forests

MDPI

Article

Color Change of Pear Wood (*Pyrus communis* L.) during Water Steam Treatment

Miljenko Klarić [1], Nikola Španić [1,*], Zlatko Budrović [2], Andreja Čunčić Zorić [3], Stjepan Pervan [1] and Kristina Klarić [1]

[1] University of Zagreb Faculty of Forestry and Wood Technology, 10000 Zagreb, Croatia; mklaric@sumfak.unizg.hr (M.K.); spervan@sumfak.unizg.hr (S.P.); kklaric@sumfak.unizg.hr (K.K.)
[2] Drvni Trak, 10000 Zagreb, Croatia; zlatko.budrovic@zg.ht.hr
[3] Hrvatske Šume d.o.o., 10000 Zagreb, Croatia; andreja.cuncic.zoric@sk.ht.hr
* Correspondence: nspanic@sumfak.unizg.hr

Abstract: Hydrothermal treatment of wood, particularly steaming with saturated water steam, is often used to achieve a more intensive and homogenous wood color or to vary its hue. However, information on pear wood (*Pyrus communis* L.) steaming is limited in the available literature. This paper investigates the influence of steaming on the color of pear wood. Green, water-saturated samples of pear wood heartwood and sapwood were steamed with saturated water steam for 24 h at 98 °C. The color of the heartwood and sapwood was assessed both visually and with a standard three-stimulus colorimeter using the CIE*L*a*b** system, and compared to the natural color of pear-wood. Additionally, FT-IR spectrometry was employed to analyze chemical changes in the wood samples. The results showed that both heartwood and sapwood experienced a decrease in lightening (*L**), an increase in redness (*a**), and a decrease in yellowness (*b**) during steaming. Furthermore, a trend toward the equalization of *L**, *a**, and *b** parameters between heartwood and sapwood over time was observed. FT-IR spectroscopy revealed that the chemical changes during steaming were primarily related to extractives and hemicelluloses, with no significant changes in cellulose and lignin. The obtained results suggest that pear wood color can be equalized to some extent by steaming and that the extent of the color change to darker tones is dependent on steaming time.

Keywords: pear wood; color modification; hydrothermal treatment; CIE*L*a*b**; FT-IR

Citation: Klarić, M.; Španić, N.; Budrović, Z.; Zorić, A.Č.; Pervan, S.; Klarić, K. Color Change of Pear Wood (*Pyrus communis* L.) during Water Steam Treatment. *Forests* **2024**, *15*, 1685. https://doi.org/10.3390/f15101685

Academic Editors: Richard Hrčka, Magdalena Broda and Vlastimil Borůvka

Received: 23 August 2024
Revised: 18 September 2024
Accepted: 19 September 2024
Published: 25 September 2024

1. Introduction

The steaming of wood is a procedure that is usually conducted in the wood processing industry for wood softening, sterilization of wood, improvement of the dimensional stability of wood, and intensification and homogenization of wood color [1,2]. As regards color, it is one of the most important qualities that influences customers of wooden products [3], especially when products are used for decorative purposes. It has been shown that, in addition to the species name, wood color notably influences customer preferences when they choose products made of wood [4]. Therefore, wood surface color, i.e., its aesthetic appearance, can remarkably affect its final market value.

The natural color of wood can vary largely within one species and especially between the heartwood and sapwood zones. The steaming of wood species that have distinctive color differences between the heartwood and sapwood, (e.g., walnut, cherrywood, etc.) is often conducted to darken the sapwood [5], thus minimizing the color difference between the heartwood and sapwood, and to additionally improve heartwood color. In the past, there were attempts to improve sapwood color through a staining action by covering wood during steaming with a layer of sawdust or bark from the same wood species, but it was of little value [1]. Furthermore, beech wood and ash wood are often steamed to minimize the color difference between false heartwood and the surrounding wood [6,7]. In the wood processing industry, steaming processes are conducted in a wide variety of steaming

chambers, and often the steam parameters (temperature, pressure, etc.) cannot be regulated. Thus, steaming is often empirically conducted based on the experience of the steaming operator and based on inherited knowledge within a company.

Wood is a complex biopolymer composite material, and changes that take place within it during hydrothermal processing are very complex and numerous. There are many factors that have an influence on color formation during the hydrothermal processing of wood i.e., from processing equipment and various process parameters to the chemical composition of certain wood species. The significant influence of time, temperature, and pressure, as well as their interaction during steaming was reported [8,9], while the possible strong impact of some inherent wood properties, especially wood moisture content, on the direction and intensity of the coloring process is indicated [10]. The heat treatment of wood also depends on the presence and the amount of oxygen and water, which facilitate different types of chemical reactions [9,11]. It was suggested that color formation during hydrothermal wood processing (kiln-drying and steaming) is caused by chemical reactions of the accessory compounds, frequently described as oxidation and condensation of phenolic extractives [10,12,13]. Likewise, above certain temperatures, color formation can be caused by the hydrolysis of hemicelluloses and induced chemical reactions of lignin molecules [8,14]. According to Sundqvist and Morén [15], both, wood polymers degradation products and extractives contribute to color formation of hydrothermally treated wood. Generally, darker color hues in most wood species are achieved after steaming, which most probably is a result of the hydrolysis of accessory compounds and raised condensed polyphenolic products [10].

Pear wood (*Pyrus communis* L.), also known as wild pearwood or pearwood, belongs to the genus *Pyrus Torunf*. of the family *Rosaceae* and the subfamily *Pomoideae*. It is found in Europe, North and East Africa, and Central Asia. The tree grows up to 10–15 m in height, with a trunk diameter of 0.6 to 0.7 m. The wood is light reddish-brown with small, dense pores and visible growth rings [16]. It has a homogeneous structure with a high density of fibers. The density of dry wood is 650–760 kg/m^3, while that of green wood is 960–1070 kg/m^3. Radial, tangential, and volumetric shrinkage rates are 4.6%, 9.1%, and 14.1%, respectively. The compressive strength is 41–60 MPa, bending strength is 77–112 MPa, and shear strength is 8–9.5 MPa. Pear wood is highly valued for its workability and versatility. It works well with tools, glues easily, and is excellent for turning and carving due to its hardness and fine texture. Drying must be slow to minimize warping; when properly dried, it retains its shape well. Although it is not naturally durable outdoors without chemical protection, pear wood is extremely suitable for various demanding applications. It is used for making tool handles, screen printing frames, woodcuts, and musical instruments (when dyed black, it can substitute for ebony) [16]. It is also used for making billiard cue handles, drawing instruments, and other precision items. However, due to its limited availability in large quantities, pear wood remains a valuable but sparsely researched wood species. In this paper, pear wood (*Pyrus communis* L.) heartwood, and sapwood color change during steaming with saturated water steam at isothermal conditions through a course of 24 h was studied. This research aims to provide a deeper understanding of the color changes in pear wood (*Pyrus communis* L.) during saturated steam treatment, focusing on both the heartwood and sapwood. The significance of this research lies in addressing the limited existing knowledge on pear wood steaming, despite its value and aesthetic appeal in decorative applications. By employing both CIE*L*a*b** color measurement and FT-IR spectroscopy (the thin-slice method), the research not only investigates the visual changes but also explores the underlying chemical alterations primarily related to extractives and hemicelluloses. The innovative aspect of this research is its systematic approach to quantifying color modification through controlled steaming processes, which could lead to optimized methods for achieving desired wood aesthetics while minimizing resource use. This work lays the groundwork for future studies aimed at refining hydrothermal treatment processes for pear wood, enhancing its marketability and application in high-value products.

2. Materials and Methods

2.1. Wood Samples Preparation

A pear wood (*Pyrus communis* L.) tree was harvested at the end of March 2012, in central Croatia (Petrinja city), and the diameter of the trunk at breast height (1.3 m) was approximately 30 cm. The end bole with a final length of 1.1 m was sawn out, and the 55-mm quarter-sawn central plank that included the pith was sawn. After sawing the log, the sapwood was clearly visible and the sapwood samples were sawn within 2 cm from the bark in a radial direction. The heartwood samples were sawn at a minimum distance of 3 cm from the sapwood in a radial direction. Sixteen heartwood and sixteen sapwood samples for steaming were additionally sawn out from the same central plank with a circular saw for a fine cut. The surface was not additionally processed mechanically because there were no traces of the cutting. The sapwood samples' dimensions were 7(L) × 2(R) × 5(T) cm, and the heartwood samples' dimensions were 5(L) × 5(R) × 5(T) cm, without significant wood defects. Before steaming, the green wood samples were submerged in deionized water (Type II, according to ASTM DS1193-06 (2011)) [17] for 25 days to achieve maximal water saturation.

2.2. Steaming of Wood Samples

Steaming was carried out within the same year (2012), immediately after the felling of the tree, on green samples. Pear wood (*Pyrus communis* L.) heartwood and sapwood saturated (with deionized water) samples were subjected to 98 °C saturated water steam, at atmospheric pressure (~100,000 Pa) in a laboratory scale steaming chamber (usable volume ~7560 cm^3). The steaming chamber interior and samples shelve were made of stainless steel and the chamber was additionally insulated from the outside. The laboratory steaming chamber was equipped with two electrical heaters (2 × 3.4 kW), which were immersed in the water tank, for water steam generation. During the steaming process, condensate was drained into the water tank and exposed to the influence of heat. Steam temperature was continuously monitored using a mercury thermometer and a thermocouple thermometer. The process was conducted for 24 h. Every 2 h, samples of the heartwood and sapwood were collected and taken out to be analyzed. During the first 8 h, two heartwood and two sapwood samples were collected, and afterward, only one sample of heartwood and one sample of sapwood were collected after every 2 h of steaming.

2.3. Colour Measurement

The color evaluation was performed on the heartwood and sapwood referent samples before the steaming procedure, and on the equilibrated heartwood and sapwood samples after steaming (after 24 h of drying at room conditions). On each sample, the maximal possible number of measurements was conducted on the radial surface (but not less than 12). A spectral photometer DATACOLOR Microflash 100d (standard illuminant D65, xenon light source, d/8° measuring geometry, 10° standard observer) was used for the color coordinates measurements. The color parameters were monitored, recorded, and evaluated in the CIE$L^*a^*b^*$ color system. Component L^* represents lightness (0 → black, 100 → white), component a^* represents chromatic coordinates on the green–red axis (negative → green, positive → red), and component b^* represents chromatic coordinates on the blue–yellow axis (negative → blue, positive → yellow). Additionally, total color differences (ΔE^*) were calculated according to Equation (1), where ΔL^*, Δa^*, and Δb^* are the differences between the initial values and the values after the steaming procedure. After the color measurement, the samples were left to dry at room conditions.

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (1)$$

2.4. FT-IR Analysis

FT-IR analysis was performed in order to determine whether steaming caused any chemical changes in the pear-wood structure and to determine the extent of those changes.

The analysis was performed by the thin-slice method using a Perkin Elmer Spectrum One FT-IR spectrometer. The FT-IR spectra between 4000 and 400 cm^{-1} were recorded on thin wood slices (40 µm, cut using microtome). The areas of absorption bands were integrated, and the ratios of characteristic absorption peaks were calculated and used to assist in data interpretation. The integration of areas was based on the "tangent skim method" as described by Timar et al. [18]. The obtained data was processed using Spectrum One Version 5.0.1.

3. Results and Discussion

3.1. Color Analysis

The trend of lightness (L^*) and the chromaticity components (a^*, b^*) during the steaming process were monitored for the heartwood and sapwood samples. The arithmetic means of the obtained results are shown in Figures 1–3. Change of lightness (ΔL^*), chromaticity components (Δa^* and Δb^*), and total color change (ΔE^*) are calculated with arithmetic means.

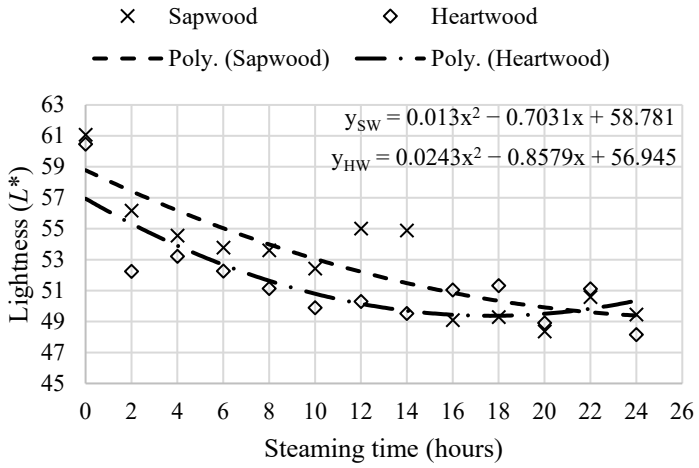

Figure 1. Heartwood and sapwood lightness (L^*) trend during the steaming process.

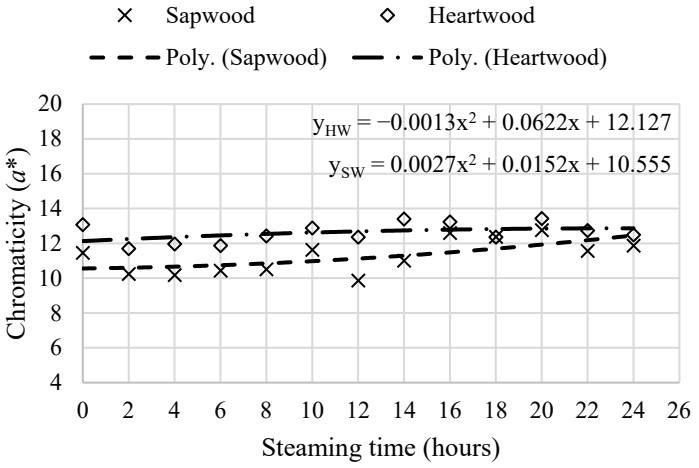

Figure 2. Heartwood and sapwood chromaticity component (a^*) trend during the steaming process.

It can be seen (Figure 1) that the initial lightness of the sapwood is somewhat higher than the lightness of the heartwood. Both, heartwood and sapwood lightness are decreasing over steaming time, while the heartwood is generally darker than the sapwood. After approximately 20 h of steaming, the lightness of the heartwood and sapwood begin to equalize.

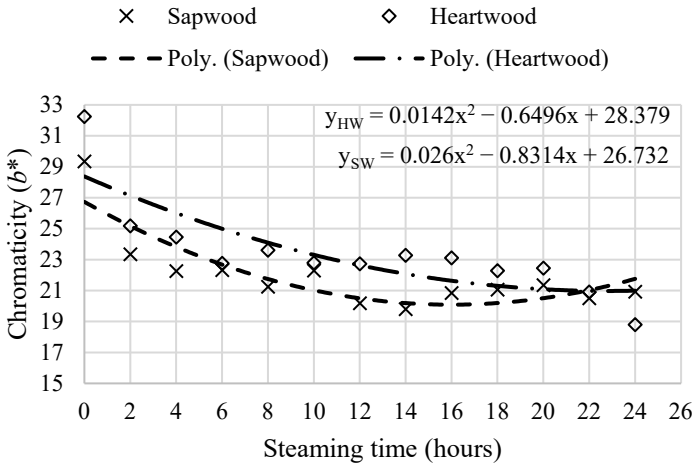

Figure 3. Heartwood and sapwood chromaticity component (b^*) trend during the steaming process.

As regards chromaticity component a^* (Figure 2), the coordinates are located on the red part of the green–red axis. Initially and during steaming, the heartwood is more red than the sapwood, while the color starts to equalize at around 16 h of steaming. The red color has a slight ascending trend over the whole steaming period.

Regarding chromaticity component b^* (Figure 3), the presence of a yellow color is more intense in the heartwood than in the sapwood during the first 14 h of steaming. However, after around 16 h of steaming, the sapwood's yellowness starts to increase, and the heartwood's yellowness continues to decrease. After 22 h of steaming, the recorded values of the heartwood and sapwood b^* component are almost equalized.

The change of lightness in the negative direction (Figure 4) of the heartwood is greater than the sapwood during the first 20 h of steaming, and afterward, the difference is less pronounced. In general, the change in lightness increases with the steaming duration in both the sapwood and heartwood.

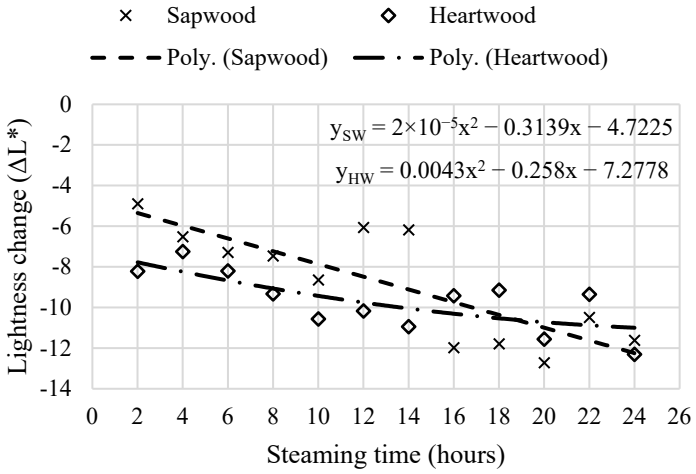

Figure 4. Heartwood and sapwood lightness (ΔL^*) change during the steaming process.

On the chromaticity axis a^* (Figure 5), color change in a positive direction is almost the same for the heartwood and sapwood till the 14th hour of steaming. Afterward, the sapwood's change is still going in a positive direction, while the heartwood's color change is in a negative direction, i.e., redness is decreasing.

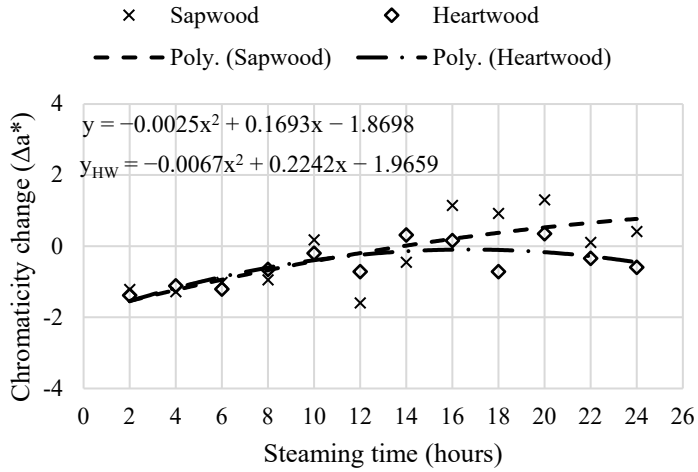

Figure 5. Heartwood and sapwood chromaticity components (Δ*a**) change during the steaming process.

On the chromaticity axis *b** (Figure 6), the change is in the negative direction, while at the beginning of the steaming process, the heartwood change is slightly more pronounced. Around the 18th hour, the heartwood color starts to change more than the sapwood.

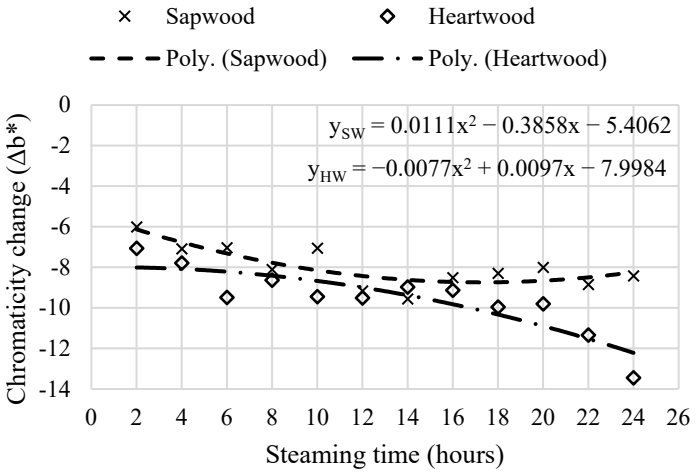

Figure 6. Heartwood and sapwood chromaticity components (Δ*b**) change during the steaming process.

Total color change Δ*E** (Figure 7) is greater for the heartwood than for the sapwood. In the middle of the steaming time, the difference between the sapwood and heartwood is somewhat decreasing, but towards the end, this difference slightly increases.

The changes in these color parameters are further analyzed and quantified using regression analysis and an ANOVA, as shown in Tables 1 and 2. The key statistical indicators for assessing the validity of the six regression models and the ANOVA used to predict the different components of the CIE*L*a*b** color space in pear wood during a 24-h steaming period are presented in Table 1. The overall significance of each regression model is confirmed by the ANOVA results, as indicated by the F-statistics and corresponding *p*-values (Pr > F). The sapwood lightness model is identified as the most statistically significant (F = 27.881, Pr > F = 0.000), while the model for the green–red axis component of the heartwood is found to be the only one not significant at the 5% level (F = 2.286, Pr > F = 0.159). It is indicated that the model predicting the lightness component (*L**) of the sapwood has the highest R^2 (0.717), suggesting the best fit to the data, while the model predicting the green–red axis component (*a**) of the heartwood has the lowest R^2 (0.172), indicating a poor fit. The coefficients for the variable "Time" are found to be significant for all models except the one predicting the green–red axis of the heartwood, confirming

that statistically significant relationships between the predictor and the dependent variable are established for all other models. In general, the models predicting the lightness and green–red axis components of the sapwood, as well as those predicting the blue–yellow axis of both the sapwood and heartwood, are considered valid for explaining the variability of the CIE*L*a*b** components, while the model for the green–red axis of the heartwood is not statistically significant.

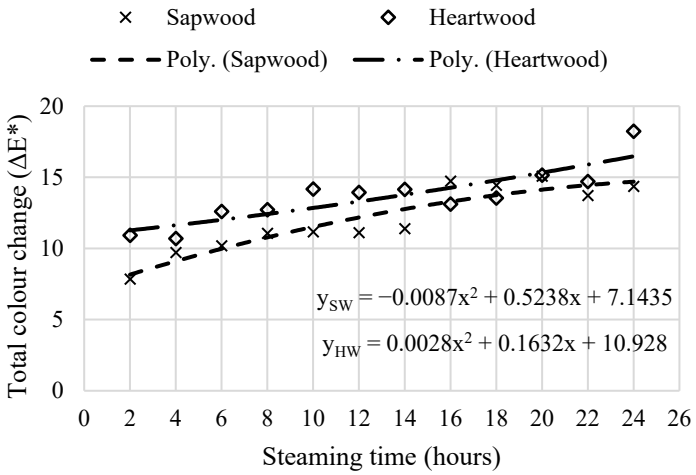

Figure 7. Heartwood and sapwood total color change (Δ*E**) during the steaming process.

Table 1. Regression analysis and ANOVA results of CIE*L*a*b** color components in the heartwood and sapwood of pear wood during a 24-h steaming.

Variable †	Mean	Std. Deviation	R^2	Adjusted R^2	F-Statistic	Pr > F	Coefficient (Time)	Std. Error (Time)	t (Time)	Pr > |t| (Time)
SW *L*	53.386	3.516	0.717	0.691	27.881	0.000	−0.391	0.074	−5.280	0.000
SW *a*	11.053	1.139	0.399	0.344	7.306	0.021	0.079	0.029	2.703	0.021
SW *b*	22.098	2.359	0.442	0.391	8.707	0.013	−0.207	0.070	−2.951	0.013
HW *L*	51.947	3.328	0.497	0.452	10.879	0.007	−0.275	0.083	−3.298	0.007
HW *a*	12.487	0.746	0.172	0.097	2.286	0.159	0.031	0.020	1.512	0.159
HW *b*	23.840	3.266	0.608	0.572	17.058	0.002	−0.308	0.075	−4.130	0.002

† The abbreviations are defined as follows: SW = sapwood, HW = heartwood, *L* = lightness (*L**) component, *a* = green–red axis (*a**) component, *b* = blue–yellow axis (*b**) component.

In Table 2, the results of both regression and ANOVA analyses are presented to evaluate the changes (Δ) in various components of the CIE*L*a*b** color space for the heartwood and sapwood of pear wood over a 24-h steaming period. The model predicting the total color change of the sapwood (Δ*E**) is found to have the highest R^2 value (0.842), indicating the best explanation for the variation in the data, while the model predicting changes in the green–red axis component (Δ*a**) of the heartwood is shown to have the lowest R^2 (0.377), suggesting a relatively weaker fit. The ANOVA results confirm that the sapwood total color change model (SW Δ*E**) is the most statistically significant, with an F-statistic of 53.138 and Pr > F < 0.0001. In contrast, the heartwood green–red axis model (HW Δ*a*) is identified as the least significant, although still statistically significant at the 5% level (F = 6.057, Pr > F = 0.034). It is observed that the coefficients for "Time" are statistically significant across all models, indicating strong relationships between the predictor and dependent variables. The different effects of the "Time" variable on each component are reflected in the direction and magnitude of the coefficients: positive impacts are observed in models such as SW Δ*a** and SW Δ*E*, while negative impacts are noted in models like SW

Δ*L** and HW Δ*b**. Overall, it can be seen that most models demonstrate a strong fit to the data, as evidenced by high R^2 values and statistically significant *p*-values.

Table 2. Regression analysis and ANOVA results of changes (Δ) in CIE*L***a***b** color components in the heartwood and sapwood of pear wood during a 24-h steaming period.

Variable †	R^2	Adjusted R^2	F-Statistic	Pr > F	Coefficient (Time)	Std. Error (Time)	t (Time)	Pr > |t| (Time)
SW Δ*L*	0.669	0.636	20.221	0.001	−0.313	0.070	−4.497	0.001
SW Δ*a*	0.554	0.510	12.428	0.005	0.105	0.030	3.525	0.005
SW Δ*b*	0.451	0.396	8.218	0.017	−0.096	0.033	−2.867	0.017
SW Δ*E*	0.842	0.826	53.138	<0.0001	0.297	0.041	7.290	<0.0001
HW Δ*L*	0.515	0.467	10.619	0.009	−0.146	0.045	−3.259	0.009
HW Δ*a*	0.377	0.315	6.057	0.034	0.050	0.020	2.461	0.034
HW Δ*b*	0.716	0.688	25.234	0.001	−0.191	0.038	−5.023	0.001
HW Δ*E*	0.739	0.713	28.36	<0.0001	0.237	0.044	5.325	<0.0001

† The abbreviations are defined as follows: SW = sapwood, HW = heartwood, Δ*L* = change in lightness (*L**) component, Δ*a* = change in green–red axis (*a**) component, Δ*b* = change in blue–yellow axis (*b**) component, Δ*E* = total color change (Δ*E**).

Regression analysis and ANOVA results (Tables 1 and 2) further support the visual observations in Figures 1–7, revealing significant relationships between steaming time and color changes in both the heartwood and sapwood. The color change during the steaming process mostly occurred and behaved as expected. A decrease in the lightness of both the sapwood and heartwood was expected. Similar results were obtained in the research of other researchers on other species, like poplar [19], spruce and Scots pine [20], and larch [21]. The red component increased, but red coloring compounds are leachable from wood during steaming, and they were found during steaming in condensate, with condensate becoming redder as steaming progressed (Figure 8). The above certainly had an effect on the reduction of the red color in the wood.

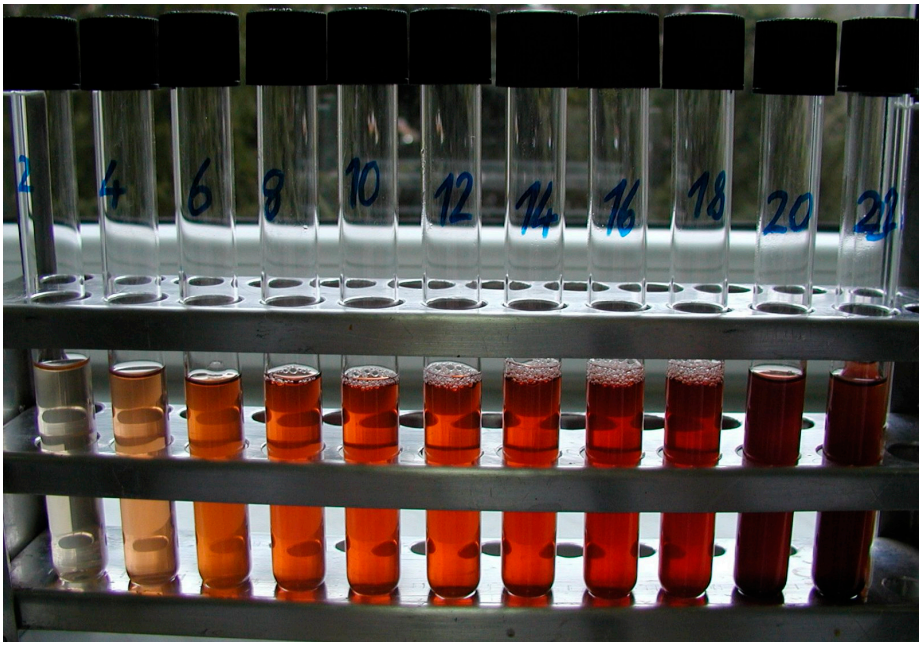

Figure 8. Cumulative condensate from the steaming chamber, extraction every two hours (left to right).

The yellow component decreases as steaming time progresses, as is expected because the wood is becoming darker and the participation of the blue color increases. The total color change increases as steaming continues. The color would probably additionally change in a few more hours of steaming, but this needs to be confirmed with additional experiments.

3.2. FT-IR Analysis Results

The FT-IR spectra of untreated and steam-treated sapwood (Figure 9) and heartwood (Figure 10) showed strong bands at around 3345 to 3350 cm^{-1} (1) related to O-H stretching (cellulose) and 2900 to 2903 cm^{-1} (2) related to C-H stretching in methyl and methylene groups. Other peaks in the fingerprint region (1800 to 800 cm^{-1}) are assigned [22–28]: 1732 to 1737 cm^{-1} (3) for C=O stretching of unconjugated ketone, carbonyl, and ester groups (xylan); 1650 cm^{-1} (4) for absorbed O-H and conjugated C-O; 1591 cm^{-1} (5) and 1501 to 1503 cm^{-1} (6) for aromatic skeletal vibrations (lignin); 1455 cm^{-1} (7) for in plane bending of OH groups in cellulose or aromatic CH deformation and asymmetric bending of CH_3 in lignin; 1422 cm^{-1} (8) for C-H in plane deformation combined with vibration of aromatic structures in lignin; 1369 to 1371 cm^{-1} (9) for symmetric C-H bending in cellulose and non-cellulosic carbohydrates (hemicelluloses); 1323 cm^{-1} (10) for vibration in C-H (cellulose) and stretching in C-O related to syringyl ring (lignin); 1231 cm^{-1} (11) for syringyl ring and C-O stretch in lignin and xylan; 1158–1160 cm^{-1} (12) for C-O-C asymmetric valence vibrations (cellulose and hemicelluloses); 1107 to 1109 cm^{-1} (13) for aromatic skeletal and asymmetric stretch of glycosidic ring; 1051 to 1056 cm^{-1} (14) for C-O valence vibrations in cellulose; 1035 cm^{-1} (15) for C-O stretching in cellulose and hemicelluloses; and 897 cm^{-1} (16) for C-H deformation in cellulose.

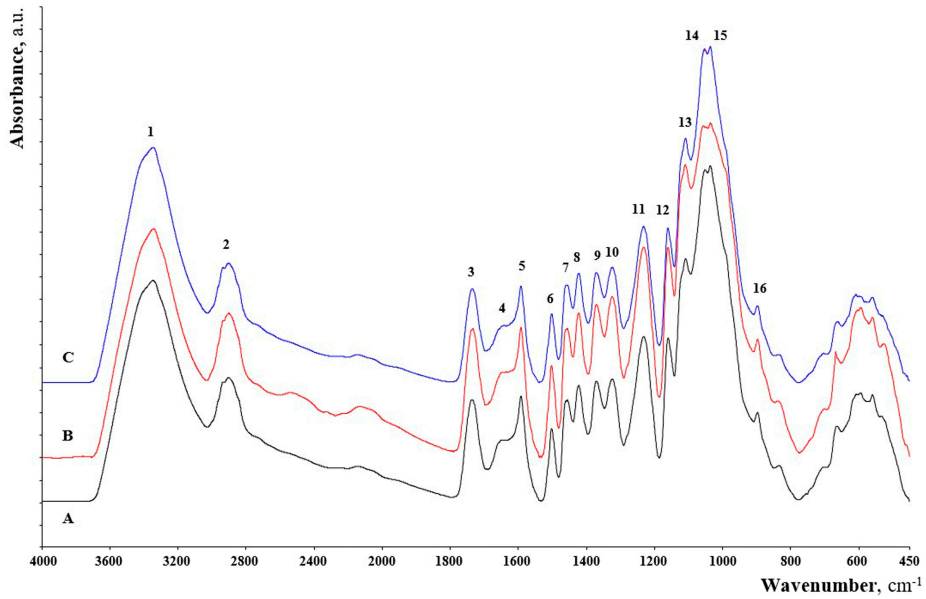

Figure 9. FT-IR spectra of un-steamed (A) and sapwood samples steamed for 12 (B) and 24 (C) hours. (Numbers 1 to 16 denote characteristic carbohydrates and lignin bands).

As FT-IR spectra in Figures 9 and 10 reveal, spectral differences between untreated and steamed sapwood and heartwood are barely visible, or there is no obvious difference. Therefore, area integration of some of the absorption bands was conducted in order to assist in the determination of chemical changes. Data used for semiquantitative evaluation of chemical changes is given in Tables 3–5.

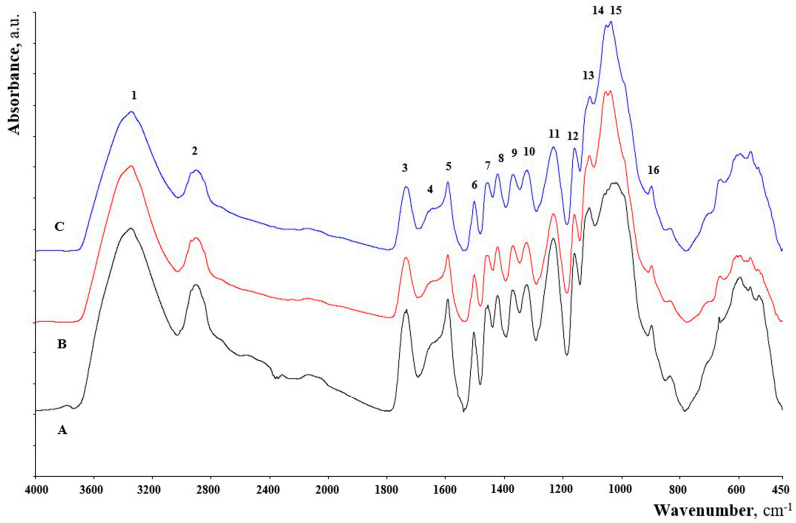

Figure 10. FT-IR spectra of un-steamed (A) and heartwood samples steamed for 12 (B) and 24 (C) hours. (Numbers 1 to 16 denote characteristic carbohydrates and lignin bands).

Table 3. Average values of integrated areas of selected absorption bands of the FT-IR spectra of sapwood.

Peak Position, cm^{-1}	Borders of Integrated Area, cm^{-1}	Integrated Areas (A)		
		Un-Steamed	Steamed for 12 h	Steamed for 24 h
3345	3706–3030	397.90	407.59	404.03
1732	1785–1693	23.15	31.00	20.85
1650	1685–1622	16.05	22.32	14.26
1501	1527–1480	7.85	11.03	8.06
1369	1393–1345	19.32	27.87	19.52

Table 4. Average values of integrated areas of selected absorption bands of the FT-IR spectra of heartwood.

Peak Position, cm^{-1}	Borders of Integrated Area, cm^{-1}	Integrated Areas (A)		
		Un-Steamed	Steamed for 12 h	Steamed for 24 h
3345	3706–3030	527.27	402.98	383.86
1732	1785–1693	35.06	21.78	22.10
1650	1685–1622	25.57	15.13	16.00
1501	1527–1480	14.45	7.92	8.92
1369	1393–1345	33.20	19.72	20.60

Table 5. FT-IR ratios of selected absorption bands.

FT-IR Ratio	Assignment	Treatment					
		Un-Steamed		Steamed for 12 h		Steamed for 24 h	
A1732/A1369	Non-conjugated carbonyl/Carbohydrates	1.20	1.06 [1]	1.11	1.10	1.07	1.07
A1501/A1369	Lignin/Carbohydrates	0.41	0.44	0.40	0.40	0.41	0.43
A1732/A1650	Non-conjugated carbonyl/Conjugated carbonyl	1.44	1.37	1.39	1.44	1.46	1.38
A3340/A1501	Hydroxyl/Lignin	50.66	36.47	36.92	50.83	50.07	42.99

[1] The first number in each column/row denotes the values obtained for sapwood and the second one for heartwood.

The data given in Table 3 reveal that the steaming process, in terms of cellulose and lignin, did not alter the surface chemistry significantly. This is supported by the fact that there are almost no differences in the ratio A1501/A1369 (lignin/carbohydrates) for both the sapwood and heartwood. However, the results suggest that the steaming process affected the sapwood and heartwood differently. Steaming caused an increase of free hydroxyl groups (decrease of the ratio A3340/A1501) and non-conjugated carbonyl groups (decrease of the ratio A1732/A1369) in the case of sapwood. These changes, which are of the opposite tendency for the heartwood, are mostly related to the hydrolysis of hemicelluloses. The opposite influence that steaming has on the sapwood and heartwood is additionally confirmed by the changes related to the non-conjugated carbonyl/conjugated carbonyl groups (A1732/A1650 ratio). Such tendencies could be explained by the fact that as the biological functions of sapwood and heartwood are different, so are the quantities and accessibility of carbohydrates and phenolic compounds in them. Generally, heartwood contains more lignin and less cellulose and holocellulose than sapwood [14,29]. As calculated values of examined ratios are somewhat similar, the influence of the method used for obtaining FT-IR spectra (thin slices) must also be taken into consideration. Nonetheless, the obtained results clearly show that the majority of chemical changes occurred in the extractives (degradation or dissolution) and hemicelluloses, and those changes are not easily/usually detectable by FT-IR [18].

Wood's natural color can vary greatly with genetic factors and environmental conditions [30], and additionally, can be significantly altered during industrial processes. During the hydrothermal treatment of wood, color changes occur mostly due to extractives, especially polyphenols [5,6], while the products of polymer degradation can participate in the formation of the color [15]. During this research, before steaming, wood samples were submerged in deionized water for 25 days to achieve their saturation with water. During submersion, a maceration extraction process took place, where some of the more polar extractives were leached out from the wood. This unintentionally caused extraction certainly had some influence on color change during steaming, where probably color change would be to some extent greater if the extraction had not occurred. However, it is well known that the initial moisture content is very important for the achievement of greater color change during steaming. Furthermore, when wood is light irradiated before heat treatment, the lightness and color component changes are intensified in comparison with non-irradiated wood, while the change was greater in the presence of water [31]. Dzurenda and Dudiak found that steamed beech wood is more resistant to photochemical reactions by UV radiation (Xenotest Q-SUN Xe-3-HS during 298 h irradiation) causing color changes in the process of natural aging [32]. Bandics et al. established that UV irradiation of steamed (100 °C, 110 °C and 120 °C) plantation poplar wood (*Populus x euramericana* cv. *Pannonia*) enhanced the redness stability and slightly reduced sensitivity of the yellow color to photodegradation, while the lightness value of the steamed samples decreased only during the first 7 h of UV irradiation and remained constant afterward [33]. It has been found that black locust, beech, and poplar after 48 h of steaming and then UV irradiation presented a greater absorption increase at 1705 cm^{-1} than the un-steamed ones, which refers to photodegradation of hemicelluloses, while only black locust had considerably reduced photodegradation sensitivity of lignin [34]. Regarding the time and temperature of steaming, higher temperatures and longer steaming times in general result in greater color changes, i.e., darkening [11,35,36]. At maple wood increases in temperature and duration of the steaming, treatment primarily affects holocellulose and extractives content, and less the content of cellulose and lignin [37]. Bandics et al. steamed poplar wood together with black locust and beech specimens (as initiators with higher extractive content compared to poplar) and showed that the presence of initiators intensified the color of poplar wood above 100 °C, especially the heartwood [38].

This research makes a significant contribution to the study of pear wood (*Pyrus communis* L.) color during saturated steam treatment. Detailed insights into the color changes of the heartwood and sapwood of pear wood throughout the 24-h steaming

process are provided. The presented results contribute to a better understanding of the effects of steaming on pear wood and can serve as a basis for further research in the field of hydrothermal wood treatment. Furthermore, the research lays the groundwork for future studies focused on optimizing the steaming process to achieve the desired aesthetic and functional properties of the wood. Additionally, the exploration of the long-term effects of steaming on the other properties of pear wood is suggested, which could further expand its applications in various industrial sectors.

4. Conclusions

It was established, that with pear-wood steaming, its heartwood and sapwood color can be to some extent equalized, while prolongation of the steaming process causes the darkening of the pear wood. The results showed that the pear wood's heartwood and sapwood lightness decreases, redness slightly increases, and yellowness decreases. The longer the steaming process lasted, the greater the overall color change. The results of FT-IR analysis showed that the chemical changes that have occurred during the steaming of the pear wood are almost solely related to the extractives and hemicelluloses, without noticeable changes in the cellulose and lignin. Therefore, it can be concluded that pear wood is suitable for color modification by steaming, but to establish the optimal duration of the process, additional laboratory and industrial investigations should be carried out.

Author Contributions: Conceptualization, M.K., N.Š., K.K., Z.B., A.Č.Z. and S.P.; methodology, M.K. and N.Š.; validation M.K., N.Š., K.K., Z.B., A.Č.Z. and S.P.; formal analysis, M.K., N.Š., K.K., Z.B. and A.Č.Z.; investigation, M.K., N.Š., Z.B. and A.Č.Z.; resources, M.K., N.Š., K.K., Z.B. and A.Č.Z.; data curation, M.K., N.Š., Z.B., A.Č.Z. and S.P.; writing—original draft preparation, M.K., N.Š. and K.K.; writing—review and editing, M.K., N.Š., K.K., Z.B., A.Č.Z. and S.P.; visualization, M.K., N.Š. and K.K.; supervision, S.P.; project administration, S.P. and M.K.; funding acquisition, M.K. and KK. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: The raw data supporting the conclusions of this article will be made available by the authors upon request.

Conflicts of Interest: Zlatko Budrović is employed by the company Drvni trak and Andreja Čunčić Zorić is employed by the company Hrvatske Šume d.o.o. Their employer's company was not involved in this study, and there is no relevance between this research and their company. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

References

1. Brauner, A.; Conway, E.M. Steaming Walnut for Color. *For. Prod. J.* **1964**, *14*, 525–527.
2. Burmester, A. Einfluß einer Wärme-Druck-Behandlung halbtrockenen Holzes auf seine Formbeständigkeit. *Holz Roh Werkst.* **1973**, *31*, 237–243. [CrossRef]
3. Sandoval-Torres, S.; Jomaa, W.; Marc, F.; Puiggali, J.R. Causes of color changes in wood during drying. *For. Stud.* **2010**, *12*, 167–175. [CrossRef]
4. Bumgardner, M.; Nicholls, D.; Donovan, G. Effects of species information and furniture price on consumer preferences for selected woods. *Wood Fiber Sci.* **2007**, *39*, 71–81.
5. Pervan, S.; Antonović, A.; Humar, M.; Straže, A.; Gorišek, Ž. Colour chemistry of steamed and boiled walnutwood (*Juglans regia* L.). *Drv. Ind.* **2006**, *57*, 127–133.
6. Tolvaj, L.; Németh, R.; Varga, D.; Molnar, S. Colour homogenisation of beech wood by steam treatment. *Drew. Wood* **2009**, *52*, 5–17.
7. Dzurenda, L.; Dudiak, M. Homogenization of the Color of Beech Sapwood and False Heartwood by the Steaming Process. *Forests* **2024**, *15*, 1009. [CrossRef]
8. Kollmann, F.; Keylwerth, R.; Kübler, H. Verfärbungen des Vollholzes und der Furniere bei der künstlichen Holztrocknung. *Holz Roh Werkst.* **1951**, *9*, 382–391. [CrossRef]
9. Navi, P.; Sandberg, D. *Thermo-Hydro-Mechanical Processing of Wood*, 1st ed.; EPFL Press: Lausanne, Switzerland, 2012; pp. 1–360.

10. Straže, A.; Gorišek, Ž.; Pervan, S.; Prekrat, S.; Antonović, A. Research on colour variation of steamed cherrywood (*Prunus avium* L.). *Wood Res.* **2008**, *53*, 77–90.
11. Németh, R.; Hill, C.A.S.; Takáts, P.; Tolvaj, L. Chemical changes of wood during steaming measured by IR spectroscopy. *Wood Mater. Sci. Eng.* **2014**, *11*, 95–101. [CrossRef]
12. Koch, G.; Puls, J.; Bauch, J. Topochemical Characterisation of Phenolic Extractives in Discoloured Beechwood (*Fagus sylvatica* L.). *Holzforschung* **2003**, *57*, 339–345. [CrossRef]
13. Klarić, M.; Oven, P.; Gorišek, Ž.; Španić, N.; Pervan, S. Yield of Stirred Cold Maceration and Extraction of Milled European Black Alder Wood and Bark using Different Solvents. *BioResources* **2016**, *11*, 9244–9254. [CrossRef]
14. Fengel, D.; Wegener, G. *Wood: Chemistry, Ultrastructure, Reactions*; Verlag Kessel: Remagen, Germany, 1989; pp. 1–613.
15. Sundqvist, B.; Morén, T. The Influence of Wood Polymers and Extractives on Wood Colour Induced by Hydrothermal Treatment. *Holz Roh Werkst.* **2002**, *60*, 375–376. [CrossRef]
16. Jirouš-Rajković, V.; Šefc, B. *Vrste Drva s Naslovnica Časopisa Drvna Industrija*; Faculty of Forestry, University of Zagreb: Zagreb, Croatia, 2019.
17. *ASTM 193-06*; Standard Specification for Reagent Water. ASTM International: West Conshohocken, PA, USA, 2011.
18. Timar, C.M.; Varodi, A.; Hacibektasoglu, M.; Campean, M. Color and FTIR analysis of chemical changes in beech wood (*Fagus sylvatica* L.) after light steaming and heat treatment in two different environments. *BioResources* **2016**, *11*, 8325–8343. [CrossRef]
19. Banadics, E.A.; Tolvaj, L. Colour modification of poplar wood by steaming for brown colour. *Eur. J. Wood Prod.* **2019**, *77*, 717–719. [CrossRef]
20. Tolvaj, L.; Papp, G.; Varga, D.; Lang, E. Effect of steaming on the colour change of softwoods. *BioRes* **2012**, *7*, 2799–2808. [CrossRef]
21. Preklet, E.; Tolvaj, L.; Banadics, E.A.; Alpar, T.; Varga, D. Colour modification and homogenisation of larch wood by steaming. *Wood Res.* **2019**, *64*, 811–820.
22. Pandey, K.K. A Study of Chemical Structure of Soft and Hardwood and Wood Polymers by FTIR Spectroscopy. *J. Appl. Polym. Sci.* **1999**, *71*, 1969–1975. [CrossRef]
23. Pandey, K.K.; Pitman, A.J. FTIR studies of the changes in wood chemistry following decay by brown-rot and white-rot fungi. *Int. Biodeterior. Biodegrad.* **2003**, *52*, 151–160. [CrossRef]
24. Colom, X.; Carillo, F.; Nogués, F.; Garriga, P. Structural analysis of photodegraded wood by means of FTIR spectroscopy. *Polym. Degrad. Stab.* **2003**, *30*, 543–549. [CrossRef]
25. Tjeerdsma, B.F.; Militz, H. Chemical changes in hydrothermal treated wood: FTIR analysis of combined hydrothermal and dry heat-treated wood. *Eur. J. Wood Wood Prod.* **2005**, *63*, 102–111. [CrossRef]
26. Gierlinger, N.; Goswami, L.; Schmidt, M.; Burgert, I.; Coutand, C.; Rogge, T.; Schwanninger, M. In situ FT-IR microscopic study on enzymatic treatment of poplar wood cross sections. *Biomacromolecules* **2008**, *9*, 2194–2201. [CrossRef] [PubMed]
27. Esteves, B.; Marques, A.V.; Domingos, I.; Pereira, H. Chemical changes of heat treated pine and eucalypt wood monitored by FTIR. *Maderas. Cienc. Tecnol.* **2013**, *15*, 245–258. [CrossRef]
28. Hao, Y.; Pan, Y.; Du, R.; Wang, Y.; Chen, Z.; Zhang, X.; Wang, X. The Influence of a thermal treatment on the decay resistance of wood via FTIR analysis. *Adv. Mater. Sci. Eng.* **2018**, 8461407. [CrossRef]
29. Chen, C.-L. Lignins: Occurrence in woody tissues, isolation, reactions, and structure. In *Wood Structure and Composition*; Lewin, M., Goldstein, I.S., Eds.; Marcel Dekker Inc.: New York, NY, USA, 1991; pp. 183–261.
30. Burtin, P.; Jay-Allemand, C.; Charpentier, J.-P.; Janin, G. Natural wood colouring proces sin Juglans sp. (*J. nigra*, *J. regia* and hybrid *J. nigra* 23 × *J. regia*) depends on native phenolic compounds accumulated in the transition zone between sapwood and heartwood. *Trees* **1998**, *12*, 258–264. [CrossRef]
31. Mitsui, K.; Takada, H.; Sugiyama, M.; Hasegawa, R. Changes in the Properties of Light-Irradiated Wood with Heat Treatment. Part 1. Effect of Treatment Conditions on the Change in Color. *Holzforschung* **2001**, *55*, 601–605. [CrossRef]
32. Dzurenda, L.; Dudiak, M. Effect of UV radiation on change in color of steamed beech wood. *Wood Res.* **2022**, *67*, 361–371. [CrossRef]
33. Banadics, E.A.; Tolvaj, L.; Varga, D. Colour Stability of Steamed Poplar Wood during Short-Term Photodegradation. *BioRes* **2019**, *14*, 8250–8256. [CrossRef]
34. Hofmann, T.; Tolvaj, L.; Visi-Rajczi, E.; Varga, D. Chemical Changes of Steamed Timber during Short-Term Photodegradation Monitored by FTIR Spectroscopy. *Eur. J. Wood Prod.* **2022**, *80*, 841–849. [CrossRef]
35. 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. [CrossRef]
36. Dzurenda, L. The Shades of Color of Quercus Robur L. Wood Obtained through the Processes of Thermal Treatment with Saturated Water Vapor. *BioRes* **2018**, *13*, 1525–1533. [CrossRef]
37. Výbohová, E.; Geffertová, J.; Geffert, A. Impact of Steaming on the Chemical Composition of Maple Wood. *BioRes* **2018**, *13*, 5862–5874. [CrossRef]
38. Banadics, E.A.; Tolvaj, L.; Varga, D. Steaming of poplar, black locust and beech timbers simultaneously to investigate colour modification effect of extractive transport. *Drewno* **2022**, *65*, 1–11. [CrossRef]