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Color changes of ash wood (*Fraxinus excelsior* L.) caused by thermal modification in air and steam

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Abstract: *Color changes of ash wood (Fraxinus excelsior L.) caused by thermal modification in air and steam.* Ash wood samples of 20x20x30 mm were subjected to thermal modification in different conditions. The thermal modification was conducted in air at 190 °C and in steam at 160 °C. For both environments modification lasted 2, 6 and 10 hours. Samples color parameters were measured before and after thermal modification on the basis of the mathematical CIELab color space model. Changes in all parameters (L, a and b) were observed, the highest in lightness (L) - darker color. The total color difference (ΔE) and chromaticity change (ΔC) were calculated for all samples. The highest value of ΔE was obtained for wood modified in the air at 190 °C for 10 h. The highest value of ΔC was obtained for wood modified in steam at 160 °C for 10 h. However, the value obtained for wood modified in the air at 190 °C for 10 h were only slightly lower.

Keywords: ash wood, CIELab color space, total color difference, thermal modification of wood

INTRODUCTION

Ash trees are common throughout Poland and are wild forest trees. About 65 species of ash trees are known to grow in our climatic conditions. Only one species has been recognised in other conditions. Ash trees are one of the oldest genera existing on earth, for more than 10 million years (Pliocene) they inhabit the planet (Tomanek 1970). Ash wood is used to make: furniture, parquets, laminated boards and floor boards, ornaments, countertops, wainscoting, veneers, facings, sports equipment and structural timber for interior construction. It is dimensionally stable, hard, easily hydrothermally treatable and easily impregnated in the sapwood zone. It glues well together and accepts paint and varnish coatings well. Ash wood is unfortunately characterized by low durability in atmospheric conditions and is not recommended for outdoor use.

Thermal modification is defined as the application of high temperatures to wood, resulting in a change in the chemical composition of the wood and the structure of its polymers. As a consequence of the process, the physical and chemical properties of the material change (Hill, 2006). Thermal modification is used to enhance the aesthetic and functional qualities of wood obtained from trees of commonly occurring species in a particular region or to increase their resistance to the damaging effects of environmental factors. In Poland, the wood of the most expensive species, such as ash, elm and oak, is also modified in order to increase its value by changing its color, increasing its hardness, resistance to biocorrosion, and moisture resistance. However, the thermal modification often encounters problems which are mainly due to the modification method which is not optimized in accordance to the species of wood which causes a number of functional defects e.g.: difficulties in adhesion of paint and varnish coatings to thermally treated wood. The use of thermally modified wood both inside and outside buildings is diverse. Most often, wood modified in this way is used for parquet flooring, facade and terrace boards, garden furniture and constructions, panelling and is also used to equip saunas (Metsä-Kortelainen, 2004). As a result of a thermal modification, the wood darkens. The color ranges from light brown

to dark brown. The change of color applies to the entire wood, not just the surface, which is very important during processing and product operation.

During the modification of spruce and oak wood, new chromophores (especially carbonyl and carboxyl groups) are formed by oxidation. The methoxyl groups and bonds in the lignin are cleaved. At higher modification temperatures lignin is condensed. Cleavage of acetyl groups from polysaccharides also occurs. The colour change is also strongly influenced by a higher proportion of extraction compounds related to the decomposition of hemicelluloses (Sikora et al. 2018).

To determine color changes a CIELab color system can be applied. CIELab is currently the most popular way to describe color and is the basis of modern color management systems. It describes color as three values: L for perceptual lightness and a and b for the four colors of unique human vision – a-axis is for green-red colors, and b-axis for blue-yellow. The CIELab space allows to quantify the color changes and makes it easier to assess the magnitude of color deviation with measurement equipment.

The study of colour changes in wood modified by thermal treatment has aroused interest. The relationship between these changes and weight loss, equilibrium moisture content and mechanical strength has been investigated (Bekhta and Niemz 2003; Patzelt et al. 2003; Brischke et al. 2007). However, the colour change is so unique for modification parameters and wood species that even many researchers investigated it the information are still not full. Especially in some works, only ΔE (total color change) is described, not focusing on single parameters (L, a, b) changes and ΔC (chromaticity change).

In this study, the effect of thermal modification in popular modification conditions - air at 190 °C and steam at 160 °C - on color change was investigated. Color change was analysed by change of L (lightness), a (green-red color change), b (blue-yellow color change) and the intensity change described by calculating ΔC and at the end the total color change by ΔE.

MATERIAL AND METHODS

Samples made from the wood of ash trees (*Fraxinus excelsior* L.) were used in this study. These samples were cut from boards obtained from the unstained part of heartwood. The material was seasoned at 20±2 °C and 65±5% relative humidity for three months. Samples of dimensions 20×20×30 mm were cut. The moisture content of wood samples was determined with the drying and weighing method (PN-77/D-04100) and was 12%. Samples with defects were excluded from the testing. The remaining samples were divided into ten groups according to their density so that both the average density of the groups was similar and each group contained a similar number of samples within a specific density range. The density was determined according to PN-77/D-04101.

A total of over 192 samples were used for the study. The average density of the groups measured for all groups was 742,2 kg/m3. The average standard deviation of the density for the groups given was 39,2 kg/m3. The average density for each group of control samples used for thermal modification. The densities are presented in Tab. 1.

Table 1. General characteristics of sample groups used for thermal modification.

Group:	**1**	**2**	**3**	**4**	**5**	**6**
Modification environment	Air			Steam		
Modification time /h	2	6	10	2	6	10
Average group density /(kg/m^3)	741,2	741,4	741,7	742,8	743	743,2
Standard deviation	40	39,7	39,3	38,7	38,6	38,6

After completion of the thermal modification process, the samples were again placed at 20±2 °C and 65±5% relative humidity for the time required for them to reach a hygroscopic equilibrium state (approximately one month) as determined by the weight changes of the individual samples.

Thermal modification of ash in the air

Thermal modification conducted in laboratory dryer with hot air circulation Three groups of samples were modified in 2, 6 and 10 hours Figure 1.

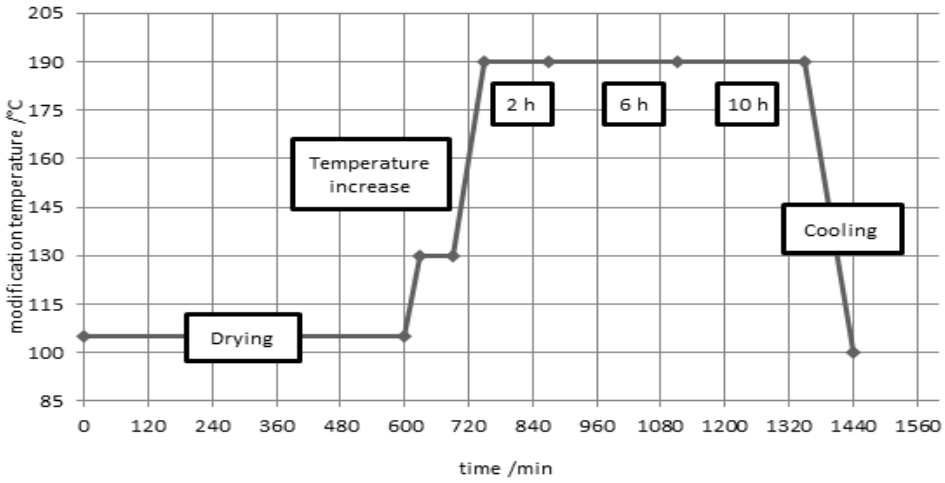

Figure 1. Ash thermal modification process flow (Gawron 2012).

Before modification samples were dried to an absolutely dry state. In the next step, the temperature was raised to 130 °C at a rate of 1 °C/min, this temperature was maintained for 30 minutes, and the temperature was raised again to 190 °C at a rate of 1 °C/min. Once the assumed modification temperature was reached in the dryer chamber, a countdown was started for the actual modification lasting 2, 6, or 10 hours. After the set time, the samples were cooled for 60 minutes, to ambient temperature, in the oven in which the modification took place.

Thermal modification of ash in water vapor

Thermal modification in steam was carried out in a specially modified aluminium vacuum laboratory dryer with a continuously open-top exhaust stack. Three groups of samples (4, 5, 6) for which the actual modification process took 2, 6, and 10 hours at 190 °C, respectively, were used for the modification.

The modification was preceded by drying the samples to an absolutely dry state. The temperature was then raised to 130 °C at a rate of 1 °C/min while bringing distilled water to the cuvette at the bottom of the drying chamber. The temperature was maintained until ¾ of the applied water volume evaporated i.e. for about 60 minutes. The next step was to raise the temperature in the dryer chamber to 190 °C at a rate of 1 °C/min. After reaching the modification temperature in the dryer chamber, the countdown of the actual modification time lasting 2, 6 or 10 hours was started. During the process, the regularly evaporated water from the bottom of the drying chamber was replenished through an additional valve made in the wall of the chamber. After the set time, the samples were cooled down to ambient temperature for 60 minutes and placed in a desiccator.

Color measurement

Measurements were made using an SP60 spectrophotometer X-Rite Europe GmbH (Regensdorf, Switzerland) using a D65 illuminant. The sensor head was 8 mm in diameter.

The results of the measurements were developed on the basis of mathematical models of color space included in the standard CIE DS 014-4.3/E:2007. The parameters analyzed were the CIE L*a*b color space, ΔL lightness, Δa red-green, Δb - yellow-blue, ΔC chromaticity change and ΔE total color change.

RESULTS AND DISCUSSION

The changes of single measured parameters (ΔL, Δa, Δb) and total color difference (ΔE) and chromaticity change (ΔC) of ash wood are presented in Table 2.

Table 2. Color changes of ash wood caused by thermal modification with standard deviation (SD).

	T	h	ΔL	SD	Δa	SD	Δb	SD	ΔC	SD	ΔE	SD
		2	-25,1	4,0	0,0	1,0	1,9	2,9	1,8	3,0	25,4	3,9
air	190	6	-29,2	3,0	-1,1	1,0	-3,1	3,4	-3,3	3,5	29,6	3,2
		10	-32,2	3,3	-1,1	0,9	-4,4	2,1	-4,6	2,2	32,6	3,3
		2	-21,2	3,7	2,3	0,5	1,4	2,4	1,8	2,3	21,5	3,6
steam	160	6	-24,3	4,2	1,8	0,7	-0,8	2,8	-0,4	2,8	24,6	4,2
		10	-27,4	3,7	1,3	0,8	-4,2	3,3	-3,8	3,4	28,0	3,8

Based on the analysis of the obtained results, it was found that the greatest change among the measured parameters (L, a, b) occurred in the case of the parameter L for all the examined modifications. The performed tests confirmed the obvious organoleptic observations that the color of wood became darker under the influence of thermal modification, both carried out in the air and steam for all process times. The tests carried out enabled us to quantify that a greater change in color in the parameter L (brightness) occurred as a result of the modification in the air at 190 °C than in steam at 160 °C. Due to the two variable parameters (environment and temperature), it cannot be determined which parameter affects and to what extent, the difference in brightness change. The value increases with the duration of modification in both environments and temperatures. The longer the modification time the greater the change in brightness. A great decrease in the L parameter (brightness) is a sign that many visible-light absorbing components are formed during thermal modification.

The average value of the Δa parameter in the case of wood thermally modified in the air after 2 hours is almost zero - 0,01. In the case of wood modified in the air at 190 °C for 6 and 10 hours, the value of the Δa parameter takes on negative values, indicating that the color changes in the direction from red to green. The opposite is true for wood modified in steam - this parameter takes on positive values, which indicates a change in color in the direction from green to red. The small value of Δa for wood after all modifications indicates that the color change on the green-red axis is also small.

The parameter Δb (color change on the blue-yellow axis) takes values higher than the parameter Δa, but strongly lower than ΔL. Interestingly, this parameter increased after 2 hours of modification (in the air at 190 °C and in steam at 160 °C) and decreased after 6 and 10 hours. A similar tendency was also observed for rubberwood (*Hevea brasiliensis*) and silver oak (*Grevillea robusta*) thermally modified in the vacuum between 210 to 240 °C for 1 to 8 hours (Srinivas and Pandey 2012). In the case of investigated ash after thermal modification, it means that the color change in the first two hours of the process is in the blue to yellow direction, while after 6 and 10 hours the change is in the yellow to blue direction. When analyzing these results, it is important to take into account the high value of the standard deviation, which shows that these results are highly scattered, there is a large variation in color change. This is a perfectly understandable thing considering the material under study - wood. Wood is a material with non-uniform color, structure and chemical composition (Krzysik 1978, Prosiński 1984, Pettersen 1984). The color change occurring during thermal modification is also heterogeneous.

Based on the calculated parameter ΔC, the change in color intensity can be determined. In the case of both thermal modifications carried out, a more intense color was obtained after 2 hours of modification compared to the color of unmodified wood. Longer modification times, that is 6

and 10 hours, caused a decrease in color intensity of the modified wood and at the same time, the color darkening mentioned above.

The total color change ΔE calculated from all measured color parameters shows how much the newly obtained wood color differs from the color of unmodified wood. Classification of ΔE depending on the average capability of humans to distinguish color difference (Witzel et al. 1973, Wright 1928, Wyszecki and Fielder 1971):

0.0 < ΔE < 0.5 no color difference
0,5 < ΔE < 1,0 difference only perceivable for experienced observers
1,0 < ΔE < 2,0 minimal color difference
2,0 < ΔE < 4,0 perceivable color difference
4,0 < ΔE < 5,0 significant color difference
5,0 < ΔE different color.

The obtained color change ΔE ranged from 21,5 to 32,6 depending on the thermal modification parameters. Other researchers obtained similar values depending on the investigated wood species and parameters of a modification. For example, Kučerová et al. (2016) for silver fir wood after thermal modification in the air for 1 hour at 200 °C determined value of color change (ΔE) 21,95, Čabalová et al. (2018) for oak wood after thermal modification in air 180 °C - 20,76 and at 200 °C determined the ΔE - 32,20, Cirule and Kuka (2015) for ash (Fraxinus excelsior) sapwood and heartwood thermal treatment t in a water vapour medium for 1 hour at 170 °C obtained values of ΔE - 50,0 and 36,1, respectively. For all samples examined, the color change obtained is perceived by the human eye as an obvious color change. This classification is mainly used for smaller color changes where it is not clear whether the color difference will be perceived by the "average" human eye. By quantifying the color change, the assessment becomes objective and repeatable in contrast to an organoleptic examination. In both environments in which ash wood was modified, the color change is greater the longer the time of modification.

Color change is a complex phenomenon and a number of parameters are used to describe it. The color change can be manifested not only in color change, but also in brightness or color intensity. The evaluation of color change effects after thermal modification gives the impression of a simple process. Especially since organoleptic evaluation seems to be obvious. However, the multitude of possible parameters indicates a high level of complexity of the issue, which needs to be analyzed in detail as it affects the consumer's perception of the final product and its commercial success.

CONCLUSIONS

Based on the conducted study of selected indicators of thermally modified ash wood color change, the following conclusions were formed:

1. The greatest change among the studied color parameters was observed for parameter L (lightness). The changes of parameters a and b showed much smaller values, with bigger changes in parameter b than in parameter a.
2. The greatest value of chromaticity change (ΔC) was obtained for wood thermally modified in the air at 190 °C.
3. The greatest value of color change (ΔE) was obtained also for wood thermally modified in the air at 190 °C.
4. The color change of all examined samples is perceived by the human eye as an obvious color change - different color (ΔE> 5,0).
5. Increasing the modification time increases the color difference regardless of the modification environment used (steam, air).

6. Thermal modification in steam at 160 °C changes the color of ash wood much more gently than a thermal modification in the air at 190 °C.
7. Ash wood can be thermally modified to obtain an attractive color.

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Streszczenie: *Zmiany barwy drewna jesionowego (Fraxinus excelsior L.) pod wpływem modyfikacji termicznej w środowisku powietrza i pary wodnej.* Próbki drewna jesionowego o wymiarach 20x20x30 mm poddano modyfikacji termicznej w różnych warunkach. Modyfikację termiczną prowadzono w środowisku powietrza w temperaturze 190 °C oraz w środowisku pary wodnej w temperaturze 160 °C. W obu środowiskach modyfikacja trwała 2, 6 i 10 godzin. Parametry barwy próbek mierzono przed i po modyfikacji termicznej na podstawie matematycznego modelu przestrzeni barw CIELab. Zaobserwowano zmiany wszystkich parametrów (L, a i b), największe w jasności (L) - ciemniejsza barwa. Dla wszystkich próbek obliczono całkowitą różnicę barw (ΔE) oraz zmianę chromatyczności (ΔC). Największą wartość ΔE uzyskano dla drewna modyfikowanego w środowisku powietrza w temperaturze 190 °C przez 10 h. Największą wartość ΔC uzyskano dla drewna modyfikowanego w środowisku pary wodnej w temperaturze 160 °C przez 10 h. Natomiast wartość ΔC uzyskana dla drewna modyfikowanego w środowisku powietrza w temperaturze 190 °C przez 10 h była tylko nieznacznie niższa.

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