EFFECT OF TREATMENT TEMPERATURE ON THE WATER UPTAKE AND VOLUMETRIC SWELLING OF ASH WOOD TREATED WITH DILUTE ACETIC ACID SOLUTIONS

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Abstract:
The free hydroxyl groups of the biopolymers that make up the cell walls of wood are responsible for the hygroscopic properties of wood. During sorption, water molecules are embedded in the cell walls of wood by building a hydrogen bond with accessibleOH groups, which leads to the swelling of wood. The effect of treatment on wood tissue leads to changes in the chemical composition of wood, thereby changing the hygroscopicity of wood. In this study, wood samples of Narrow-leaved Ash were treated by adding 3%, 6% and 9% of aqueous solution of acetic acid, calculated relative to the dry matter of wood at temperatures of 100°C and 120°C for a period of 1h. The water uptake and volumetric swelling of the treated wood samples and the control (untreated) group of samples were examined during 48h of immersion in distilled water. It was found that in the first 10h of immersion all treated samples absorbed a larger amount than the control group, after which the intensity of water uptake of these samples decreased. After 48h, they generally absorbed less water than the untreated samples. In addition, it was found that all the treated samples, regardless of the conditions of treatment, had less volumetric swelling of the samples than the control group during the study period, even during periods of intense water uptake.

Key words: water uptake; volumetric swelling; ash wood; temperature treatment; acetic acid.
INTRODUCTION

Hygroscopic moisture is located in the cell walls of wood and its maximum content is the fiber saturation point that represents the wood moisture content at which the cell walls are saturated with water and cannot continue to increase moisture content. The increase in moisture content of wood i.e. hygroscopic moisture creates empty space between molecules that are the building blocks of the cell walls (microfibrils) due to the insertion of water molecules between them, which leads to changes in cell wall dimensions, or swelling of wood (Hill et al. 2006). In the area above the fiber saturation point, water is free in the lumens of cells and in macrocapillaries. The change of free moisture does not cause dimensional changes in wood (Šoškić and Popović 2002).

The size of changes in wood dimensions is proportional to the change in the number of water molecules absorbed in the cell wall, or the number of accessible hydrophilic hydroxyl (-OH) groups in cellulose, hemicellulose and lignin, which are potential sites for the formation of hydrogen bonds with absorbed water molecules (Walker et al. 2006, Hill et al. 2006).

Dimensional instability of wood and wood products is a major problem and has been a subject of many investigations for decades. Recent researches have been examining the impact of dealing with the extraction of hemicelluloses on water absorption and dimensional stability of wood. Their results indicate a great influence of the presence of hemicelluloses on water absorption and reduction of hygroscopicity of wood after extraction of the hemicelluloses (Zhang et al. 2011, Paredes et al. 2008).

Hemicelluloses are holders of the majority of free -OH groups, and the most hydrophilic chemical constituent of wood. At the same time, due to their amorphous branching structure and low level of polymerization reactions hemicelluloses are most susceptible to hydrolytic degradation (Janežić- Stevanović 1990). Of course, depending on the conditions of the treatments applied, changes in the structure of other biopolymers building the cell wall are also possible.

Depending on the conditions of the treatment applied, in addition to the partial removal of hemicelluloses effects achieved may include: removal of part of the lignin, reduction in the crystallinity and the degree of polymerization of cellulose, the removal of acetyl groups and the like (Mosier et al., 2005). Treatments of wood at low or moderate temperatures and pressures result in a small amount of products of degradation, which increases with an increase in other reaction parameters (temperature, pressure, duration of treatment) (Sievers and Zacchi 1995). One of the main effects of treatment of wood at low pH, including hot water treatments (Allen et al. 2001, Amidon et al. 2006, Garrote et al. 2001, Yoon et al. 2008) and treatment with diluted acids (Jacobsen et al. 1999, Kumar et al. 2009, Mosier et al. 2005) is the removal of significant amounts of hemicelluloses from wood tissue. According to the literature most frequently used treatments in researches are the ones using sulfuric acid concentrations in the range of 0.5 to 1.5% at a temperature of 120-160°C, followed by hydrochloric, nitric and phosphoric acid.

This paper investigates the effect of treatment with aqueous solution of acetic acid, by adding 0.03, 0.06 and 0.09g of acetic acid/g dry weight of wood at temperatures between 100 and 120°C on the water uptake and volumetric swelling of wood.

MATERIALS AND METHODS

For the purposes of this study according to a standard methodology, a Narrow-leaved ash (Fraxinus angustifolia Vahl. Ssp. Pannonica Soo & Simon) stem aged 72 years was sampled in the area of Morović, Republic of Serbia. The cellulose content in ash wood was 46.70% on average, and the lignin content was 22.42%. The mean value of ash content was 0.33g, while the content of the extractive in the toluene/ethanol solvent was on average 4.62%, and 5.59% in the hot water (Popović and Radošević 2010).

Preparation and characterization of the samples

Wood samples of dimensions 5 (tangential) x 20 (radial) x 150 (axial) mm, were cut at different positions on the stem. These samples were immediately marked in order to know the position they held in the tree (Fig. 1). The samples were air-dried for 30 days at 20°C in order to achieve uniform moisture content. After their weight was stabilized, all the samples were measured on a digital scale accurate to 0.01g, and then sorted into seven groups (six groups of samples and the seventh control group, which served to compare the effects of the treatment). There were 24 samples in each group.

Fig. 1
Ash samples prepared
R - radial direction (20mm), A - axial direction (150mm), T - tangential direction (5mm)
While sorting, attention was paid to maintain an equal number of samples from all positions on a stem in each group, so that all seven groups of samples were of similar properties, and comparable. At the same time, to ensure the same conditions of treatment in each autoclave, care was taken to keep the weights of these seven groups roughly equal.

Thirty boards were randomly selected from the remaining samples for the determination of moisture content, density and porosity of ash wood. The moisture content was determined by the gravimetric method, according to ISO 3130:1975, by drying the samples in a ventilation kiln at 103±2°C to constant weight. Before and after drying, the samples were measured on a digital scale accurate to 0.01g. After drying of the samples their dimensions were measured. The width and length were measured using a standard gage and thickness using a micrometer accurate to 0.01mm. On the basis of these data, mean values of moisture content, density and porosity of ash wood were calculated.

Moisture content was calculated according to the formula:

$$W_{waps} = \frac{m - m_o}{m_o} \cdot 100 \%$$  \hspace{1cm} (1)

$W_{waps}$ - absolute moisture content, in %
$m$ - weight of an air-dried sample, in g
$m_o$ - weight of the sample after drying to constant weight, in g

The mean value of the moisture content of air-dried samples was 10.34%, with a minimum and maximum value of 9.69% and 10.70%, respectively and a standard deviation of 0.2648.

The density of each sample in the oven-dry state ($\rho_o$) was calculated using the formula:

$$\rho_o = \frac{m_o}{V_o} \cdot 100 \ [g/cm^3]$$  \hspace{1cm} (2)

$\rho_o$ - wood density in the oven-dry state, in g/cm$^3$
$m_o$ - weight of the sample after drying to constant weight, in g
$V_o$ - volume of the sample after drying to constant weight, in g

Volumetric porosity of wood depends on the wood density of each sample and it was calculated for each sample using the formula:

$$P_z = \left( 1 - \frac{\rho_o}{\rho_{ds}} \right) \cdot 100 \ [%]$$  \hspace{1cm} (3)

$P_z$ - volumetric porosity of wood, in %
$\rho_o$ - wood density in the oven-dry state, in g/cm$^3$
$\rho_{ds}$ - bulk density of wood substance, in g/cm$^3$, which is 1.5g/cm$^3$

Treatments

The treatments of wood were performed in a device with six separate autoclaves that rotate in an oil bath. Since we took care to maintain the same weight (with a tolerance of ±0.1g) of samples in each of the six autoclaves it also enabled for the volume of fluid in all autoclaves to be the same, that is, to maintain identical conditions in each autoclave during the isochoric process.

Glacial acetic acid (CH$_3$COOH) with 99.5% purity was used for the treatment in the form of an aqueous solution with the addition of 0.03, 0.06 and 0.09g acetic acid/g of dry weight of wood to keep the hydromodule constant and appropriate for the ratio wood:liquid = 1:5. The amount of water present in the air-dried wood samples was taken into account in the calculation. The samples of Narrow-leaved ash wood were treated with solutions prepared for 60min at two temperatures: 100°C and 120°C.

After treatment the autoclaves were removed from the rotating coil of the oil bath and cooled in a water bath to room temperature. The samples were removed from the autoclaves and rinsed with water until reaching a neutral pH and they were air-dried.

Water uptake and swelling of the treated and control samples were tested during 48 hours by immersing the samples in plastic tubs filled with distilled water, in accordance with the requirements of ISO 4859:1997. Plastic mesh partitions were placed in the tubs so that the samples would not be in contact. During the test the water temperature was maintained at 20±1°C. Before immersion the samples had been dried to a constant weight in a ventilation kiln at a temperature of 103±2°C. After cooling in an exicator, the weight and dimensions of samples were measured to an accuracy of 0.01g and 0.01mm.
During the first 10h of immersion the samples were hourly taken out from the water, their surface was wiped with filter paper, and their weight and dimensions were measured to an accuracy of 0.01g and 0.01mm. After the measurements the samples were returned to the water. In the same way the weight and dimensions of the samples were measured after 24 and 48h of being in water.

On the basis of measurements of the weight and dimensions of the samples during 48h of immersion in water, the values of water uptake (%) and volumetric swelling (%) of each of the tested samples, in all measurement intervals were calculated according to the forms:

\[ m = \frac{m_t - m_o}{m_o} \times 100 \% \]  
(4)

- \( m \) - water uptake, in %
- \( m_0 \) - weight of an oven dry sample, in g
- \( m_t \) - weight of a sample at the time of measurement during immersion, in g

\[ V = \frac{V_t - V_o}{V_o} \times 100 \% \]  
(5)

- \( V \) - volumetric swelling, in %
- \( V_0 \) - volume of an oven dry sample, in mm\(^3\)
- \( V_t \) - volume of a sample at the time of measurement during immersion, in mm\(^3\)

Statistical analysis was performed by the t-test at a confidence level of 95%.

RESULTS AND DISCUSSION

The mean value of density of ash wood in the oven dry state is 666.96kg/m\(^3\), with a minimum value of 566.78kg/m\(^3\) and a maximum value of 790.28kg/m\(^3\).

The mean value of volumetric porosity of ash wood in the oven dry state is 55.54%. The minimum value is 47.31% and the maximum value is 62.21%.

On the basis of the mean values of water uptake and volumetric swelling, a diagram of correlation of the water uptake (%) and the time of immersion (h) (Fig. 2) was produced, as well as the diagrams of correlation of volumetric swelling (%) and the time of immersion (h) and the water uptake (%) (Fig. 3, 4 and 5).

Water uptake

Fig. 2 shows that the intensity of water uptake during the first 10h of immersion is higher in all treated samples compared to the group of control samples. The statistical analysis performed by a t-test showed that differences in the amount of water uptake between the group of treated samples and the control group were significantly different during the first 2-6h of immersion in the samples treated at the temperature of 100°C, and in the case of samples treated at the temperature of 120°C for nearly the entire period of immersion. However, after 24h of immersion in the samples treated with an aqueous solution of acetic acid by adding 0.03g and 0.06g CH\(_3\)COOH/g of dry weight of wood at 120°C, the intensity of water uptake of decreased, and they absorbed less water than the control group. In the other treatments applied this phenomenon was observed much earlier, i.e. after 10h of immersion. After 48h of immersion the values of water uptake in all the treated samples were in the 51.66 - 53.84% range and significantly lower than the mean values of the control group (58.31%), except in the samples treated by adding 0.03g and 0.06g of an aqueous solution of acetic acid/g of dry weight of wood at 120°C, whose values amounted to 58.49% and 56.28%. 

The effect of temperature treatment on water uptake of Narrow-leaved ash wood treated for 1h with dilute solutions of acetic acid by adding 0.03g (a), 0.06g (b) 0.09g and (c) of acetic acid/g of wood dry weight

A more intensive water uptake of the treated samples can be explained by an increase in their porosity due to the effect of the treatment. Paredes et al. (2009) also found that micropores appeared and the volume of pores in the cell wall increased, due to the harsh conditions of treatment of strand chips with hot water in the digester for 45 to 90 minutes, because in their research they obtained higher values of water uptake in the samples of OSB boards made from chips that had previously been extracted with hot water. In their research Zhang et al. (2011) explained the increased water uptake of the samples of pine chips extracted with hot water during 30 and 60 minutes at temperatures of 140, 155 and 160°C by the presence of large pores and numerous pores which promote capillary movement of water in the treated wood. In addition, Lantican et al. (1965) and Nicholas and Thomas (1968) considered that in addition to increasing porosity the treatments could lead to increased permeability of the treated samples compared to the control ones.

Since ash wood samples that were treated with the addition of an aqueous solution of acetic acid at a concentration of 0.03 and 0.06g/g of dry weight of wood at a temperature of 120°C showed a significantly higher water uptake compared to the group of samples treated at a temperature of 100°C during 48h of immersion, it can be concluded that the higher treatment temperature (120°C) caused greater changes in the structure of the wood tissue samples. However, Fig. 2 clearly shows that the higher temperature of the treatment with the aqueous solution of acetic acid at a concentration of 0.09g/g of dry weight of wood had no effect on the increase in the amount of water uptake by the samples treated, because the samples treated at 100°C and 120°C showed approximately the same water uptake during the whole study period. On the basis of the differences in the amount of water absorbed by the treated samples tested it can be concluded that the effect of temperature treatment on water uptake of ash wood decreases with increasing concentrations of acetic acid.

Volumetric swelling

Fig. 3, 4 and 5, clearly show that all the treatments applied had an effect on a decrease in the volumetric swelling of ash wood, throughout the period of immersion. After 48h of immersion in water the treatments reduced the average volumetric swelling by 17.5-24.5%. Since the observed difference in the values of swelling of the treated group and the untreated samples was statistically significant, it could be concluded that the hygroscopic nature of the Narrow-leaved ash wood changed due to changes in chemical characteristics that occurred as the effect of the treatment. It is possible that the treatments affected the removal of hemicelluloses from the wood tissue as the most hydrophilous chemical constituent of the cell wall with the largest number of free-OH groups that are able to build hydrogen bonds with water molecules absorbed and cause swelling of the wood. The fact that during the observed immersion period all the samples treated showed less volumetric swelling, in spite of absorbing more water than the control samples suggested that in addition to chemical changes treatments also caused structural changes in the wood tissue, and the appearance of micropores in the cell wall. Other researchers have obtained similar results on the impact of pre-treatment on the swelling of wood. Paredes et al. (2008) observed that the OSB panels made of strand chips of red maple wood, which had previously been extracted with hot water, showed significantly less thickness swelling compared to the untreated OSB samples, although they absorbed more water than the untreated ones during the first 24h of immersion.

The samples that were treated with an aqueous solution with the addition of acetic acid at a concentration of 0.03g/g of dry weight of wood at temperatures of 100 and 120°C showed the volumetric swelling of about 14% after 48h of immersion. Almost the same value of volumetric swelling after 48h of immersion, was shown by the samples treated with an aqueous solution of acetic acid at the concentrations of 0.06 and 0.09g/g of dry weight of wood at a temperature of 120°C. With the same treatments at a temperature of 100°C slightly lower swelling value of about 12.8% was obtained. On the basis of these
results it can be concluded that the treatment at a temperature of 120°C with an aqueous solution with the addition of 0.03g of acetic acid/g of dry weight of wood is more efficient in achieving the dimensional stability of ash wood, because the increase in the concentration of acetic acid solution at this temperature does not lead to a decrease in the degree of volumetric swelling of the wood. Lower temperatures of the treatment are more favourable, when using solutions with higher concentrations of acetic acid. Increasing of the acid with the addition of more than 6g/g of dry wood is not justified, because it increases the cost of treatment, and does not lead to a further improvement of dimensional stability of ash wood.

**Fig. 3**
Volumetric swelling time dependence (a) and its relation with water uptake (b) for the control group and for the samples treated at the temperatures of 100°C and 120°C with the addition of the aqueous solution of acetic acid at a concentration of 0.03g/g of wood dry weight.

**Fig. 4**
Volumetric swelling time dependence (a) and its relation with water uptake (b) for the control group and for the samples treated at the temperatures of 100°C and 120°C with the addition of the aqueous solution of acetic acid at a concentration of 0.06g/g of wood dry weight.

**Fig. 5**
Volumetric swelling time dependence (a) and its relation with water uptake (b) for the control group and for the samples treated at the temperatures of 100°C and 120°C with the addition of the aqueous solution of acetic acid at a concentration of 0.09g/g of wood dry weight.
In Fig. 3a, 4a and 5a it can also be noted that all samples swell extensively during the first 10h of examination. In this period, the control samples swell up most and absorb a minimum amount of water (Fig. 2), while the samples treated at 120°C absorb the largest quantity of water and swell less than the control ones, but more than the ones treated at 100°C. Starting from the tenth hour of immersion onwards, the intensity of swelling of all groups of samples is reduced. A further decrease swelling is more pronounced in the treated samples, because their porous structure facilitates the penetration of water, which leads to faster achievement of saturation of the cell walls in comparison with the control samples.

After 24h of immersion the samples treated with solutions of acetic acid at 100°C cease to swell even though the water uptake process continues. In these samples maximum swelling is achieved if the water uptake is about 45% (Fig. 3b, 4b and 5b). However, the samples treated at a temperature of 120°C reach saturation at higher values of water uptake (about 48%). The exceptions were samples treated with a solution of acetic acid at a concentration of 0.09g/g of dry weight of wood at 120°C that reach saturation at the same amount of water uptake (45%) and the samples treated at 100°C. A higher water uptake and swelling after 48h of testing of the samples treated at 120°C compared to samples treated at 100°C suggests that the higher temperature of the treatment produced not only the increase in the volume of voids in the wood tissue, but it probably led to major changes in the chemical structure of the treated samples. Also, severe treatment conditions probably reduce the degree of cellulose crystallinity, thus creating new -OH groups responsible for the wood swelling, especially at the higher concentrations of the acid solution.

Hosseinaei et al. (2011) also indicated this possibility since they found increased concentrations of sugars and other products of degradation with increasing time and temperature of treatment in the extraction of the hydrolyzate resulting from the extraction of pine strand chips with hot water at 140, 155 and 170°C for 30 and 60 minutes. They found the presence of mannose, galactose, xylose, acetic acid and glucose in the composition of the hydrolyzate suggesting the hemicellulose depolymerization as the main reaction that takes place in this system. However, an increased proportion of glucose and cellulbiose in the hydrolyzate resulting from the extraction for 60min at a temperature of 170°C indicates the degradation of cellulose.

Due to the facilitated movement through the damaged parts of wood tissue caused by acids and high temperature, the water absorbed during the first 24h of immersion was mainly in the form of free water that filled the voids and cracks and penetrated the cell walls more slowly.

CONCLUSIONS
The results obtained in this study by examining the volumetric swelling of the wood of Narrow-leaved ash treated with aqueous solutions of acetic acid prepared by adding 0.03, 0.06 and 0.09g of acid/ g of dry wood and the ratio wood:water = 1:5 at the temperatures of 100 and 120°C for a period of 1h indicate that:

- Using slightly-acidic treatments with solutions of acetic acid could improve the dimensional stability of ash wood, as all treatments led to a reduction in the volumetric swelling of the samples throughout the period of immersion. After 48h of immersion, the treatments reduced the degree of volumetric swelling of the tested wood by an average of 17.2-24.6%.
- The degree of improvement of dimensional stability depends on the treatment conditions. The treatment with an aqueous solution of acetic acid with the addition of 0.06g/g of dry wood at a temperature of 100°C proved to be the best, because it decreased the volumetric swelling of the ash samples treated by approximately 24.6% compared to the untreated wood, after 48h of the immersion in water.
- The results obtained regarding the volumetric swelling of ash wood indicate that greater dimensional stability is achieved at a lower temperature of the treatment when the solutions with higher concentrations of acetic acid are used.
- The different behavior in terms of water uptake during 48h of immersion in the groups of samples treated with the addition of an aqueous solution of 0.06g and 0.03g of acetic acid, and groups of samples treated with the addition 0.09g of acetic acid / g of dry wood weight at the change of the treatment temperature.
- Results of water uptake on treated samples suggest that the increases in the concentration of the acetic acid solution decreases the the effect of the temperature treatment on the water uptake treated samples.
- Taking into account the results presented in this paper, it can be concluded that the extraction of hemicelluloses could be considered as a potential method of reducing the hygroscopicity of wood.

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