

Article

Changes in the Physical and Chemical Properties of Alder Wood in the Process of Thermal Treatment with Saturated Water Steam

Michal Dudiak * and Ladislav Dzurenda

Faculty of Wood Sciences and Technology, Technical University in Zvolen, T.G. Masaryka 24, 96001 Zvolen, Slovakia; dzurenda@tuzvo.sk

* Correspondence: xdudiak@is.tuzvo.sk; Tel.: +421-45-520-6367

Abstract: The paper presents changes in color and selected physico-chemical properties of alder (*Alnus glutinosa*) wood during the process of thermal treatment of the wood with a saturated steam-air mixture or saturated water steam in the temperature range $t = 95\text{--}125\text{ }^{\circ}\text{C}$ for $\tau = 3$ to 12 h. During the process of thermal treatment of alder wood, the original light white-gray color changes depending on the temperature and time of modification to soft reddish-brown to dark brown color shades. Color changes of alder wood expressed in the form of the total color difference are in the range of values $\Delta E^* = 2.7\text{--}31.7$. Measurements of the density of thermally treated alder wood in the dry state indicate that due to the thermal treatment of alder wood, the density decreases by $\rho \leq 4.6\%$ compared to the average density of native alder wood. Due to the hydrolysis of hemicelluloses, in the process of thermal treatment of wet alder wood, its acidity changes in the range of values: $\text{pH} = 4.9$ to 3.1. Analyses of ATR-FTIR spectroscopy indicate changes in alder wood extractants and hemicellulose degradation. A decrease in unconjugated and an increase in conjugated carbonyls was observed at all temperatures of thermal modification of alder wood. Measurements indicate changes in the lignin of alder wood and the fact that as the temperature increases, the formation of new carbonyls increases, which is reflected in the change of the chromophoric system.

Keywords: alder wood; acidity; color difference; density; ATR-FTIR spectroscopy; thermal treatment; saturated water steam



Citation: Dudiak, M.; Dzurenda, L. Changes in the Physical and Chemical Properties of Alder Wood in the Process of Thermal Treatment with Saturated Water Steam. *Coatings* **2021**, *11*, 898. <https://doi.org/10.3390/coatings11080898>

Academic Editor: Marko Petric

Received: 24 June 2021

Accepted: 22 July 2021

Published: 27 July 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Wood placed in an hot water, saturated water steam or saturated humid air environment heats up and its physical, mechanical and chemical properties change. Targeted physical-mechanical changes are achieved by thermal treatment of wood used in the production of veneers, plywood, bentwood furniture, or pressed wood [1–3].

In addition to targeted physico-mechanical changes, thermal treatment of wood with saturated steam also creates conditions for chemical reactions, such as water-soluble extraction processes, hydrolysis of alder wood hemicelluloses, depolymerization of polysaccharides and chemical changes in lignin causing modification of the beech wood chromophore system [4–11]. While in the past, color changes of darkening in the technological process of wood steaming were used to remove unwanted color differences between light white and dark cores, or to remove unwanted color spots caused by steaming, browning or molding, in recent times research has focused on targeted color changes wood of individual domestic woody plants in more or less pronounced color shades, with the purpose of imitating exotic woods [12–18].

The aim of the work is to determine the change of color, density and acidity of alder wood in the technological process of wood color modification with saturated water steam in the temperature range $t = 95\text{--}125\text{ }^{\circ}\text{C}$ during $\tau = 3\text{--}12$ h as well as the dependence of the total color difference of alder wood (ΔE^*) in the color space $CIE\ L^*a^*b^*$ on the temperature

and the duration of the thermal treatment. Changes in absorption spectra observed using FTIR analysis help explain the color changes of alder wood occurring during the thermal treatment process.

2. Material and Methods

2.1. Material

A number (320) of alder (*Alnus glutinosa* L.) wood pieces in the form of blanks with dimensions: thickness (h) = 38 mm, width (w) = 90 mm and length (d) = 750 mm was divided into four groups of 80 pieces in each group, which represents 20 pieces of blanks for a given thermal treatment time. The initial moisture content of the wet alder wood was in the range of values: $w = 58.7\% \pm 5.1\%$. Group 1 blanks were not thermally treated. The other blanks were divided into three groups and thermally treated with a saturated steam-air mixture with a temperature of $t = 95 \pm 2.5$ °C and thermally treated with saturated steam at $t = 115$ °C, $t = 125$ °C, for $\tau = 3, 6, 9$ and 12 h. Thermal treatment of alder wood with saturated steam was performed in a pressure autoclave APDZ 240 (Himmasch AD, Haskovo, Bulgaria) installed at Sundermann Ltd., Banská Štiavnica (Slovakia).

2.2. Thermal Treatment of Alder Wood

The conditions in the pressure autoclave during the thermal treatment of alder wood with saturated steam with marked sampling intervals during the thermal treatment in are shown in the diagram in Figure 1.

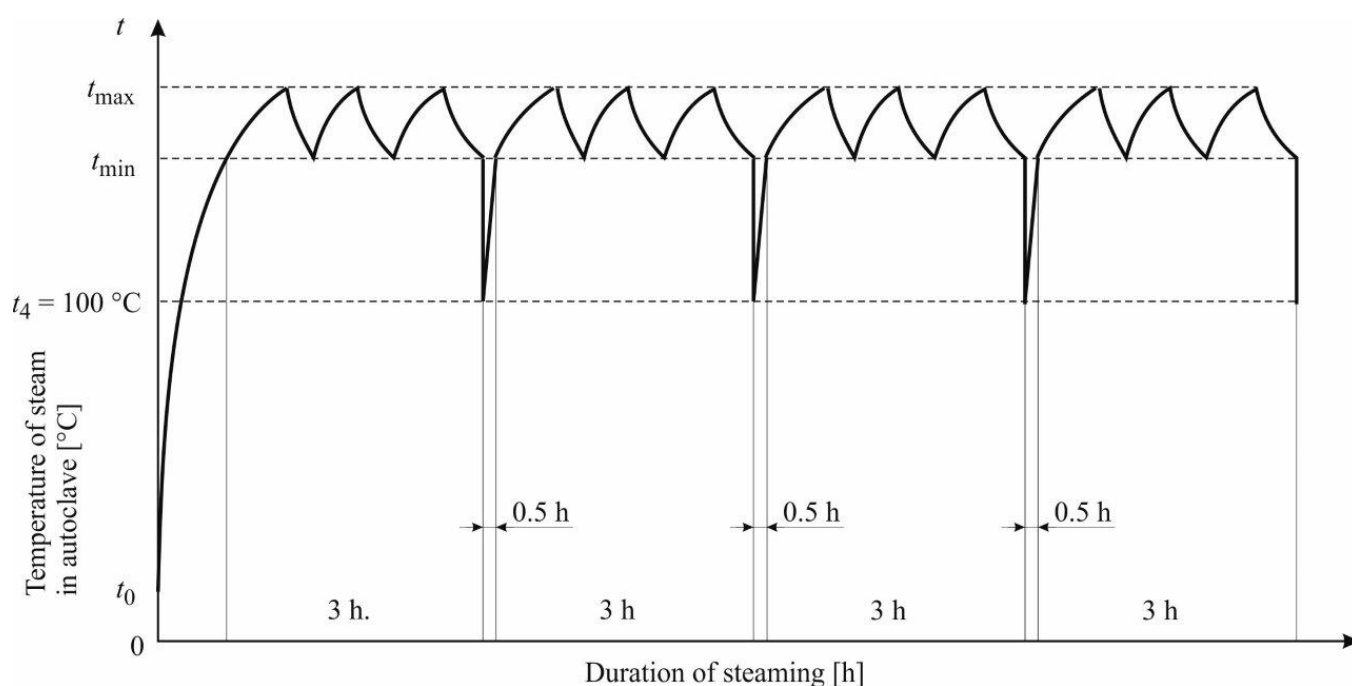


Figure 1. Diagram color modification of alder wood with saturated water steam.

The thermal alder wood color modification process was performed in a pressure autoclave at atmospheric pressure with a saturated steam-air mixture or saturated with steam at a pressure higher than atmospheric pressure. The temperatures t_{max} and t_{min} are the temperature interval in which saturated steam is fed into the autoclave for the implementation of the technological process. The 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, allowing the pressure device to be opened safely and samples to be taken after a specified time of thermal treatment.

The modes of thermal treatment of alder wood with saturated steam-air mixture (Mode I) and saturated water steam (Mode II, Mode III) are listed in Table 1.

Table 1. Modes of color modification of alder wood with saturated steam-air mixture and saturated water steam.

Modes	t_{min} (°C)	t_{max} (°C)	t_4 (°C)	Length of Time Wood Is Exposed to Color Modification			
Mode I	92.5	97.5	-				
Mode II	112.5	117.5	100	$\tau_1 = 3$ h	$\tau_2 = 6$ h *	$\tau_3 = 9$ h *	$\tau_4 = 12$ h *
Mode III	122.5	127.5	100				

Note: * After individual time periods of color modification, exactly according to the determined diagram (course), 0.5 h must be added to the given time of thermal modification of alder wood color. This time between the individual sections of the modification serves to reduce the pressure for safe opening of the autoclave and manipulation for selection of one group of modified blanks from the autoclave, closing and pressurization of the autoclave with saturated steam.

Native and color modified alder wood was dried to a final moisture content $w = 12 \pm 0.5\%$. Drying was carried out by low-temperature drying in a conventional hot-air dryer: KAD 1 $\times$ 6 (KATRES s.r.o., Jihlava, Czech Republic) with an emphasis on preserving the acquired wood color in individual regimes and times. Subsequently, the surface of dry blanks was machined on a FS 200 milling machine (BENET Trading, Kvasiny, Slovakia).

2.3. Determination of Alder Wood Density

Test specimens for measuring density with the following dimensions were made from native and thermally treated blanks in individual modes and times: dimensions $h = 15$ mm; width $w = 50$ mm; length $d = 100$ mm. The produced samples were dried in a laboratory oven (UM110m, MEMMERT, Niedersachsen, Germany) at a temperature of $T = 103 \pm 2$ °C to constant weight according to the standard [19]. The density of the alder wood in each mode and time of treatment was determined on the dried samples. The principle of measuring density was to weigh the sample in air and in liquid (distilled water). The determination of the density of alder wood was carried out on the device: Set-for measuring the density of solids (KIT 128, RADWAG, Kraków, Poland), with built-in software designed for measuring and evaluating the density of solids, including wood [20].

2.4. Determination of Moisture Content before and after the Thermal Treatment Process

The moisture content of the alder wood was determined before applying the thermal treatment process by random selection of 15 samples. The moisture content of five pieces of thermally treated blanks was also determined in individual modes and times after their cooling to the ambient temperature. The moisture content of the wet alder wood was determined by the gravimetric method according to the standard [19].

2.5. Measurement of Alder Wood Acidity

The acidity of wet alder native and thermal treated wood was measured using a SI 600 pH meter with a functional Lance FET + H probe (Sentron, Roden, The Netherlands). 3 measurements were performed on all samples in the middle of the thickness of the blank and 100 mm from the front of the blank. Using an cordless drill (DCD791NT, DeWalt, Frankfurt, Germany), a 12 mm diameter hole was made at the measuring point. The drilled wet sawdust was pushed back into the hole with a glass rod, where the LanceFET + H sensor head was inserted. After about 60 s of stabilization, the pH value was read on a SI 600 pH meter (Sentron, Roden, The Netherlands) [21].

2.6. Color Measurement of Modified Alder Wood

The color identification of the thermally treated as well as untreated alder wood in the CIE $L^*a^*b^*$ color space was determined using a Color Reader CR-10 colorimeter (Konica Minolta, Tokyo, Japan). The measurement was performed on the loading and side surfaces at a distance of 300 mm from the front of the blanks. A D65 light source with an illuminated area of 8 mm was used. The color was evaluated based on the changes in the color space

CIE $L^*a^*b^*$ on the luminance coordinate L^* , color coordinates: red a^* , yellow b^* . The value of the total color difference is described by the following equation:

$$\Delta E^* = \sqrt{(L_2^* - L_1^*)^2 + (a_2^* - a_1^*)^2 + (b_2^* - b_1^*)^2} \quad (1)$$

where: L_1^*, a_1^*, b_1^* values on the coordinates of the color space of the surface of dried milled thermally untreated alder wood, L_2^*, a_2^*, b_2^* values on the coordinates of the color space of the surface of dried milled thermally treated alder wood.

2.7. Analysis of Changes in Lignin-Cellulose Matrix of Wood ATR-FTIR Spectroscopy

The original and thermally treated alder wood samples were analysed by ATR-FTIR spectroscopy. The measurements were carried out using a iS10 FTIR spectrometer (Nicolet, Thermo Fisher Scientific, Madison, WI, USA) equipped with a Smart iTR attenuated total reflectance (ATR) accessory. The resolution was set at 4 cm^{-1} , 32 scans were recorded for each analysis, and the wavenumber range was from 4000 to 650 cm^{-1} . Six analyses were performed per sample. The spectra were evaluated using the OMNIC 8.0 software.

2.8. Statistical Processing of Measured Data

Graphical and mathematical dependences of $\Delta E^* = f(t, \tau)$ and $\text{pH} = f(t, \tau)$ were determined from the measured data of the total color difference ΔE^* and acidity of wood pH using the program STATISTICA 12 (V12.0 SP2), in the temperature range: $t = 95\text{--}125^\circ\text{C}$ and time $\tau = 3\text{--}12 \text{ h}$. The program processing of the measured results partially eliminated the influence of measurement errors caused by wood heterogeneity and the direct pH measurement method [21].

3. Results and Discussion

Physical properties of *Alnus glutinosa* wood such as moisture and acidity of wet wood before the thermal treatment process, as well as wood density, coordinates color space CIE $L^*a^*b^*$ in the dry state are given in Table 2.

Table 2. Measured values of density, coordinates color space CIE $L^*a^*b^*$ of dry wood, moisture and acidity of wet wood: Alder.

Wood	Dry Alder Wood			Wet Alder Wood		
	Density Wood ρ_0 (kg·m ⁻³)	Coordinates of Color Space CIE $L^*a^*b^*$			Moisture Content w (%)	Acidity pH (-)
		L^*	a^*	b^*		
Alder	522.8 ± 30.4	78.3 ± 2.3	9.2 ± 1.6	22.6 ± 1.2	62.9 ± 2.3	4.9 ± 0.2

The measured values of the density of alder wood in the dry state are the average values of the density of healthy alder wood, which is not damaged by fungi or molds. Similar values of alder wood density for the territory of Central Europe are given in [22–24]. Based on the above statement, it is possible to follow the analyzed changes in the properties of alder wood achieved by thermal treatment in individual regimes as representative (standard).

The results of laboratory work determining the density of thermally treated alder wood over time and at individual temperatures of saturated water steam in the dry state are given in Table 3.

Table 3. Average density values of dry thermally treated alder wood.

Thermal Treatment Mode	Statistical Characteristics of Dry Wood Density			
	$\rho_0 \text{ (kg}\cdot\text{m}^{-3}\text{)}$	$s \text{ (kg}\cdot\text{m}^{-3}\text{)}$	$v_x \text{ (\%)}$	$N \text{ (-)}$
Mode I	513.7	25.1	4.9	20
Mode II	510.4	22.5	4.4	20
Mode III	503.6	21.7	4.3	20

where: ρ_0 —measured average values of alder wood density; s —standard deviation of measurement; v_x —coefficient of variation (relative degree of variability); N —number of measurements performed.

The presented results show that the density of thermally treated alder wood decreases with increasing temperature. The stated changes in the densities of color-modified alder wood do not exceed the limits of the natural tolerance of alder wood densities, which in the Central European area is: $\rho_0 = 450\text{--}510\text{--}600 \text{ kg}\cdot\text{m}^{-3}$.

The moisture values of thermally treated alder wood after cooling the wood to ambient temperature are given in Table 4.

Table 4. Average values of alder wood moisture content in the thermal treatment process.

Thermal Treatment Mode	Time of Thermal Modification of Alder Wood			
	3 h w (%)	6 h w (%)	9 h w (%)	12 h w (%)
Mode I	58.6 ± 1.9	59.2 ± 1.2	58.5 ± 1.0	57.9 ± 1.1
Mode II	59.3 ± 1.2	58.9 ± 1.4	58.2 ± 1.2	56.9 ± 1.1
Mode III	58.5 ± 1.6	57.0 ± 1.1	56.1 ± 1.1	53.8 ± 0.9

The decrease in the moisture content of alder wood by $\Delta w = 9.1\%$ is caused by evaporation of water from the wood into the saturated water steam environment in the autoclave during cooling to $t = 100^\circ\text{C}$ before removing the wood from the autoclave and evaporation of water from wood to the atmosphere during cooling of wood to ambient temperature of air. The source of heat for evaporation and vaporization of water from wood is the heat accumulated during the heating of wood to the required technological temperature [25,26].

The acidity values of wet alder wood measured by the direct method of pH measurement before the thermal treatment process and during the thermal treatment during the technological process measured at 3, 6, 9, 12 h time intervals after listed in Table 5.

Table 5. Measured average pH values of alder wood in the process of thermal treatment.

Modes Thermal Treatment	Time of Thermal Modification of Alder Wood			
	3 h pH	6 h pH	9 h pH	12 h pH
Mode I	4.8 ± 0.2	4.7 ± 0.1	4.5 ± 0.3	4.4 ± 0.2
Mode II	4.0 ± 0.2	3.8 ± 0.3	3.7 ± 0.2	3.5 ± 0.2
Mode III	3.9 ± 0.3	3.4 ± 0.2	3.1 ± 0.2	3.1 ± 0.1

The acidity of wet alder wood $\text{pH} = 4.9 \pm 0.2$ is in accordance with the literature range of $\text{pH} = 5.5\text{--}4.8$ [7,21,27,28]. According to the literature, the free water found in the lumens of moist wood cells is a dilute aqueous solution of sugars, organic acids and salts of calcium, magnesium, potassium, sodium and inorganic acids, which are transported by the root system to the living tree during its growth [29–32]. The decrease in the acidity of alder wood during the process of thermal treatment with saturated steam is a confirmation of the known knowledge about the decrease in the pH of wet wood depending on the temperature and time of treatment [6,8,21,33,34]. From the measured pH values of alder wood during thermal treatment in the range of temperatures $t = 95\text{--}135^\circ\text{C}$ and time $\tau = 3\text{--}12 \text{ h}$ using a statistical program, the mathematical (Equation (2)) and graphical dependence (Figure 2) of the change in acidity in the process of thermal treatment was determined:

$$\text{pH} = 4.9042 + 0.0258 \cdot t + 0.0365 \cdot \tau - 0.0003 \cdot t^2 - 0.0014 \cdot t \cdot \tau + 0.004 \cdot \tau^2 \quad (2)$$

where: t —temperature of the saturated water steam $^\circ\text{C}$, τ —time of thermal modification of wood color in hours.

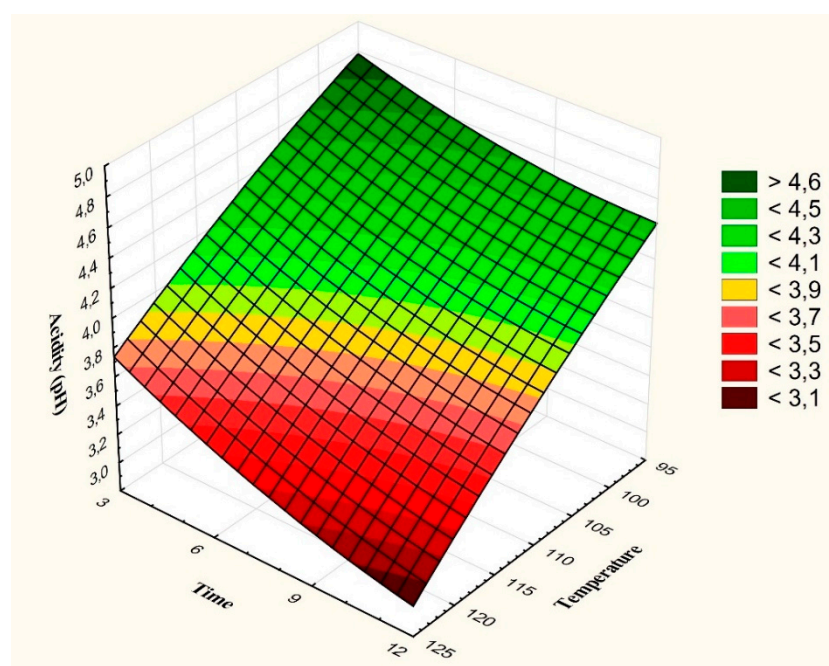


Figure 2. Correlation of the pH value of wet alder wood and the temperature of saturated water steam t and the time τ .

The light white-gray color of alder wood with a yellowish tinge of untreated wood was identified in the color space CIE $L^*a^*b^*$ with values on the luminance coordinate $L_0^* = 78.3 \pm 2.3$ and color coordinates: $a_0^* = 9.2 \pm 1.6$; $b_0^* = 22.6 \pm 1.2$. The measured values on the color coordinates of untreated alder wood are comparable with the values reported previously by other authors [14,35,36].

The process of thermal treatment of alder wood changes the color to soft reddish-brown to dark brown color shades achieved in *III* mode after 12 h of thermal treatment. The color saturation of alder wood depends on the moisture content of the wood, the temperature of saturated water steam and the duration of the technological process. The degree of coloration of alder wood in individual modes and times is declared by Figure 3.

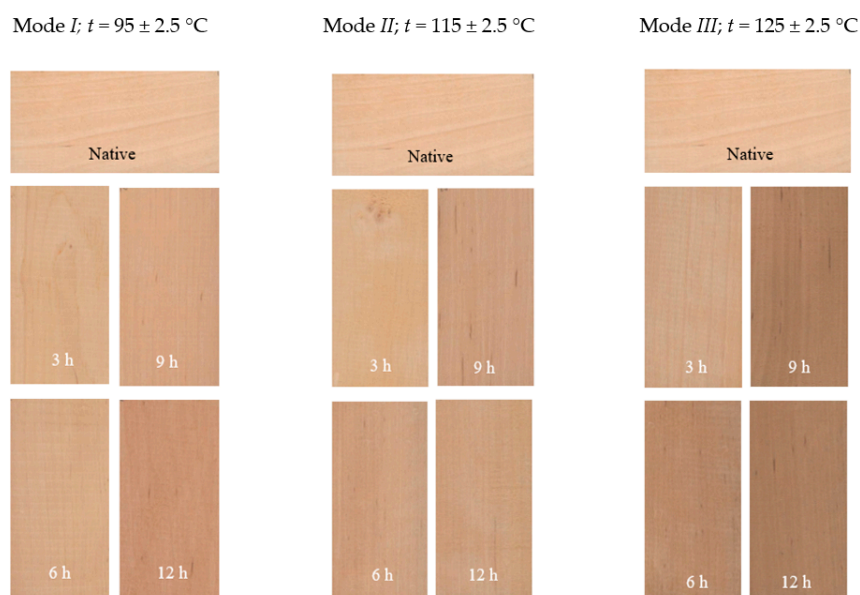


Figure 3. Changes in the color of alder wood during thermal modification.

A PERFECTION V850 PRO scanner EPSON with a scan quality of 1200 dpi was used to visually evaluate the color changes of alder wood color samples after the alder wood thermal treatment process using different modes and times.

Visual inspection of the thermally treated alder wood on the loading surfaces and in the middle of the side surfaces of the sawn blanks, as well as color measurements with the Color Reader CR-10 colorimeter on these surfaces showed that the wood is evenly colored throughout the cross section after 3 h thermal treatment of mode I ($t_I = 95 \pm 2.5^\circ\text{C}$). The full-volume coloring of alder wood is realized thanks to the rapid heating of the wood in a pressure autoclave to the required technological temperature with saturated steam over the entire volume of the autoclave, as well as over the entire cross section of the material [16,37]. Rapid heating of the material creates suitable conditions for the processes of extraction of water-soluble substances, hydrolysis of polysaccharides, as well as changes in the structure of lignin of alder wood causing modification of the chromophoric system.

The measured values of the color of the alder wood during the thermal treatment on the luminance coordinate L^* and the color coordinates: a^* —the coordinate of the red color, b^* —the coordinate of the yellow color as well as the total color difference ΔE^* are given in Table 6.

Table 6. Measured color values on the coordinates L^* , a^* , b^* in the CIE color space $L^*a^*b^*$, as well as the values of the total color difference ΔE^* of alder wood during the process of thermal modification of wood color.

Thermal Treatment Temperature	Coordinates CIE $L^*a^*b^*$	Time of Thermal Modification of Alder Wood			
		3 h	6 h	9 h	12 h
$t_I = 95 \pm 2.5^\circ\text{C}$	L^*	76.1 ± 1.8	73.3 ± 1.4	70.5 ± 1.9	68.6 ± 0.8
	a^*	10.4 ± 1.1	11.7 ± 0.8	12.2 ± 1.0	12.5 ± 0.7
	b^*	22.0 ± 0.9	21.5 ± 0.7	20.8 ± 0.8	20.5 ± 0.7
	ΔE^*	1.1	4.2	7.0	8.9
$t_{II} = 115 \pm 2.5^\circ\text{C}$	L^*	72.2 ± 1.6	65.9 ± 1.2	61.7 ± 1.1	57.4 ± 1.2
	a^*	11.4 ± 0.8	12.6 ± 0.6	12.8 ± 0.6	12.9 ± 0.5
	b^*	19.2 ± 0.7	18.6 ± 0.5	18.4 ± 0.6	18.3 ± 0.4
	ΔE^*	5.8	11.9	15.9	20.1
$t_{III} = 125 \pm 2.5^\circ\text{C}$	L^*	64.8 ± 1.7	57.4 ± 1.2	51.2 ± 1.1	47.4 ± 1.7
	a^*	11.8 ± 0.7	12.3 ± 0.6	12.5 ± 0.5	13.1 ± 0.6
	b^*	19.3 ± 0.6	17.2 ± 0.5	16.6 ± 0.5	16.3 ± 0.4
	ΔE^*	12.6	20.2	26.4	30.2

From the measured values on the luminance coordinate L^* it follows that the luminosity of native alder wood $L_0^* = 78.3$ has a decreasing tendency depending on temperature and time, where during thermal treatment with temperature t_{III} = luminosity decreased by up to $\Delta L_3^* = -30.9$. The decrease in the lightness of alder wood with the increase in the temperature of the saturated steam is not directly proportional. At higher temperatures of the heat treatment process, the decrease in brightness is greater and the darkening of alder wood is more pronounced.

The reduction of the values on the light coordinate L^* is in accordance with the knowledge about wood darkening in thermal and hydrothermal technological processes, such as wood steaming declared in the works: [13,14,16,17,20,38–41], or drying with warm humid air, resp. superheated steam [18,42].

Changes in the chromatic coordinate of red a^* have an increasing tendency. The value of the red color of native wood $a_0^* = 9.2$ increases during 12 h in a thermal process with the temperature $t_I = 95 \pm 2.5^\circ\text{C}$ to the value of $a_3^* = 12.5$, at the temperature of saturated steam $t_{II} = 115 \pm 2.5^\circ\text{C}$ to $a_3^* = 12.9$ and at water steam temperature $t_{III} = 125 \pm 2.5^\circ\text{C}$ to $a_3^* = 13.1$. The magnitudes of the changes on the red coordinate of a^* are significantly smaller compared to the changes on the luminance coordinate of L^* . A comparison of the effects of the parameters: temperature and duration of the technological process shows that increasing temperature has a greater effect on the increase of values than time. The

largest increase in Δa^* values, manifested by the red-brown shade of alder wood, is at the temperature of saturated water steam $t_{II} = 115 \pm 2.5$ °C.

On the yellow color coordinate b^* , the values have a slightly decreasing tendency depending on the saturated water vapor temperature and the modification time. The most significant decrease is at temperature $t_{III} = 125 \pm 2.5$ °C. Color-modified wood loses a yellowish tinge compared to uncooked alder wood.

Changes in the color of alder wood in the thermal process, in addition to changes in individual coordinates in the color space CIE $L^*a^*b^*$, are analyzed by the total color difference ΔE^* . The dependence of the change in the total color difference ΔE^* on the temperature t and time τ of alder wood during heat treatment of wood at saturated water steam temperatures in the range from $t = 95$ to 135 °C and time $\tau = 3$ – 12 h, is shown in the form of a 3D diagram in Figure 4 and is mathematically described by equation (Equation (3)):

$$\Delta E^* = 160.1885 - 3.2688 \cdot t - 1.6125 \cdot \tau + 0.0162 \cdot t^2 + 0.0362 \cdot t \cdot \tau - 0.0639 \cdot \tau^2 \quad (3)$$

where: t —temperature of the saturated water steam °C, τ —time of thermal modification of wood color in hours.

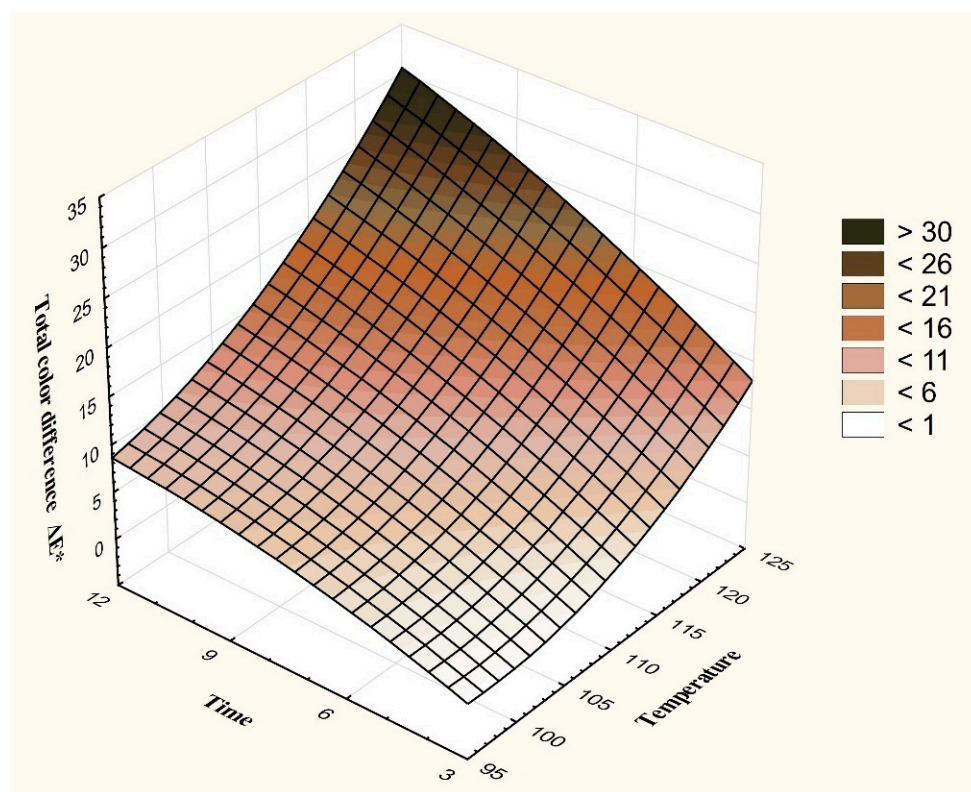


Figure 4. Dependence of the total color difference ΔE^* on the temperature of saturated water steam and the time of thermal modification.

During the process of thermal modification of wet alder wood, the formation of acetic acid and formic acid occurs depending on the temperature and time, as well as the degradation of polysaccharides through oxidation of carbohydrates, pectin and dehydration of pentoses to 2-furaldehyde. Free radicals and phenolic hydroxyl groups begin to form in lignin, which results in the formation of new chromophoric groups causing a change in the color of the wood [4–7,43]. Said changes, in the form of ATR-FTIR analyzes after 6 and 12 h, are shown in Figures 5 and 6

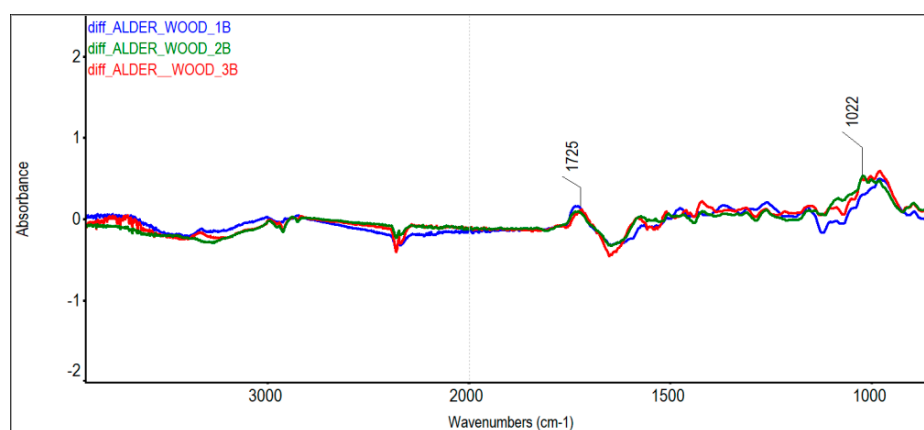


Figure 5. Absorption difference spectra of alder wood after 6 h of thermal modification.

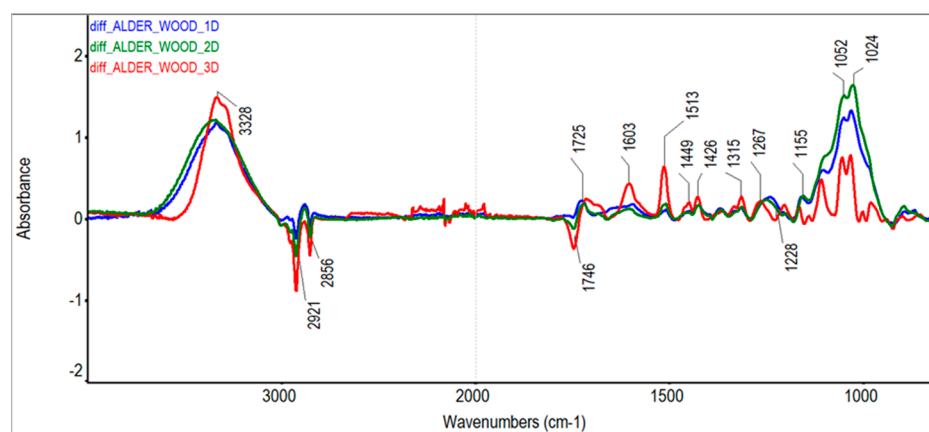


Figure 6. Absorption difference spectra of alder wood after 12 h of thermal modification.

The differences in ATR-FTIR absorption spectra were used to further elucidate the changes in chemical substances of alder wood during thermal treatment. In the spectra, there were monitored the changes of the functional groups and bonds responsible for the color changes of the thermal treatment wood [44,45].

According to our assumptions, more significant changes in the intensity of the absorption bands were recorded in the spectrum of wood thermal treatment for a long time. In the spectra of wood after 12 h of thermal treatment (Figure 6), positive bands at 3500 to 3200 cm^{-1} suggest an increase of intermolecular hydrogen bonds via devolatilization of original extractive substances and the changes in the carbohydrate components of wood—mainly from the significant degradation of hemicelluloses and the subsequent dehydration reactions. The positive bands at 1603 and 1513 cm^{-1} suggested the changes of the lignin and forming of the quinone structures in alder wood with elevated thermal treatment temperature.

Of interest are the changes observed in the region of 1750 – 1650 cm^{-1} , which correspond to the vibrations of carbonyl and carboxyl groups. At both treatment times, an increase in the intensity of the bands at 1725 cm^{-1} can be observed, to approximately the same extent. This suggested a formation of new carbonyl or carboxyl groups presumably due to hydrolysis and oxidative transformation of polyphenols to dark color polymers, which is in agreement with increase in green-red color coordinate a^* [46]. However, only in the case of samples thermal treatment for 6 h (Figure 5), a decrease in absorbance at 1651 cm^{-1} was observed, which indicated a loss of conjugated carbonyls in polysaccharides [42]. In the case of samples thermal treatment for 12 h (Figure 6), a decrease in absorbance at 1746 cm^{-1} is showed, whereby the decrease is more pronounced at higher treatment temperatures.

4. Conclusions

- (1) The process of thermal treatment of alder wood changes the color from the original light white-gray color with the coordinates: $L^* = 76.8 \pm 2.3$; $a^* = 9.6 \pm 1.6$; $b^* = 22.3 \pm 1.2$ for soft reddish-brown tones with coordinates: $L^* = 57.4 \pm 1.2$; $a^* = 12.9 \pm 0.5$; $b^* = 18.3 \pm 0.4$ to dark brown shades with coordinates: $L^* = 47.4 \pm 1.7$; $a^* = 13.1 \pm 0.6$; $b^* = 16.3 \pm 0.4$.
- (2) The density of thermally treated alder wood decreases with increasing temperature in the range of average values $\rho_0 = 513.7\text{--}503.6 \text{ kg}\cdot\text{m}^{-3}$. The stated changes in the densities of color-modified alder wood do not exceed the tolerance limits of the densities of native alder wood, which is in the Central European area: $\rho_0 = 450\text{--}510\text{--}600 \text{ kg}\cdot\text{m}^{-3}$.
- (3) During the technological process of wood modification, the acidity of the wood changes, which is more pronounced at a higher saturated steam temperature and for a longer time. The change is from pH = 4.9 for native alder wood to pH = 3.1 in mode III after 12 h of modification.
- (4) The differential spectrum of alder wood samples showed significant changes in the extractives as well as degradation of hemicelluloses. A decrease in unconjugated bonds and an increase in conjugated carbonyls was observed at all steaming temperatures. The findings also confirmed changes in alder lignin.

Author Contributions: M.D. designed the whole study; M.D. and L.D. conducted data collection, modeling and results analysis; M.D. wrote the original draft paper; L.D. revised and edited the paper. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by project APVV-17-0456 “Thermal modification of wood with saturated water steam for purposeful and stable change of wood color”.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: This experimental research was carried out under the grant project APVV-17-0456 “Thermal modification of wood with saturated water steam for purposeful and stable change of wood color”.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Kollmann, F.; Gote, W.A. Principles of wood sciences and technology. *Solid Wood* **1968**, *1*, 257–274.
2. Sergovskij, P.S.; Rasev, A.I. *Hydrothermal Treatment and Conservation of Wood*; Lesnaja Promyšlennost: Moskva, Russia, 1987; p. 360.
3. Trebula, P. *Drying and Hydrothermal Treatment of Wood*; Technical University in Zvolen: Zvolen, Slovakia, 1986; p. 255.
4. Fengel, D.; Wegener, G. *Wood: Chemistry, Ultrastructure, Reactions*, 2nd ed.; Walter de Gruyter: Berlin, Germany, 1989; p. 613.
5. Bučko, J. *Hydrolysis Processes*; Technical University in Zvolen: Zvolen, Slovakia, 1995; p. 116.
6. Hon, D.S.N.; Shiraishi, N. Weathering and photochemistry in wood. In *Wood and Cellulosic Chemistry*, 2nd ed.; MarcelDekker: New York, NY, USA, 2001; pp. 513–546.
7. Solár, R. *Wood Chemistry*; Technical University in Zvolen: Zvolen, Slovakia, 2004; p. 101.
8. Sundqvist, B.; Karlsson, O.; Westremark, U. Determination of formic-acid and acid concentrations formed during hydrothermal treatment of birch wood and its relation to color, strength and hardness. *Wood Sci. Technol.* **2006**, *40*, 549–561. [\[CrossRef\]](#)
9. Kačíková, D.; Kačík, F. *Chemical and Mechanical Changes of Wood during Thermal Treatment*; Technical University of Zvolen: Zvolen, Slovakia, 2011; p. 71.
10. Výbohová, E.; Kučerová, V.; Andor, T.; Balážová, Ž.; Veľková, V. The effect of heat treatment on the chemical composition of ash wood. *Bioresources* **2018**, *4*, 8394–8408. [\[CrossRef\]](#)
11. Geffert, A.; Výbohová, E.; Geffertová, J. Changes in the chemical composition of oak wood due to steaming. *Acta Fac. Xylologiae Zvolen* **2019**, *1*, 19–29.
12. Molnar, S.; Tolvaj, L. Colour homogenisation of different wood species by steaming. In *Interaction of Wood with Various Forms of Energy*; Technical University in Zvolen: Zvolen, Slovakia, 2002; pp. 119–122.
13. Tolvaj, L.; Nemeth, R.; Varga, D.; Molnar, S. Color homogenisation of beech wood by steam treatment. *Drewno* **2009**, *52*, 5–17.
14. Dzurenda, L. Colouring of beech wood during thermal treatment using saturated water steams. *Acta Fac. Xylologiae Zvolen* **2014**, *56*, 13–22.

15. Dzurenda, L. The shades of color of *Quercus robur* L. wood obtained through the processes of thermal treatment with saturated water vapor. *BioResources* **2018**, *13*, 1525–1533. [\[CrossRef\]](#)
16. Dzurenda, L. Hues of *Acer platanoides* L. resulting from processes of thermal treatment with saturated steam. *Drewno* **2018**, *61*, 165–176.
17. Dzurenda, L. Colour modification of *Robinia pseudoacacia* L. during the processes of heat treatment with saturated water steam. *Acta Fac. Xylologiae Zvolen* **2018**, *60*, 61–70.
18. Barański, J.; Klement, I.; Vilkovská, T.; Konopka, A. High temperature drying process of beech wood (*Fagus sylvatica* L.) with different zones of sapwood and red false heartwood. *Bioresources* **2017**, *12*, 1861–1870. [\[CrossRef\]](#)
19. STN EN 13183–1. *Moisture Content of a Piece of Sawn Timber—Part1: Determination by Oven Dry Method*; Slovenian Institute for Standardization: Ljubljana, Slovenia, 2003.
20. Dudiak, M. Modification of maple wood colour during the process of thermal treatment with saturated water steam. *Acta Fac. Xylologiae Zvolen* **2021**, *63*, 25–34.
21. Geffert, A.; Geffertová, J.; Dudiak, M. Direct method of measuring the pH value of wood. *Forests* **2019**, *10*, 852. [\[CrossRef\]](#)
22. Požgaj, A.; Chovanec, D.; Kurjatko, S.; Babiak, M. *Wood Structure and Properties*; Bratislava: Príroda, Slovakia, 1997; p. 485.
23. Makovíny, I. *Useful Properties and Use of Different Types of Wood*; Technical University in Zvolen: Zvolen, Slovakia, 2010; p. 104.
24. Kuriatko, S. *Wood Quality Parameters Determining Its Final Use*; Technical University in Zvolen: Zvolen, Slovakia, 2010; p. 352.
25. Dzurenda, L.; Deliiski, N. Analysis of moisture content changes in beech wood in the steaming process with saturated water steam. *Wood Res.* **2000**, *45*, 1–8.
26. Dzurenda, L. The effect of moisture content of black locust wood on the heating in the saturated water steam during the process of colour modification. In *Proceedings of the XXI International Scientific Conference—The Application of Experimental and Numerical Methods in Fluid Mechanics and Energy*, Rajec Teplice, Slovakia, 25–27 April 2018; Volume 168.
27. Sanderman, W.; Rothkamm, M. The determination of pH values of woods and their practical importance. *Holz Roh-Werkst.* **1959**, *17*, 433–441.
28. Irle, M. pH and Why You Need to Know It. *Based Panels International*. 2012. Available online: <http://www.wbpionline.com/features/ph-and-why-you-need-to-know-it/> (accessed on 20 August 2012).
29. Čudinov, B.S.; Stepanov, V.L. Phasenzusammensetzung der wassers in gefrorenem holz. *Holztechnologie* **1968**, *9*, 14–18.
30. Blažej, A.; Šutý, L.; Košík, M.; Krkoška, P.; Golis, E. *Chémia Dreva [Wood Chemistry]*; ALFA: Bratislava, Slovakia, 1975; p. 221.
31. Zevenhoven, M. *Ash-Forming Matter in Biomass Fuels*; Åbo Akademi University: Turku, Finland, 2001.
32. Pňakovič, L.; Dzurenda, L. Combustion characteristics of fallen fall leaves from ornamental trees in city and forest parks. *Bioresources* **2015**, *10*, 5563–5572. [\[CrossRef\]](#)
33. Melcer, I.; Melcerová, A.; Solár, R.; Kačík, F. *Chemistry of Hydrothermal Treatment of Deciduous Trees*; College of Forestry and Wood Technology in Zvolen: Zvolen, Slovakia, 1989.
34. Laurová, M.; Mamonová, M.; Kučerová, V. *Process of Partial Hydrolysis of Beech Wood (Fagus sylvatica L.) by Steaming and Cooking*; Technical University in Zvolen: Zvolen, Slovakia, 2004; p. 59.
35. Babiak, M.; Kubovský, I.; Mamoňová, M. Color Space of Selected Domestic Trees. In *Interaction of Wood with Various Forms of Energy*; Technical University in Zvolen: Zvolen, Slovakia, 2004; pp. 113–117.
36. Meints, T.; Teischinger, A.; Stingl, R.; Hassmann, C. Wood colour of central European wood species: CIELAB characterisation and colour intensification. *Eur. J. Wood Prod.* **2017**, *75*, 499–509. [\[CrossRef\]](#)
37. Dzurenda, L.; Geffert, A.; Geffertová, J.; Dudiak, M. Evaluation of the process thermal treatment of maple wood saturated water steam in terms of change of pH and color of wood. *Bioresources* **2020**, *15*, 2550–2559.
38. Varga, D.; Van der Zee, M.E. Influence of steaming on selected wood properties of four hardwood species. *HolzRoh. Werkst.* **2008**, *66*, 11–18. [\[CrossRef\]](#)
39. Hadjiski, M.; Deliiski, N. Advanced control of the wood thermal treatment processing. *Cybern. Inf. Technol. Bulg. Acad. Sci.* **2016**, *16*, 176–197. [\[CrossRef\]](#)
40. Banski, A.; Dudiak, M. Dependence of color on the time and temperature of saturated water steam in the process of thermal modification of beech wood. In *AIP Conference Proceedings*; AIP: College Park, MD, USA, 2019.
41. Dzurenda, L.; Dudiak, M. Cross-correlation of color and acidity of wet beech wood in the process of thermal treatment with saturated steam. *Wood Res.* **2021**, *66*, 105–116. [\[CrossRef\]](#)
42. Klement, I.; Marko, P. Colour changes of beech wood (*Fagus sylvatica* L.) during high temperature drying process. *Wood Res.* **2009**, *54*, 45–54.
43. Geffert, A.; Geffertová, J.; Výboňová, E.; Dudiak, M. Impact of steaming mode on chemical characteristics and color of birch wood. *Forests* **2020**, *11*, 478. [\[CrossRef\]](#)
44. Poletto, M.; Zattera, A.J.; Santana, R.M.C. Structural differences between wood species: Evidence from chemical composition, FTIR spectroscopy, and thermogravimetric analysis. *J. Appl. Polym. Sci.* **2012**, *126*, E336–E343. [\[CrossRef\]](#)
45. Zhang, P.; Wei, Y.; Liu, Y.; Gao, J.; Chen, Y.; Fan, Y. Heat-induced discoloration of chromophore structures in Eucalyptus lignin. *Materials* **2018**, *11*, 1686. [\[CrossRef\]](#) [\[PubMed\]](#)
46. Chen, Y.; Tshabalala, M.A.; Gao, J.M.; Stark, N.M.; Fan, Y.M. Color and surface chemistry changes of extracted wood flour after heating at 120 °C. *Wood Sci. Technol.* **2014**, *48*, 137–150. [\[CrossRef\]](#)