulp were noticeably improved. A number of papers have dealt with peroxide activated delignification of unbleached pulps, recycled paper, and other lignocellulosics (Chen 1996, 1997; Sun et al. 2002). Pulping in aqueous ammonia/hydrogen peroxide, yielding pulp with negligible content of residual lignin, has also been reported (Efanov and Averin 2004). Promising results with a stepwise treatment of hard- and softwoods with sodium hydroxide followed by delignification with peroxymono-sulfate and by the subsequent alkaline extraction of delignified wood has also been reported (Minor and Springer 1993, 1995).

Much attention has been paid to estimation of the influence of alkali on the swelling of individual anatomical elements in wood, its uniform impregnation, diffusion of alkali and chemicals in wood, consumption of alkali via deacetylation and neutralisation of polyuronides, and to deacetylation kinetics of hardwoods (Zanuttini and Marzocchi 1997; Zanuttini et al. 1999; Constanza and Constanza 2002; Malkov et al. 2003; Zanuttini et al. 2003; Constanza and Zanuttini 2004; Zanuttini et al. 2005). All the studied phenomena concerning impregnation of chips at different temperatures, its uniformity, kinetic equations, and mathematical models for diffusion of chemicals and deacetylation products in wood may serve for optimising conditions of alkaline semi-chemical and chemical pulping. However, the obtained knowledge may be useful also from the viewpoint of alkaline pretreatment of wood prior to pulping.

The aim of this paper was to study the effect of alterations in the selected physical properties of hornbeam wood resulting from its pretreatment by white-rot fungi and by stepwise sodium hydroxide/hydrogen-peroxide (per-acetic acid) pretreatments on its digestibility under conditions of kraft cooking.

EXPERIMENTAL

Materials
Wood species

Model specimens of hornbeam wood (*Carpinus betulus* L.) were prepared from three 30 cm long sections, taken in 1 m distance from each other, from the middle part of the tree trunk 85-90 years of age. Dimensions of the specimens were 2.5x2.5x1.0 cm. The longer dimensions were in radial and tangential directions, and the shorter one in the direction parallel to grain.

Methods
Biotic pretreatments of wood

White-rot fungi *Trametes versicolor* (Lineus), Quelet (Stamm CTB 863 A) - erosive strain, *Phanerochaete chrysosporium* (K 3)-Burds 242 - erosive strain, and

Ceriporiopsis subvermispora (CBS – 374.636) - lignin-selective strain were used for bio-degradations. The pretreatments lasted 30 days at a temperature of 30 $^{\circ}$C and 90 % air humidity. The specimens with initial moisture content of 6.40 % were sterilised by a 5-min boiling in 1 % solution of D-glucose in de-ionised water.

Abiotic pretreatments of wood

For the pretreatments a comparable series of specimens preliminarily immersed into 0.0155 M solution of Chelaton III in de-ionised water (48 h) in their wet state were used. The pretreatments comprised 48-h impregnation of the specimens by 2.5 % NaOH (initial concentration), then their surface was rinsed with distilled water (2 x 200 ml), and this was followed by 72-h duration oxidation steps with the following media: **1.** - 7.5 % H_2O_2; **2.** - 7.5 % H_2O_2 with dicyandiamide as an activator (0.028g/g of o. d. wood.); **3.** - 8 % per-acetic acid; and **4.** - 4 % per-acetic acid. The ratio of wood to the agent was always 1:5, and the temperature was maintained at 20 $^{\circ}$C. A bio-mimetic delignification of the test specimens was also performed as a standard to compare the efficacy of pretreatments. The 4-aminopyridine/tertialbutyl-hydroperoxide/Cu^{2+} complex proposed by Messner et al. (2000) was used. Concentration of the system components represented a 1.5 multiple of that applied by Messner et al. The ratio of wood to solution of the complex was 1:16, and the time of treatment at a temperature of 55 $^{\circ}$C was 72 h.

Physical properties of wood

- Facial swelling of horn-beam wood specimens prior to pretreatments was calculated from their dimensions in radial and tangential direction after 48 hours duration dipping in de-ionised water with the addition of Chelaton III (0.0155 mol.l^{-1}). To remove the air from wood and promote its penetration, two 10-min vacuum treatments at 10 kPa were carried out at the beginning of soaking. Swelling of the specimens after pretreatments was measured instantly after rinsing their surface with de-ionised water.

- The facial area of sound and pretreated specimens in their air-dry state was calculated from their radial and tangential dimensions. Drying of the specimens was performed cautiously at the ambient temperature. The final moisture content varied from 6.36 to 6.50 %. [Swelling and "shrinking" were not measured according to the Standards. The reason for this was an inconvenience of their determination at 0 or 12 % moisture contents of wood and different dimensions of the specimens. Recalculation of the data to normalised moisture would distort them in the case of pretreated specimens.]

- Coefficients of axial permeability of sound and pretreated hornbeam wood were determined at a constant pressure gradient according to the method of Regináč et al. (1977), based on the application of the Darcy law. The monitoring temperature was 20 $^{\circ}$C, and de-ionised water was used as a medium. The measurements were carried out on the specimens saturated with water after a 48-hour immersion in the de-ionised water at 20 $^{\circ}$C.

- Diffusion coefficients of sound and pretreated specimens saturated with de-ionized water were determined under pseudo-stationary conditions from the conductivity of an electrolyte passing through them into the monitoring chamber. The method proposed by Reinprecht and Makovíny (1989, 1990) was used for the determinations.

- The conductivity in the chamber initially containing de-ionized water was measured at 5 min intervals in the first 60 min period of the pseudo-stationary process. Sodium chloride was used as an electrolyte in order to avoid deacetylation and neutralization of acidic groups of sound wood occurring when alkali solution is used. After the measurements, sodium chloride was removed from the specimens by continual washing in de-ionized water. The specimens were further immersed into 2.5 % NaOH at 20 ^{o}C for 48 h, and their impregnation was promoted by a vacuum. In the case of the two-step pretreatment, a 72-h action of 7.5% H_2O_2 at 20 ^{o}C followed. The chemicals from the pretreated specimens were removed prior to measurements by washing with de-ionized water until the conductivity of de-ionized water and the extract from a 3-h cold water extraction (6 specimens/100 ml of water) was practically equal (0.029-0.031 μS for water, and 0.045-0.055 μS for the extracts).
- Kinetics of facial swelling of the test specimens was monitored by a contact method based on the PC processing of the data continually collected at 1s intervals (Solár et al. 2006). For determination of the swelling kinetics, 3 specimens from each series were used. Criteria for the specimens selection were the density, number, and orientation of annual rings, and in case of the pretreated specimens also the weight loss close to mean of that from the corresponding pretreatment. The initial moisture content in wood was 3.2 %, and the temperature of monitoring 20 ^{o}C.

RESULTS AND DISCUSSION

Table 1deals with the weight loss and axial permeability of wet horn-beam wood specimens degraded by the selected strains of white rot fungi.

Table 1. Weight Loss (Δm), Facial Swelling and Coefficient of Axial Permeability (K) of Hornbeam Wood Before and After a 30-day Degradation by the White-Rot Fungi (n = 33 for sound wood, and 15 for bio-degraded wood)

Pretreatment	Property			
	Δ m (%)	Swelling (%)	K (m^{-2})	Δ K (%)∗
Sound wood	-	**16.58**	**1.55E-11**	-
Std.	-	1.036	4.02E-12	-
v (%)	-	6.25	26.1	-
T. versicolor	**16.51**	**16.2**	**1.01E-11**	**-34.80**
Std.	1.98	0.69	1.40E-12	9.04
v (%)	11.99	4.24	13.90	26.00
P. chrysosporium	**10.86**	**15.93**	**1.02E-11**	**-33.90**
Std.	2.01	0.92	1.21E-12	7.78
v (%)	18.54	5.78	11.80	23.00
C. subvermispora	**10.94**	**17.07**	**0.81E-11**	**-47.51**
Std.	2.54	0.87	3.29E-12	21.23
v (%)	23.26	5.12	40.50	44.70

∗ expressed as a difference between the coefficients of permeability of a series of sound and pretreated specimens; for this reason the data may be of indicative value only.

As follows from the table, a 30-day fungal pretreatment of the comparable series of hornbeam wood specimens influenced their final <u>facial swelling</u> negligibly, and variability of the data was very low.

Bio-degradation of the specimens was accompanied by their <u>weight loss</u>, which was almost equal after application of *P. chrysosporium* and *C. subvermispora*. The effect of *T. versicolor* was more pronounced, and the fungus decomposed 16.5 % of a substrate. Relatively high variation coefficients of the data concerning wood degraded by lignin-selective fungus *C. subvermispora* hint at an uneven action of this agent (Table 1).

Despite relatively deep weight loss of wood due to bio-degradations, and as it can be assumed also increased porosity of wood, the biodegradation reduced the <u>axial permeability</u> of the specimens with moisture content above FSP, markedly. In this respect the most effective fungus was the lignin-selective *C. subvermispora*. Deep reduction in the permeability of wet hornbeam wood degraded by *P. chrysosporium* (Δ K -51.16 %) was also reported by Solár at al. (2001). On the contrary, the permeability of such a material in air-dry state was for 39 % higher as compared to permeability of sound wood.

Table 2. Weight loss (Δ m), Facial Swelling, and Coefficients of Axial Permeability (K) of Comparable Series of Hornbeam Wood Pretreated by Different Alkaline/Oxidative and Bio-mimetic Media (n =15, initial moisture content $w_{abs.} = 6.35$ %)

Pretreatment	Property						
	Δ m (%)	Swelling of sound wood (%)	Swelling in 2.5 % NaOH (%)	Swelling due to pretreatment (%)	K – sound wood (m^2)	K – pretreated wood (m^2)	Δ K (%)
2.5%NaOH	**8.67**	**16.58**	**20.51**	-	**1.56E-11**	**0.95E-11**	**- 36.45**
Std.	0.87	**1.04**	1.55	-	2.96E-12	2.98E-13	8.61
v (%)	10.05	**6.25**	7.56	-	18.99	31.33	23.62
2.5%NaOH /7.5%H_2O_2	**11.69**	**16.74**	**20.48**	**20.82**	**1.32E-11**	**0.86E-11**	**- 34.92**
Std.	2.26	1.04	1.36	1.16	4.74E-12	2.97E-12	11.54
v (%)	19.37	6.19	6.75	5.57	36.20	34.60	33.05
2.5%NaOH /7.5%H_2O_2/activ.	**10.53**	**16.81**	**20.32**	**20.69**	**1.44E-11**	**0.95E-11**	**- 34.17**
Std.	0.78	1.84	1.18	1.40	5.42E-12	3.75E-12	4.41
v (%)	7.37	10.95	5.82	6.75	37.50	39.53	12.90
2.5% NaOH /8 % CH_3COOOH	**15.05**	**16.44**	**20.66**	**19.58**	**1.50E-11**	**1.07E-11**	**- 28.7**
Std.	1.74	1.1	1.24	1.28	4.86E-12	3.66E-12	9.71
v (%)	11.54	6.67	5.99	6.56	32.40	34.21	33.82
2.5%NaOH /4 % CH_3CO-OOH	**11.78**	**16.40**	**20.58**	**19.33**	**1.65E-11**	**1.11E-11**	**- 32.73**
Std.	0.95	1.36	149	1.59	5.89E-12	3.68E-12	8.50
v (%)	8.06	8.28	7.22	8.21	35.70	33.13	25.98
Bio-mimetic system	**7.20**	**16.12**	-	**18.95**	**1.43E-11**	**0.85E-11**	**- 40.71**
Std.	0.66	0.79	-	0.86	2.29E-12	1.89E-12	8.02
v (%)	9.19	4.87	-	4.54	16.00	22.20	19.70

The abiotic pretreatments of hornbeam wood led to similar <u>weight loss</u> as fungal pretreatments, however in a much shorter time (Table 2). The pretreatment of wood with 2.5% sodium hydroxide followed by oxidation with 8% per-acetic acid caused its deep (15%) weight loss. The combined alkaline treatment followed by action of hydrogen peroxide led to weight loss of approximately 11%. The effect of bio-mimetic delignification on the weight loss was less pronounced (Δ m = 7.2%).

Apparently higher values of <u>facial swelling</u> and weight loss of by alkali-pretreated hornbeam wood give rise to an assumption of its deeply diminished "reduced density ($\rho_{red.\ min.}$ = mo/$V_{w\ max.}$)" at a moisture content above FSP.

The general opinion concerning increased final swelling of wood pretreated by alkali is, that it results from splitting of acetyl groups from glucuronoxylans (hardwoods) and glucomannans (softwoods) in the cell wall. Deacetylation leads to diminished concentration of intermolecular hydrogen bonds between acetyl and hydroxyl groups of polysaccharides and improves accessibility of wood for water (Sjoström and Haglund 1961; Sumi et al. 1964). Co-occurring, and contributing to swelling of wood in the alkaline media, however, might be also the cleavage of benzyl-ether and ester bonds in the lignin-polysaccharide matrix of wood described by Fengel and Wegener (1984), together with cleavage of phenolic α-O-4 alkyl-aryl bonds in the lignin macromolecules (Gierer 1980).

Chemical pretreatments, similarly as the fungal ones, also substantially reduced the <u>axial permeability</u> of hornbeam wood. However, the pretreatment with 4-aminopyridine/TBH-peroxide/Cu^{2+} bio-mimetic complex caused the deepest drop in this property of wood. The diminished permeability of the pretreated hornbeam wood may result from swelling of the cell walls inside and outside the lumina, thus reducing their cross-sectional area in the vessels. This mode of swelling of the cell walls in hornbeam wood degraded by *P. chrysosporium* had been evaluated statistically, and reported by Solár et al. (2001). A similar phenomenon was observed by Maximino et al. (1988), using microscopy of poplar fibers short-term swelled in 5% solution of sodium hydroxide.

In Table 3 the <u>diffusion coefficients</u> of sound and the chemically pretreated hornbeam wood determined in direction parallel to grain are presented.

Table 3. Diffusion Coefficients (D) of the "Pseudo-Stationary" Process for Sound and Chemically Pretreated Hornbeam Wood in Axial Direction (n = 6)

Sample	D ($m^2.s^{-1}$)	Std.	v (%)
Sound wood	**0.81 E-7**	1.82 E-8	22.49
Wood pretreated by 2.5 % NaOH (48 h, 20 ^{o}C)	**1.55E-7**	5.91 E-8	38.13
Sound wood	**1.23E-7**	4.26 E-8	34.61
Wood pretreated by 2.5% NaOH /7.5 %H_2O_2 (72 h, 20°C)	**2.09E-7**	7.78 E-8	37.27

The pretreatment of horn-beam wood with 2.5% water solution of sodium hydroxide increased its diffusion coefficient to a 1.92 multiple in the first 60-min phase of the pseudo-stationary process. In case of the specimens treated with 2.5% sodium hydroxide and then 7.5% hydrogen peroxide, a similar increase in the value of diffusion

coefficient was observed. Increase in the coefficients of diffusion of wood pretreated by alkali might result from the swollen ultra-structure of the cell walls saturated with an excessive amount of water (Tables 3 and 4). High concentration of water in the cell walls may promote their easier penetration and faster motion of the ions and water-soluble molecules. If this assumption is correct, then the enhanced diffusion may overcompensate for the negative influence of diminished permeability of wood pretreated by alkali on the transport processes in wood.

The uptake of water by the chemically pretreated specimens was by 26 to 30% higher compared to that by the sound ones after 198-hour immersion in de-ionised water (Table 4).

Table 4. Coefficient of Axial Permeability (K), Final Facial Swelling (F) and Uptake of Water by Sound, Pretreated, and Pretreated - Washed Specimens of Hornbeam Wood (n = 6)

Sample	Property		
	K (m^2)	F (%)	g H$_2$O/100 g o. d. wood
Sound wet wood: control (48 h in H$_2$O)	**1.60E-11**, v = 19.82 %	-	-
" control (198 h in H$_2$O)	1.45E-11, v = 17.10 %	**17.28**, v = 5.11 %	**108.15**, v = 3.28 %
Sound wet wood (48 h in H$_2$O)	**1.58E-11**, v = 18.67 %	16.25, v = 6.42 %	103.23, v = 1.60 %
Pretreated wood (48 h in NaOH)	-	20.57, v = 5.59 %	136.50, v = 1.65 % ∗
Pretreated - washed wood	**1.00E-11**, v = 13.22 %	**20.76**, v = 5.22 %	**135.96**, v = 1.76 %∗
Sound wet wood (48 h in H$_2$O)	**1.36E-11**, v = 11.28 %	16.75, v = 3.93 %	104.34, v = 2.43 %
Pretreated wood (48 h NaOH/72 h H$_2$O$_2$)	-	21.45, v = 4.20 %	135.78, v = 2.58 %∗
Pretreated - washed wood	**0.80E-11**, v = 12.71 %	**21.95**, v = 4.11 %	**140.97**, v = 2.82 %∗

∗   weight loss of the specimens due to pretreatment by NaOH was **9.20 %**, in the combined NaOH/H$_2$O$_2$ pretreatment it equaled to **12.53** %, and **1.52** % weight loss resulted from 198 h dipping in H$_2$O. The data were used for computation of water uptake by the pretreated and untreated specimens immersed in water

In our opinion, the alkaline pre-treatment of wood may positively influence penetration of a liquor into the chips in early stages of an alkaline cook due to enhanced diffusion of pulping chemicals into their relaxed structure (Table 3). On the other hand, increased diffusion coefficients determined for wood pretreated by alkali may also contribute to a higher rate of transport of delignification products from chips into the liquor during pulping. If the data concerning diffusion of ions through wood in the axial direction indicate its increase after alkaline pretreatment, the same might be expected for their diffusion in its transverse directions.

Figures 1 and 2 express kinetics of facial swelling of sound and pretreated hornbeam wood. The plots were constructed from the mean values obtained by

monitoring of three selected specimens representing each kind of the pretreatment. The diffusion coefficients and the uptake of water by the specimens of wood pretreated by white-rot fungi were not determined. The reason for that was a markedly increased content of residual lignin in the resulting kraft pulps (Solár et al. 2008).
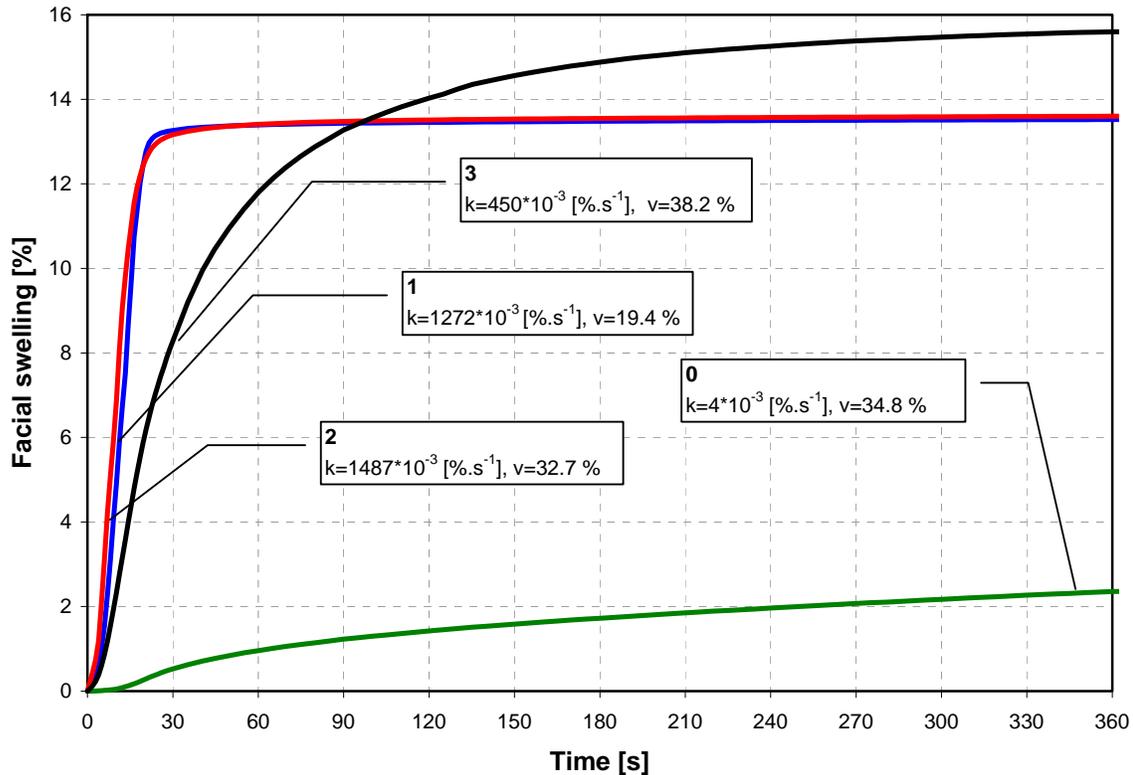
Fig. 1. Kinetic plots and relative rate constants of facial swelling of hornbeam wood pre-treated with white-rot fungi; 0-sound wood, 1– *T. versicolor*, 2 – *P. chrysosporium*, 3 – *C. subvermispora* (moisture content w $_{inic.}$ = 3.2 %, t = 20 ^{o}C)

The comparison of plots in Fig. 1 hints at a far more than two orders higher rate of the initial phase of facial swelling of wood pretreated by the white-rot fungi. In our opinion, this phenomenon is a reflection of an extremely high initial rate of interactions in the system "dry bio-degraded wood/polar liquid". Such a behavior of bio-degraded wood may be due to its high porosity and higher free surface energy on the interface of wood, water, and air (Solár et al. 2001 and 2003).

Reduction in radial and tangential dimensions of the bio-degraded specimens in drying to initial moisture content (w $_{abs.}$ = 6.4 %) was very moderate compared to that of chemically pretreated ones, and varied between 5 to 7 % according to the fungus used.
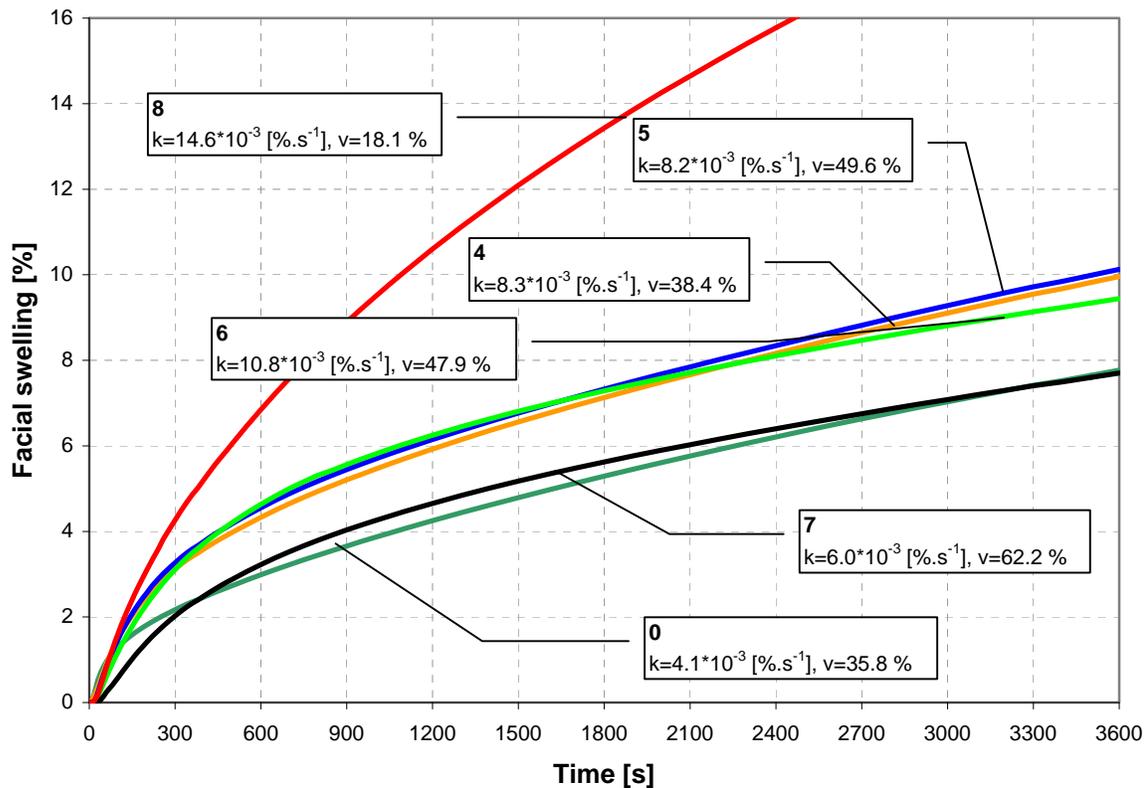
Fig. 2. Kinetic plots and rate constants of facial swelling of hornbeam wood pre-
treated chemically: 0 – sound wood, 4 - NaOH/H_2O_2, 5 – NaOH/H_2O_2 and
activator, 6 – NaOH/8 % per-acetic acid, 7 - NaOH/4 % per-acetic acid,
8 – bio-mimetic system (moisture content $w_{inic.}$= 3.2 %, t = 20 ^{o}C)

Chemical and bio-mimetic pretreatments influenced the kinetics of facial swelling
of wood to much a lesser degree. The relative rate constant of facial swelling in these
cases reached maximally only a multiple of four times that determined for sound wood
(Fig. 2).

In the case of chemically pretreated specimens a deep reduction of linear
dimensions in drying and their negligibly changed porosity resulted in a slowed down
rate of wood/water interactions.

Data concerning the reduction of the specimens' dimensions in radial and
tangential directions due to their drying to initial moisture content are presented in Table
5. In the case of the pretreated specimens the data are informative only, due to their very
high variability.

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Table 5. Reduction in Dimensions of Sound and Chemically Pretreated Hornbeam Wood Specimens Due to Drying to Initial Moisture Content (%) (n = 15)

Pretreatment		Reduction in dimensions (%)		
		Radial	Tangential	Facial
Sound wood dipped in water	(198 h, 20 ^{o}C)	0.35	0.44	0.79 (v =36 %)
2.5 % NaOH	(48 h, 20°C)	11.08	24,49	32.86
2.5 % NaOH/7.5 % H_2O_2	(48/72 h, 20°C)	11.10	23.41	31.91
2.5 % NaOH/7.5 % H_2O_2/ activator	(48/72 h, 20°C)	11.13	23.42	31.94
2.5 % NaOH/7.5 % H_2O_2/ activator	(48/24 h, 55°C)	12.14	24.64	33.79
2.5 % NaOH/8 % per-acetic acid	(48/72 h, 20°C)	16.06	30.26	41.46
Cu^{2+}/TB-OOH/4-aminopyridine system (72 h, 55 ^{o}C)		2.75	6.11	8.69

The deep "shrinkage" of wood pretreated by alkali, by alkali and hydrogen peroxide, or by alkali and per-acetic acid might result from formation of a high number of hydrogen cross-links arising in its ultrastructure during drying.

The data in Tables 2 and 5, and Fig. 3 illustrate the alterations in the shape of sound and pretreated hornbeam wood in air-dry and by the polar liquids saturated state.
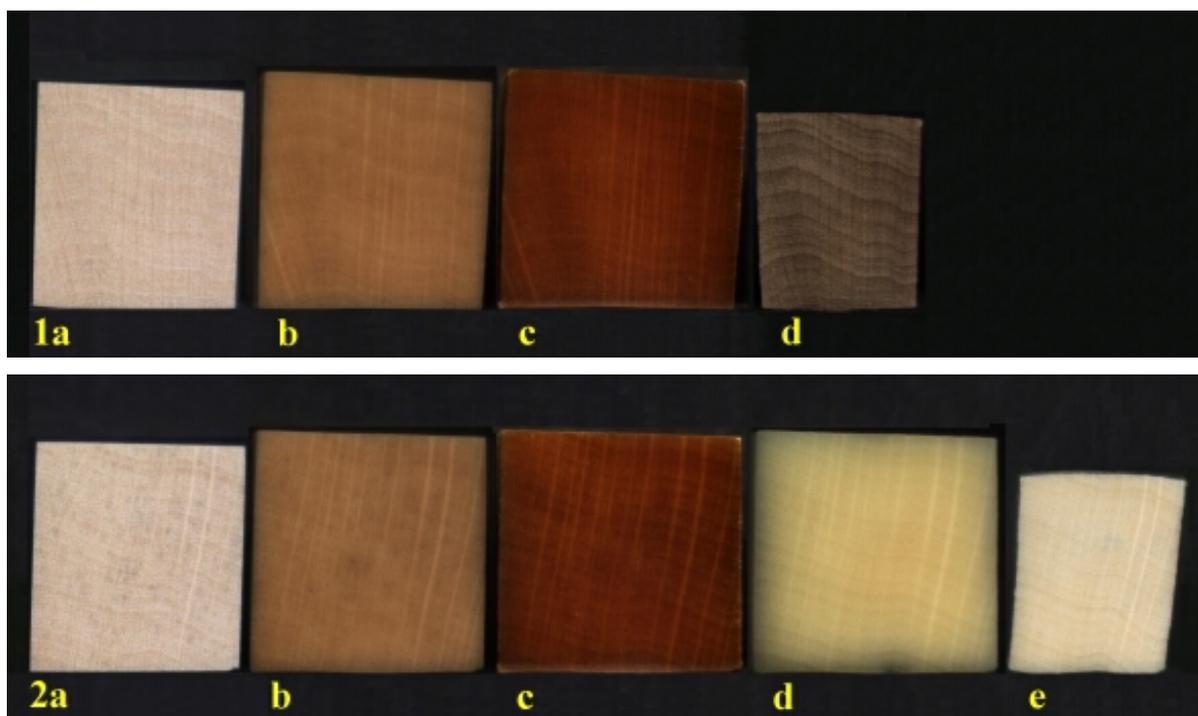
Fig. 3: Specimens of sound and pretreated hornbeam wood in air-dry and wet states (w>FSP)**:**
    1 a) air-dry sound wood, **b)** wet sound wood, **c)** wood pretreated by NaOH, **d)** pretreated air-dry wood (w $_{abs.}$ = 6.41%)
    2 a) air-dry sound wood, **b)** wet sound wood, **c)** wood pretreated by NaOH, **d)** wood after peroxide step, **e)** pretreated air-dry wood (w $_{abs.}$ = 6.48 %)

CONCLUSIONS

Pretreatment of hornbeam wood by the applied strains of white-rot fungi, by alkali solutions, or alkali solutions in combination with hydrogen peroxide, respectively caused a number of alterations in its physical properties. Some of them may play an important role in mechanical, semichemical, and chemical processing of wood to pulps.

From the viewpoint of transport of chemicals in the pretreated hornbeam wood, an interesting finding is a deep reduction in axial permeability, regardless whether the test specimens were pretreated in biotic or abiotic mode.

On the other hand, all abiotic pretreatments resulted in an extreme final swelling of wood, accompanied by marked increase in water uptake. An excessive amount of water present in the released and swollen ultra structure of wood combined with its diminished "reduced density" affects positively the diffusion of chemicals through the cell walls and may overcompensate the diminished permeability of the pretreated wood.

Pretreatment of the specimens by white-rot fungi increased the kinetics of wood/water interactions to an extreme degree; however in the case of chemically pretreated specimens the increase was less pronounced. The effect of the rate of air-dry wood/water interactions (expressed in kinetics of facial swelling of wood) on the course of alkaline pulping is not easy to estimate unambiguously due to the complex nature of these interactions (influence of porosity of wood, polarity of its surface, concentration of inter-molecular hydrogen bonds among wood constituents, free surface energy, etc.).

At the end, it is necessary to state that the chemical pretreatments of hornbeam specimens were carried out under pseudo-stationary conditions with a series of comparable specimens with regular dimensions. In the case of "large scale" pretreatments in the pulp mill, or during alkaline pulping of wood the situation is more complicated. Impregnation of industrial chips under conditions different from those used in the laboratory may provide to some extent different alterations in their properties. The differences might be due to chips dimensional heterogenity and absence of vacuum used in the laboratory to promote the impregnation. Despite this statement the obtained laboratory data may insinuate trends in the alterations of chips properties resulting from their large scale pretreatment.

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