Evaluation of the Process Thermal Treatment of Maple Wood Saturated Water Steam in Terms of Change of pH and Color of Wood

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Changes in maple wood's pH and color (*Acer pseudoplatanus*) were evaluated before and after thermal treatment process with saturated water steam. Maple wood was thermally treated at temperatures: t_I = 105 ± 2.5 °C, t_{II} = 125 ± 2.5 °C, and t_{III} = 135 ± 2.5 °C for $\tau \leq 12$ hours. Direct pH measurement of maple wood with a moisture content above the fiber saturation point (FSP) was performed using a pH-meter SI 600 with a Lance FET + H puncture probe. The polynomial dependence of pH and total color difference ΔE^* on temperature t time τ was calculated by statistical processing of measured results. The correlation between the total color difference ΔE^* of maple wood in the process of thermal color modification and the pH value is expressed y the equation: $\Delta E^* = 4.5516 \cdot (pH)^2 - 48.405 \cdot (pH) + 134.35$. This dependence is a suitable tool for assessing the achieved color change based on the change of wood pH in the technological process.

Keywords: Wood; Maple; Acidity; Colour difference; Thermal treatment; Saturated water steam

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INTRODUCTION

The lumens of wet wood cells contain a dilute aqueous solution of sugars, organic acids and salts of calcium, magnesium, potassium, sodium inorganic acids, which are transported to the living tree by the root system; as a result this solution has some acidity (Čudinov and Stepanov 1968; Blažej *et al.* 1975; Zevenhoven 2001; Pňakovič and Dzurenda 2015). The wood acidity of deciduous, scattered-porous species with moisture above the saturation point (BNV) is in the pH range of 5.5 to 4.8 (Sandermann and Rothkamm 1956; Irle 2012; Solár 2004; Geffert *et al*. 2019). The pH is a measure of the concentration of H+ ions in solution and is used to determine the acid, neutral, or basic behavior of a chemical reaction. The pH values are very important physiological parameters for plants, humans, and animals. In production processes, the change in acidity is used to control technological processes.

Wet wood located in the environment of hot water, saturated water steam, or saturated humid air is heated, and its physical, mechanical, and chemical properties change. Changes in physico-mechanical properties are used in the technology of steam bending and boiling during veneers and plywood, bent furniture, or pressed wood manufacturing processes (Kollmann and Gote 1968; Sergovskij and Rasev 1987; Melcer *et al*. 1989).

The effect of thermal on wet wood is also initiated by chemical changes in wood. The first chemical reactions include partial hydrolysis of hemicelluloses and extraction of water-soluble substances (Fengel and Wegener 1989; Bučko 1995; Laurová *et al.* 2004;

Solár 2004; Sundqvist *et al*. 2006; Samešová *et al.* 2018). Depending on the temperature and duration of action of the hydrolysis products, which are acetic acid and formic acid, degradation of polysaccharides occurs. During the thermal treatment of wood, dehydration of pentoses to 2-furaldehyde as well as oxidation of carbohydrates also occur. New chromophoric groups begin to form in lignin, causing the wood to change color (Fengel and Wegener 1989; Bučko 1995; Hon and Shiraishi 2001; Solár 2004; Sundqvist *et al.* 2006; Geffert *et al.* 2019).

The aim of this paper is to determine changes in acidity of maple wood during the technological process of wood color modification by saturated water steam in the temperature range t = 105 to 135 °C at time τ = 3 to 12 h. This paper aims to determine the dependence of total color change of maple wood (ΔE^*) in CIE L^* a^* b^* at the pH value of maple wood obtained by the thermal treatment process. The dependence of the total color difference ΔE^* on the pH of maple wood is a suitable tool for evaluating the achieved color shade before further technological processing.

EXPERIMENTAL

Material

Maple wood (*Acer pseudoplatanus*) in the form of blanks with dimensions: thickness of 40 mm, width of 90 mm, and length of 750 mm in 260 pieces was divided into 13 groups of 20 pieces in one group. The initial moisture content of wet maple wood was in the range of values: W = 54.7 to 58.2 %. Group 1 blanks were not thermally treated. The other blanks were divided into 12 groups of 20 pieces each and thermally treated with saturated water steam at t = 105 °C, t = 125 °C and t = 135 °C for 3, 6, 9 and 12 h. Thermal treatment of maple wood with saturated water steam was carried out in a pressure autoclave APDZ 240 (Himmasch AD, Haskovo, Bulgaria) installed at Sundermann s.r.o. Banská Štiavnica (Slovakia).

Methods

The conditions of thermal treatment of maple wood with saturated water steam indicating the sampling time intervals during the thermal treatment v are shown in Fig. 1.

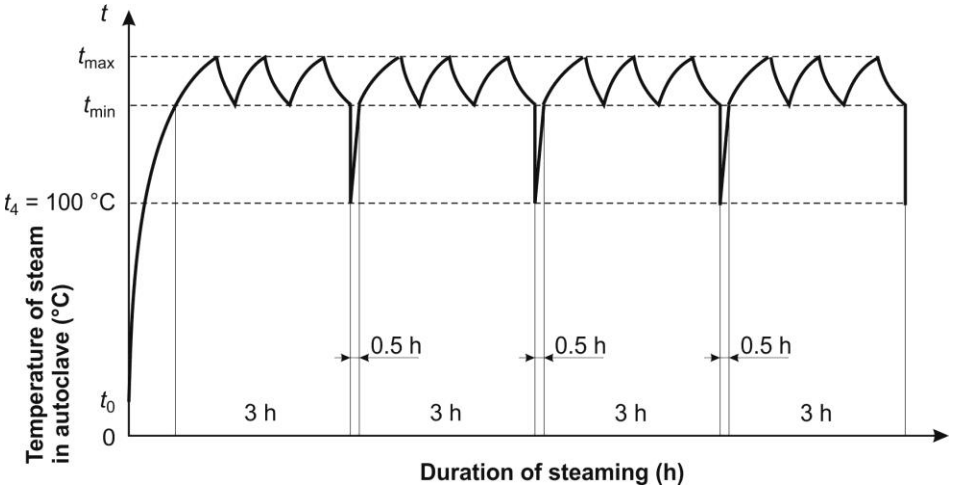

Fig. 1. Mode of colour modification of maple wood with saturated water steam

The thermal process of maple wood color modification was performed in an APDZ 240 autoclave (Himmasch AD, Haskovo, Bulgaria) at a higher saturated water steam pressure than atmospheric pressure. Saturated water steam temperatures in individual color adjustment modes are given in Table 1. The temperatures t_{max} and t_{min} are the temperature intervals at which saturated water steam is fed into the autoclave to carry out the technological process. Temperature t_4 is the temperature of the saturated water steam in the autoclave after the water steam pressure in the autoclave has been reduced to atmospheric pressure to allow safe opening of the pressure equipment and sampling after the time thermal treatment 3, 6, 9, and 12 h.

Table 1. Modes of Color Modification of Maple Wood with Saturated Water Steam

Temp. of Saturated Water Steam	t_{min}	t_{max}	t_4	Length of Time Wood is Exposed to Color Modification			
Mode I	102.5	107.5	100	τ_1 = 3 h	τ_2 = 6 (+0.5[a]) h	τ_3 = 9 (+1.0[a]) h	τ_4 = 12 (+1.5[a]) h
Mode II	122.5	127.5	100				
Mode III	132.5	137.5	100				
* Note: [a] time for taking out the specimens							

The moisture content and pH of the wet thermally treated wood were determined by taking samples from the autoclave and cooling the wood to ambient temperature. The moisture content of wet maple wood above the fiber saturation point (BNV) was measured using an FMD6 moisture meter (Brookhuis Micro-Electronic, Netherlands).

The pH of wet maple wood was measured using a pH-meter SI 600 with a Lance FET + H puncture probe (Sentron, Roden, Netherlands). A hole with a diameter of 12 mm was created using an accu drill (DeWalt DCD791NT, Germany). Drilling sawdust was pressed into the hole and the LanceFET + H sensor head (Geffert *et al.* 2019) was inserted into the wet sawdust. After about 60 seconds of stabilization, the pH value was read on a SI 600 pH-meter (Sentron, Roden, Netherlands).

Color-modified maple wood with saturated water steam treatment technology is used as a material for the production of furniture, flooring or interior tiles in a dry state. For this reason, samples of uncooked and thermally treated maple wood were dried by a gentle drying regime to a final moisture content of W = 12 ± 0.5%. Subsequently, the surface of the dry blanks was machined on a FS 200 (BENET Trading, Kvasiny, Slovakia) milling machine.

The color of thermally treated maple wood in the CIE L^* a^* b^* color space was determined using the Color Reader CR-10 (Konica Minolta, Japan). A D65 light source with an illuminated area of 8 mm was used. Color was evaluated based on changes in CIE L^* a^* b^* color space at the coordinates of L^* brightness and C^* (chroma) color saturation, and ΔE^* overall color difference.

Chroma C^* is the integration of the red a^* and yellow b^* coordinate values projected into the chromatic plane of the cylindrical color space. Chroma C^* was calculated according to Eq. 1,

$$C^* = \sqrt[2]{a^{*2} + b^{*2}} \quad (1)$$

where, a^* is the value of the chromatic coordinate of red color, and b^* is the value of the chromatic coordinate of yellow color.

The total color difference value is described by the equation,

$$\Delta E^* = \sqrt{\left(L_2^* - L_1^*\right)^2 + \left(a_2^* - a_1^*\right)^2 + \left(b_2^* - b_1^*\right)^2} \quad (2)$$

where, L^*_1, a^*_1, and b^*_1 are values on the color space coordinates of the surface of dried milled thermally untreated maple wood. Likewise, L^*_2, a^*_2, and b^*_2 are values on the color space coordinates of the surface of dried milled thermally treated maple wood.

Using the STATISTICA 12 program (V12.0 SP2, USA), graphical and mathematical dependences of pH = f (t, τ) and $\Delta E^* = f$ (t, τ) were determined from the measured data in the temperature range: t = 105 to 135 °C and time τ = 3 to 12 h. The programmatic processing of the measured results partially eliminated the effect of measurement errors due to wood heterogeneity and a direct pH measurement method (Geffert *et al.* 2019).

RESULTS AND DISCUSSION

Moisture content W and pH values of maple wood before thermal treatment and during thermal treatment of maple wood after cooling to ambient temperature were measured at regular intervals of 3 h, at times 3, 6, 9, and 12 h (Table 2).

Table 2. Average Values of Moisture Content and pH of Maple Wood in the Process of Wood Thermal Treatment

Temperature of Saturated Water Steam	Time of Thermal Modification of Maple Wood									
	0 h		3 h		6 h		9 h		12 h	
	W (%)	pH	W (%)	pH	W (%)	pH	W (%)	pH	W (%)	pH
t_I = 105 ± 2.5 °C	58.2	5.1	47.6	4.8	46.3	4.7	46.5	4.6	44.8	4.2
t_{II} = 125 ± 2.5 °C	54.7	4.9	44.6	4.1	45.3	3.9	44.9	3.5	44.7	3.3
t_{III} = 135 ± 2.5 °C	56.9	5.0	46.5	3.9	45.8	3.6	46.0	3.3	44.3	3.3

The changes in the pH of maple wood during 3 to 12 h of saturated steam treatment with temperatures t_I = 105 ± 2.5 °C, t_{II} = 125 ± 2.5 °C, and t_{III} = 135 ± 2.5 °C are shown in Fig. 2.

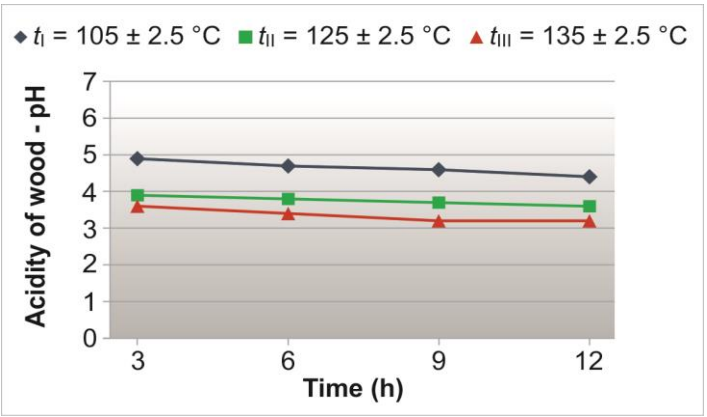

Fig. 2. The change in the acidity of maple wood during the thermal modification ode of colour modification

Due to the chemical reactions taking place in the maple wood in the thermal treatment process, the pH value of the wet wood decreased and the color of the maple wood changed. The drop in the pH of maple wood shows that the temperature is more pronounced for the pH change than the time. From the point of view of effective wood color modification, a time interval of 3 to 12 h is important when significant color changes occur.

The moisture values of the thermally treated maple wood after cooling to ambient temperature were lower than the moisture of the wood before the thermal treatment. Reduction of maple wood moisture content by ΔW = 8.9 to 12.2 % is caused by evaporation of water from wood to saturated water steam in autoclave during cooling to temperature t = 100 °C before sampling from autoclave and vaporization of water from wood to atmosphere during cooling of wood to ambient air temperature. The source of heat for evaporation and vaporization of water from wood is the heat accumulated during the heating of the wood to the required technological temperature (Dzurenda and Deliiski 2000).

Based on the measured pH values of maple wood during thermal treatment of wood at temperatures of saturated water steam in the range of t = 105 to 135 °C and time τ = 3 to 12 h, the dependence of the change of pH on temperature and time was processed in a 3D diagram (Fig. 3.).

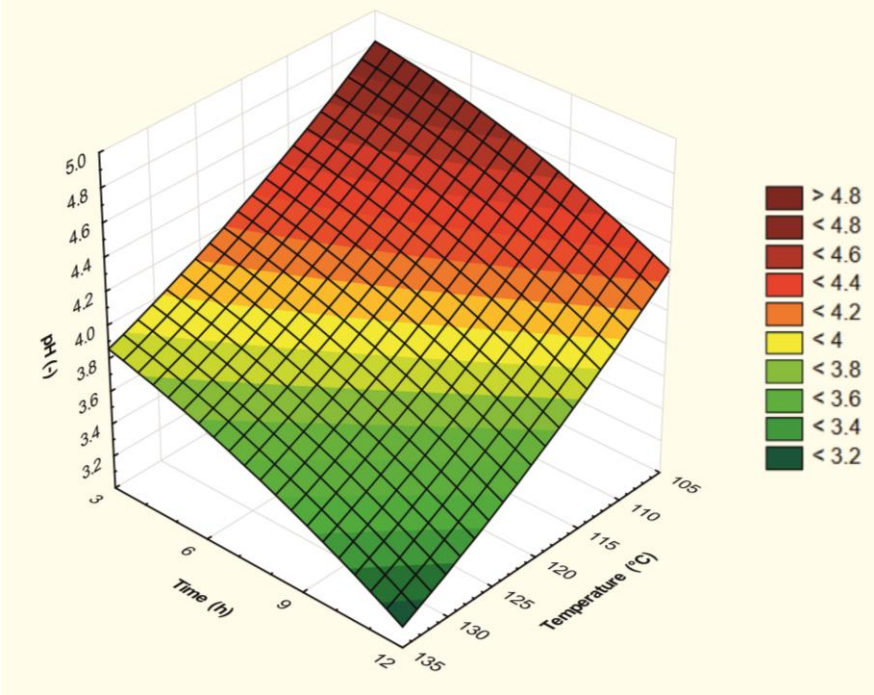

Fig. 3. Correlation of the *pH* value of wet maple wood and the temperature of saturated water steam *t* and the time *τ*

The dependence of the pH of wet maple wood on the temperature of the saturated water steam t and the time τ is described by the formula,

$$\text{pH} = 12.19 - 0.1003 \cdot t + 0.0517 \cdot \tau + 0.0003 \cdot t^2 - 0.0006 \cdot t \cdot \tau + 0.0037 \cdot \tau^2 \quad (3)$$

where t is the temperature of the saturated water steam °C, and τ is the time during which the wood is exposed to colour modification in hours.

The purpose of the maple wood thermal treatment process is to modify the original white to light white-yellow color to pale-brown to dark-brown color shades. The degree of coloring of maple wood by steam treatment with water steam depends on the temperature and duration of the technological process, as shown in Fig. 4. Information on changes in color of maple wood during thermal treatment in the form of decreasing values on the L^* coordinate, increase in color saturation (chroma) C^* and total color difference ΔE^*, is given in Table 3.

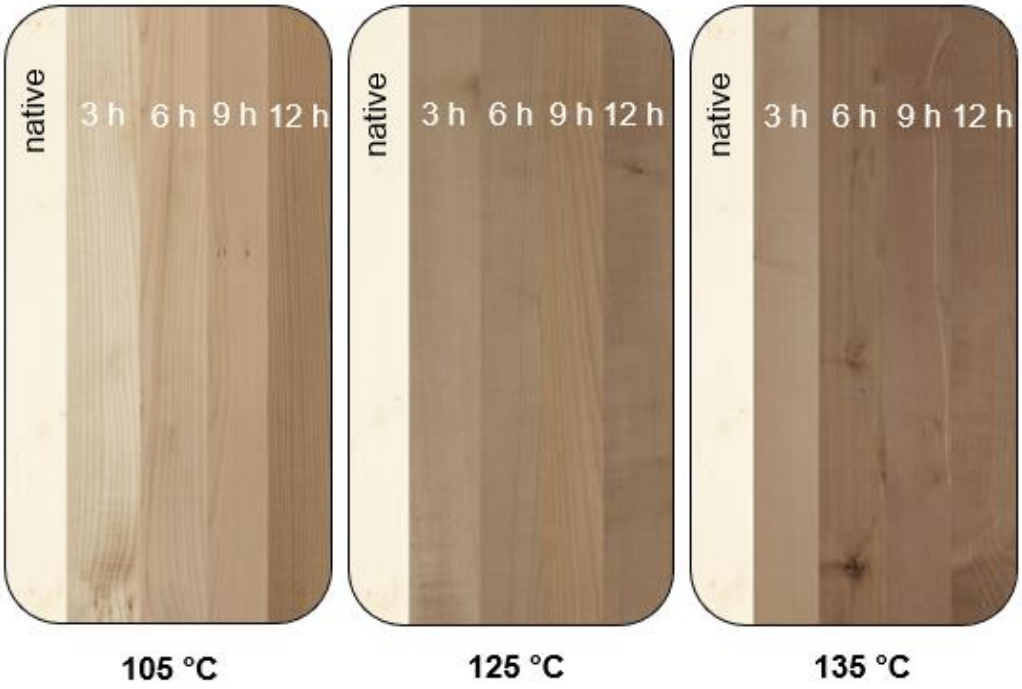

Fig. 4. Changes in the colour of maple wood during thermal modification

Table 3. Measured Values of Lightness (L^*), Chroma (C^*) and Total Color Difference (ΔE^*) of Maple Wood in Thermal Treatment of Wood Color Modification with Saturated Water Steam

Time (h)	Temperature of Saturated Water Steam								
	t_I = 105 ± 2.5 °C			t_{II} = 125 ± 2.5 °C			t_{III} = 135 ± 2.5 °C		
	Lightness L^*, Chroma C^* and Total Color Difference ΔE^*								
	L^*	C^*	ΔE^*	L^*	C^*	ΔE^*	L^*	C^*	ΔE^*
0	86	17.4	---	86	17.4	---	86	17.4	---
3	81	19.6	5.5	75	20.0	11.3	69	20.2	17.2
6	79	19.8	7.4	73	20.1	13.3	65	20.5	21.2
9	77	21.1	9.7	70	20.6	16.3	62	20.8	24.2
12	76	21.8	10.9	69	20.9	17.4	59	21.3	27.3

The decrease in values of the coordinate of lightness L^* of thermal treated wood is in line with reports of wood darkening in technological processes such as wood steaming (Dianisková *et al.* 2008; Tolvaj *et al.* 2009, 2010; Hadjiski and Deliiski 2016; Dzurenda 2013, 2018b,c; Banadics and Tolvaj 2019), or high temperature wood drying in a superheated steam environment (Klement and Marko 2009; Baranski *et al.* 2017; Klement *at al.* 2019).

The increase in color (chroma) of thermally treated C^* is significantly smaller compared to the decrease in lightness of maple wood. The greatest increase in chroma C^* is observed in the first 3 h of thermal wood treatment. Further enhancement of color (chroma) C^* and decrease in luminance L^* are reflected in the darkening of the brown shade of maple wood declared by increasing the numerical values of the total color difference ΔE^*.

From the mathematical analyzes of the magnitude of changes in the color differences ΔE^* and the pH value of maple wood in the thermal treatment process, the dependence of pH = f (ΔE^*) was derived in Fig. 5. This dependence makes it possible to identify the degree of coloring of maple wood through the pH of thermally treated maple wood and can be described by the relationship:

$$\Delta E^* = 4.5516 \cdot (pH)^2 - 48.405 \cdot (pH) + 134.35 \quad (4)$$

Equation (4) describes with sufficient accuracy the tested thermal treatment range t = 105 to 135 °C and time τ = 3 to 12 h.

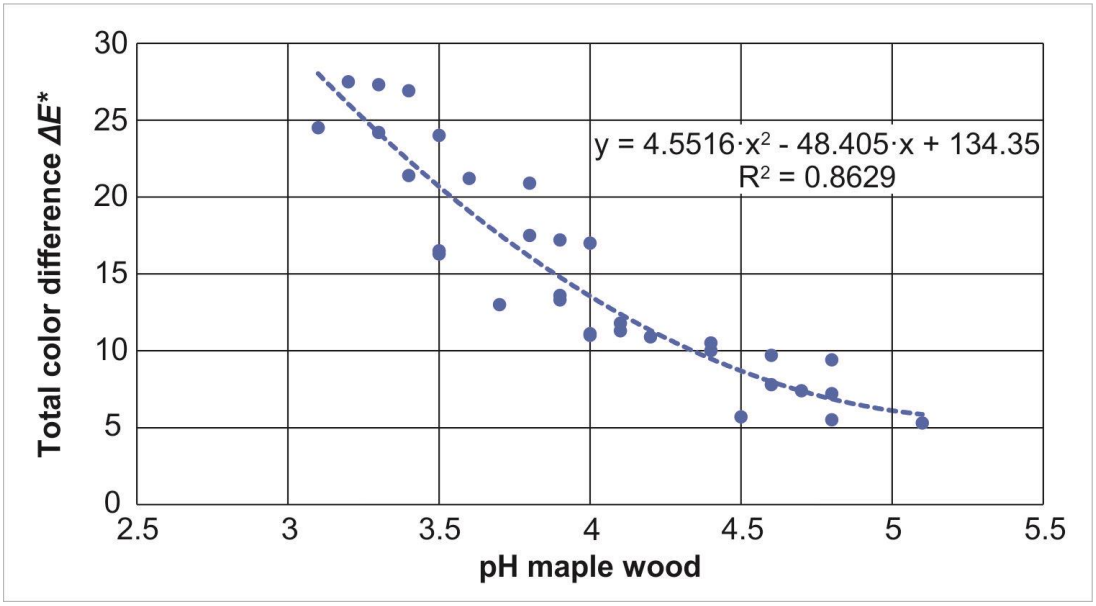

Fig. 5. Dependence *pH* of maple wood on total color difference ΔE^*

The determined dependence of color change expressed by the total color difference ΔE^* on the pH of maple wood is a suitable tool for evaluation of the achieved color shade before further technological processing.

CONCLUSIONS

1. Results were obtained for the change of pH of the wood of *Acer pseudoplatanus* in the process of thermal treatment of wood with saturated water steam at temperatures: t_I = 105 ± 2.5 °C, t_{II} = 125 ± 2.5 °C, and t_{III} = 135 ± 2.5 °C for τ = 12 h.
2. During the process of thermal treatment, the pH changed from 5.1 to 3.3.
3. Correlation between pH of wet maple wood during the thermal treatment process saturated water steam and temperature t and time τ of exposure to color modification were described using the equation:

$$pH = 12.19 - 0.1003 \cdot t + 0.0517 \cdot \tau + 0.0003 \cdot t^2 - 0.0006 \cdot t \cdot \tau + 0.0037 \cdot \tau^2.$$

4. The dependence of the total color change of ΔE^* on maple wood on the pH of maple wood in the interval of values pH = 3 to 5.5 is described by the equation:

$$\Delta E^* = 4.5516 \cdot (pH)^2 - 48.405 \cdot (pH) + 134.35.$$

ACKNOWLEDGMENTS

This experimental research was prepared within the grant project (APVV-17-0456) "Termická modifikácia dreva sýtou vodnou parou za účelom cielenej a stabilnej zmeny farby drevnej hmoty" as the result of the authors contributions as well as the considerable assistance from the APVV agency.

REFERENCES CITED

Banadics, E. A., and Tolvaj, L. (2019). "Color modification of poplar wood by steaming for brown color," *European Journal of Wood and Wood Products* 77(4), 717-719. DOI: 10.1007/s00107-019-01397-9

Blažej, A., Šutý, L., Košík, M., Krkoška, P., and Golis, E. (1975). *Chémia Dreva* [*Chemistry of Wood*], ALFA, Bratislava, Slovakia.

Barański, J., Klement, I., Vilkovská, T., and Konopka, A. (2017). "High temperature drying process of beech wood (*Fagus sylvatica* L.) with different zones of sapwood and red false heartwood," *BioResources* 12(1), 1861-1870. DOI: 10.15376/biores.12.1.1761-1870.

Bučko, J. (1995). *Hydrolýzne procesy* [*Hydrolysis Processes*], Technical University in Zvolen, Zvolen, Slovakia.

Čudinov, B. S., and Stepanov, V. L. (1968). "Phasenzusammensetzung der Wassers in gefrorenem Holz," *Holztechnologie* 9(1), 14-18.

Dianisková, M., Babiak, M., and Tolvaj, L. (2008). "Color homogenisation of cherrywood (*Cerasus avium* L.) and black locust (*Robinia pseudoaccacia* L.) during steaming," *Wood Research* 53(4), 45-58.

Dzurenda, L., and Deliiski, N. (2000). "Analysis of moisture content changes in beech wood in the steaming process with saturated water steam," *Wood Research* 45(4), 1-8.

Dzurenda, L. (2013). "Modification of wood colour of *Fagus sylvatica* L. to a brown-pink shade caused by thermal treatment," *Wood Research* 58(3), 475-482.

Dzurenda, L. (2018b). "Hues of *Acer platanoides* L. resulting from processes of thermal treatment with saturated steam," *Drewno* 61(202), 165-176. DOI: 10.12841/wood.1644-3985.241.11

Dzurenda, L. (2018c). "Colour modification of *Robinia pseudoacacia* L. during the processes of heat treatment with saturated water steam," *Acta Facultatis Xylologiae* 60(1), 61-70. DOI: 10.17423/afx.2018.60.1.07

Fengel, D., and Wegener, G. (1989). *Wood- Chemistry, Ultrastructure, Reactions*, Walter de Gruyte, Berlin, Germany.

Geffert, A., Geffertová, J., and Dudiak, M. (2019). "Direct method of measuring the pH value of wood," *Forests* 10(10), 852. DOI: 10.3390/f10100852

Hadjiski, M., and Deliiski, N. (2016). "Advanced control of the wood thermal treatment processing," *Cybernetics and Information Technologies*, Bulgarian Academy of Sciences 16(2), 176-197.

Hon, N. S. D., and Shiraishi, N. (2001). *Wood and Cellulosic Chemistry*, CRC Press, New York, NY, pp. 928.

Irle, M. (2012). "pH and why you need to know it," (http://www.wbpionline.com/features/ph-and-why-you-need-to-know-it/), Accessed 20 August 2012.

Klement, I., and Marko, P. (2009). "Colour changes of beech wood (*Fagus sylvatica* L.) during high temperature drying process," *Wood Research* 54 (3), 45-54.

Klement, I., Vilkovska, T., Baranski, J., and Konopka, A. (2019). "The impact of drying and steaming processes on surface color changes of tension and normal beech wood," *Drying Technology* 37(12), 1490-1497. DOI: 10.1080/07373937.2018.1509219

Kollmann, F., and Gote, W. A. (1968). *Principles of Wood Sciences and Technology, Vol. 1. Solid Wood*, Springer Verlag, Berlin, Germany.

Laurová, M., Mamonová, M., and Kučerová, V. (2004). *Proces parciálnej hydrolýzy bukového dreva (Fagus sylvatica* L.*) parením a varením* [*Process of Partial Hydrolysis of Beech Wood (Fagus sylvatica* L.*) by Steaming and Cooking*], Technical University in Zvolen, Zvolen, Slovakia.

Melcer, I., Melcerová, A., Solár, R., and Kačík, F. (1989). *Chémia hydrotermálneho spracovania dreva listnatých drevín* [*Chemistry of Hydrothermal Treatment of Deciduous Trees*], College of Forestry and Wood Technology in Zvolen, Zvolen, Slovakia.

Pňakovič, Ľ., and Dzurenda, L. (2015). "Combustion characteristics of fallen fall leaves from ornamental trees in city and forest parks," *BioResources* 10(3), 5563-5572. DOI: 10.15376/biores.10.3.5563-5572.

Samešová, D., Dzurenda, L., and Jurkovič, P. (2018). "Kontaminácia kondenzátu produktmi hydrolýzy a extrakcie z tepelného spracovania bukového a javorového dreva pri modifikácii farby dreva [Contamination of water by hydrolysis products and extraction from the thermal treatment of beech and maple timber during modification the color of wood]," *Chip and Chipless Woodworking Processes* 11(1), 277-282.

Sanderman, W., and Rothkamm, M. (1959). "The determination of pH values of woods and their practical importance," *Holz Roh- Werkstoff* 17, 433-441.

Sergovskij, P. S., and Rasev, A. I. (1987). *Gidrozermicheskaya obrobotka i konservironaniye drevesiny* [*Hydrothermal Treatment and Conservation of Wood*], Lesnaja promyslennost, Moscow, Russia.

Solár, R. (2004). *Chémia dreva* [*Wood Chemistry*], Technical University in Zvolen, Zvolen, Slovakia.

Sundqvist, B., Karlsson, O., and Westremark, U. (2006). "Determination of formic-acid and acid concentrations formed during hydrothermal treatment of birch wood and its relation to color, strength and hardness," *Wood Science Technology* 40(7), 549-561. DOI: 10.1007/s00226-006-0071-z.

Tolvaj, L., Nemeth, R., Varga, D., and Molnar, S. (2009). "Colour homogenisation of beech wood by steam treatment". *Drewno.* 52(181), 5-17.

Tolvaj, L., Molnar, S., Nemeth, R., and Varga, D. (2010). "Color modification of black locust depending on the steaming parameters," *Wood Research* 55(2), 81-88.

Zevenhoven, M. (2001). *Ash-forming Matter in Biomass Fuels*, Åbo Akademi University, Turku, Finland.

Article submitted: December 4, 2019; Peer review completed: January 24, 2020; Revised version received and accepted: February 17, 2020; Published: February 20, 2020.
DOI: 10.15376/biores.15.2. 2550-2559