

## SURFACE CHANGES OF BEECH AND PINE WOOD UNDER THE INFLUENCE OF UV RADIATION

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### ABSTRACT

The influence of UV radiation on two different types of wood – European beech (*Fagus sylvatica* L.) and Scots pine (*Pinus sylvestris* L.) was studied. The chemical composition of the original wood of the monitored woods (TEE, holocellulose, cellulose and lignin) was determined by standard analytical procedures. Changes in color characteristics (brightness, lightness  $L^*$ , green-red coordinate  $a^*$ , blue-yellow coordinate  $b^*$  and total color difference  $\Delta E^*$ ) were measured at the irradiation times of 30, 60, 90, 120 and 150 minutes. Chemical changes in the surface layers of irradiated wood were monitored by ATR-FTIR spectroscopy. Chemical analysis of the monitored wood samples showed higher content of cellulose, lignin and extractives and at the same time lower content of holocellulose and also hemicelluloses in pine wood than in beech wood, which affected the differences in the color changes of irradiated wood. More significant color changes were observed in pine wood compared to beech wood. A decrease in brightness was 37% of the absolute value for pine and 31% for beech, a decrease in lightness  $L^*$  was 11% for pine and 9.7% for beech, and the total color difference  $\Delta E^*$  was 15.0 for pine and 11.3 for beech. The biggest color changes of color characteristics were recorded after the first 30 minutes of irradiation. The changes in the FTIR spectra of the surface of the irradiated wood showed that UV radiation caused the degradation of lignin and the formation of conjugated and unconjugated carbonyls and quinoid structures responsible for yellowing the wood surface. A decrease in the ratio of the absorbance A1510/A1370 (lignin / carbohydrates) was most significant after the first 30 minutes of irradiation (30% for pine and 43% for beech). However, an increase in carbonyl content was more significant in pine (3-fold increase) compared to beech (2-fold increase). The dependence of the ratio of "relative" lignin absorbances and carbonyls on the total color difference  $\Delta E^*$  in both monitored woods showed a linear increasing trend in the case of carbonyls and a slightly decreasing trend in the case of lignin.

**Key words:** beech, pine, UV radiation, chemical characteristics, CIEL<sup>\*</sup>a<sup>\*</sup>b<sup>\*</sup> color space, ATR-FTIR spectroscopy, lignin degradation, carbonyl formation.

### INTRODUCTION

Wood is a natural material with a cellular structure, which represents a complicated complex of heterogeneous macromolecular substances. The main components are: cellulose (35–50%), hemicellulose (20–35%), lignin (15–35%) and accompanying components (3–10%) (BUČKO 2001). There is a significant difference between the chemical composition in the wood of broad-leaved and coniferous trees. While the wood of coniferous trees contains

more cellulose, lignin and accompanying substances, the wood of broad-leaved trees contains more hemicelluloses.

The wood retains its original appearance for a long time, structure and properties under suitable exposure conditions. While in atmospheric conditions it undergoes permanent degradation processes under the influence of a number of abiotic factors. Sunlight is one of the most aggressive factors in wood damage (REINPRECHT 1998, KUBOVSKÝ *et al.* 2018).

HON and IFJU (1978) proved that different types of radiation penetrate only to very small depths of wood. While visible radiation (400 to 750 nm) penetrates to a depth of 200  $\mu\text{m}$ , UV radiation with wavelengths below 400 nm penetrates to a maximum of 75  $\mu\text{m}$ .

After absorption of the light quantum by wood, primary free radicals are formed, which are highly reactive and cause secondary radical chain reactions. These reactions can also cause chemical reactions in the deeper layers of wood. FEIST and HON (1984) state that the secondary degradation process takes place to a depth of about 2,500  $\mu\text{m}$ .

The degradation reactions indicated by visible radiation take place on the surface of lignocellulosic materials under long-term exposure. They are manifested by a change in the physical properties and color of their surface. Many wooden buildings, tiles, fences, roof shingles, or facade elements of buildings are long-term exposed to negative external influences, which cause the aging of wood and shorten its shelf-life. The root-cause of these changes is the interaction of wood components with radiation - especially with its ultraviolet (UV) component – as a result of a complex of chemical changes of lignin, polysaccharides and extractives. The magnitude of the changes depends on the chemical composition of the wood and the duration of UV radiation on its surface. Numerous oxidation and degradation reactions result to formation of new chromophores and changes of wood color.

The wood constituents show different capacities with respect to absorbing UV radiation. According to NORRSTRÖM (1969) lignin contributes 80-95%, the carbohydrates 5-20%, and the extractives about 2% to the absorption coefficient. The UV absorption occurs at chromophoric structural elements within the molecular network of lignin, such as phenolic hydroxyl groups,  $\alpha$ -carbonyl group, conjugated double bond, quinone, biphenyl or free radicals.

Photodegradation of wood is related to the interaction of lignin with the UV component of light. Lignin is extremely susceptible to UV radiation. The site of absorption is aromatic ring, unsaturated bonds and lignin carbonyl groups. The absorbed energy quantum is transferred to less stable chemical bonds and causes their homolytic cleavage (e.g.  $\beta$ -alkyl-aryl ether bonds (FENGEL and WEGENER 1984, HON and CHANG 1984, SOLÁR 2004). The resulting radicals – phenoxy-benzyl, hydroperoxide postulate both depolymerization and condensation reactions of lignin. New chromophoric structures are created and the wood darkens from yellow to brown shades.

The interaction of polysaccharides with the UV radiation leads to weight loss, depolymerization and, in the case of cellulose, also to a reduction in the  $\alpha$ -cellulose content. The chromophoric group in the interaction of cellulose with electromagnetic radiation is believed to be the grouping of oxygen atoms on the C1 carbon of the glucopyranose unit (formation of C1, C4 radicals). The resulting radicals react with oxygen to form unstable peroxy radicals causing the formation of other radicals (C2, C3, C5, C6). At the same time, the aldehyde and primary alcohol groups of the cellulose end units are oxidized, which after decarboxylation are converted to D-xylopyranose and D-arabinopyranose units (FENGEL and WEGENER 1984, SOLÁR 2004). High UV absorption and the strong capability of lignin autooxidation retard the photolytic degradation of cellulose (NORRSTRÖM 1969).

New chromophoric groups are formed simultaneously in the wood components (carbonyls, carboxyls, peroxides, hydroperoxides, quinoid structures and conjugated double

bonds), which increase the possibilities for the absorption of additional light quanta and the intensification of the photodegradation process (REINPRECHT 1998, SOLÁR 2004).

FEIST (1990) points to the high degradation of lignin and hemicelluloses in the surface layers of maple wood during accelerated aging. The erosion of the wood surface is related to the density of the wood and the lignin content.

Extractive wood components can also act as UV absorbers - they scavenge free radicals and are subject to photooxidation reactions. They are also slowing the photodegradation of lignin (CHANG *et al.* 2010, 2014).

The aim of the work was to compare the effect of UV radiation on two different types of wood – European beech (*Fagus sylvatica* L.) and Scots pine (*Pinus sylvestris* L.), which differ significantly in their chemical composition, and to determine the dependence of changes in color characteristics (brightness,  $L^*$ ,  $a^*$ ,  $b^*$ ,  $\Delta E^*$ ) with irradiation time as a consequence of chemical changes on the surface of irradiated wood.

## MATERIAL AND METHODS

The untreated beech and pine wood without defects, i.e. without knots, resin canals, biological damage or other defects was used for the experiments in which the main components of the wood were determined by standard chemical processes:

Ethanol–toluene solubility of wood	ASTM D 1107-96. Standard Test Method for Ethanol-Toluene Solubility of Wood – the determination of the ethanol-toluene soluble content of wood, which is a measure of the waxes, fats, resins, and oils, plus tannins and certain other ether-insoluble components
Polysaccharide fraction (holocellulose)	Method according to Wise – the action of $\text{NaClO}_2$ in acetic acid on sawdust after ethanol extraction [KAČÍK and SOLÁR 2000]
Cellulose	Kürschner–Hoffer method – repeated treatment with a mixture of nitric acid and ethanol [KAČÍK and SOLÁR 2000]
Lignin	ASTM D 1106 – 96. Standard Test Method for Acid Insoluble Lignin in Wood – two-stage treatment with sulfuric acid.

Samples of beech and pine (heart) wood with the dimension of  $100 \times 100 \times 20$  mm were used to monitor color changes depending on the time of exposure to UV radiation.

Wood samples (one piece from each tree species) were exposed to intense UV radiation by device Sirius UVIR with mercury lamp (125W) at time intervals 30, 60, 90, 120 and 150 minutes under normal laboratory conditions. The distance of samples from the UV radiation source was  $20 \pm 2$  cm (STN 50 0376). (Notice: mercury lamp is a strong UV emitter suitable for studying photodegradation employing short exposure times (TIMAR *et al.* 2016, TOLVAJ and VARGA 2012).

Brightness of irradiated wood samples was determined by device Leukometer for measuring reflectance according to STN ISO 3688 (brightness is defined by the reflectivity of the surface of the measured sample, expressed in % of the reflectivity of the basic brightness normal - magnesium oxide (MgO) - measured for an effective wavelength of  $457 \pm 5$  nm). Brightness of each sample were measured 10-times.

Surface color of irradiated wood samples was determined using the color reader CR-10, which is defined by the coordinates of the CIEL<sup>\*</sup> $a^*b^*$  color space ( $L^*$ ,  $a^*$ ,  $b^*$ ) and is evenly

perceptible over a wide range of colors (ISO 11664-4, HRČKA 2013, DZURENDA 2018). Color parameters  $L^*$ ,  $a^*$ ,  $b^*$  of each sample were measured 10-times and total color difference  $\Delta E^*$  was determined by the equation:

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

$(L_2^* - L_1^*)$  change the value of the white-black coordinate (lightness)

$(a_2^* - a_1^*)$  change the value of the green-red coordinate

$(b_2^* - b_1^*)$  change the value of the blue-yellow coordinate.

The surface of the beech and pine samples was subsequently analysed by the ATR-FTIR technique and the chemical changes of the main components on the surface of the wood were characterized by evaluating the obtained spectral records.

Fourier transform-infrared (FTIR) spectroscopy measurements were carried out using a Nicolet iS10 FTIR spectrometer equipped with Smart iTR attenuated total reflectance (ATR) sampling accessory with diamond crystal (Thermo Fisher Scientific). The resolution was set at  $4 \text{ cm}^{-1}$ , 32 scans were recorded for each analysis in an absorbance mode at the wavenumber range from  $4000 \text{ cm}^{-1}$  to  $650 \text{ cm}^{-1}$ . Four analyses were performed at four locations per sample, the average spectra from obtained spectra were created for each sample. The evaluating of spectra using the OMNIC 8.0 software (Thermo Fisher Scientific) was performed.

## RESULTS AND DISCUSSION

Basic chemical analysis was performed for a more detailed characterization of the examined beech and pine wood, which included the determination of the content of extractives (TEE), holocellulose, cellulose and lignin. The content of hemicelluloses was calculated as the difference from the content of holocellulose and cellulose (Table 1).

**Tab. 1 Chemical characteristics of beech and pine wood.**

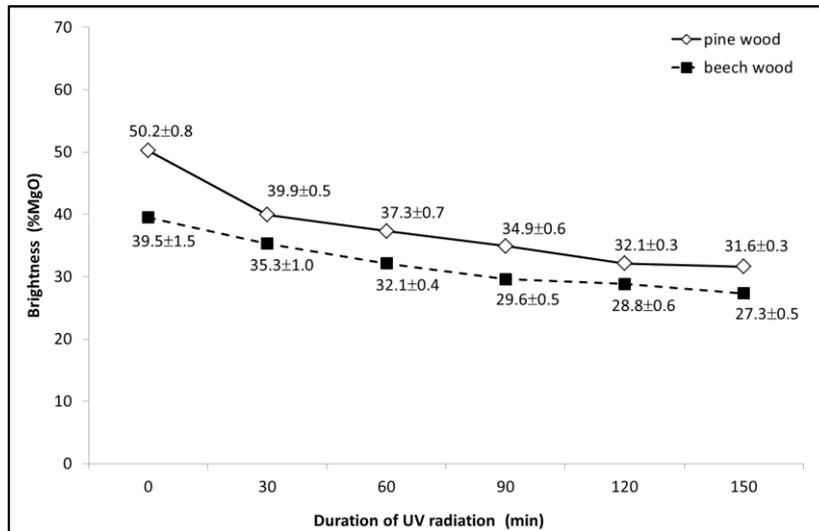
Wood sample	TEE (%)	Holocellulose (%)	Cellulose (%)	Hemicelluloses (%)	Lignin (%)
Beech	1,8	78,6	45,5	33,1	22,7
Pine	5,2	73,1	47,3	25,8	25,6

Chemical analysis of the monitored samples of beech and pine wood confirmed the generally known differences between the wood of coniferous and broad-leaved trees - more cellulose, lignin and extractives, but overall less polysaccharides (holocellulose) in the wood of coniferous trees than in the wood of broad-leaved trees.

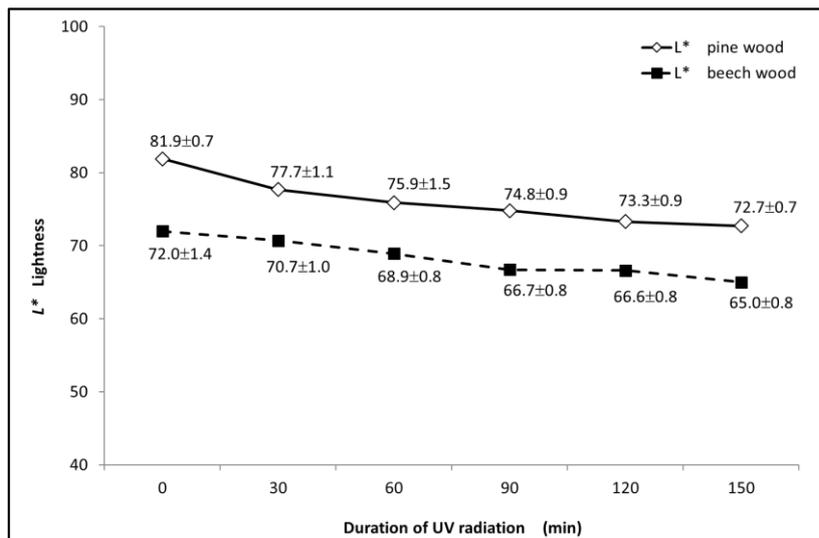
The exposure of the wood surface to UV radiation reduced the brightness. The pine sample showed a higher original brightness than the beech sample. Prolonged exposure to UV radiation decreased the brightness values of both trees (Fig. 1). The largest decrease in brightness was recorded after the first 30 minutes of irradiation, while in beech the value of brightness decreased by 4.2% MgO, in pine wood by up to 10.3% MgO. The total decrease in the brightness of the wood surface in the observed time of UV exposure (150 min) was 18.6% MgO for pine and 12.2% MgO for beech.

The evaluation using color coordinates - lightness  $L^*$  (black-white),  $a^*$  (green-red) and  $b^*$  (blue-yellow) in the color space  $CIE L^* a^* b^*$  represents more objective expression of color changes on the wood surface.

The  $L^*$  coordinate, characterizing the lightness of the measured surface, was higher in the case of pine wood in the entire observed irradiation time range. During the 150-minutes exposure, it decreased by 9.2 (by 11%), while in beech the decrease in lightness was by 7.0 (by 9.7%) (Fig. 2).



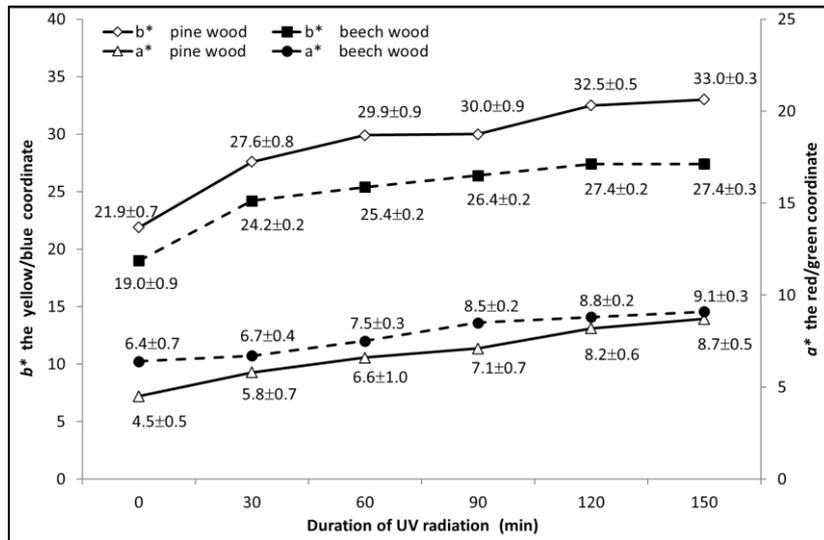
**Fig. 1** Changes in the brightness of the wood surface during irradiation.



**Fig. 2** Changes in the lightness of the wood surface during irradiation.

Changes in the coordinates  $a^*$  and  $b^*$  at 30 minute UV intervals are shown in Fig. 3. Larger changes (shifts in color space) were registered for pine wood.

The  $a^*$  coordinate, characterizing the position in the green-red part of the color space, reported higher values in the original beech sample and also in the whole monitored irradiation range than in the pine. The  $a^*$  coordinate shifted to the red area due to UV radiation in both woody plants. Pine increased from an average of 4.5 to 8.7 (1.9-fold increase) and beech from 6.4 to 9.1 (1.4-fold increase). The shift of the  $a^*$  coordinate to the red region is associated by some authors with the content and photodegradation of extractive substances (PERSZE and TOLVAJ 2012, TIMAR *et al.* 2016).



**Fig. 3** Changes in color coordinates  $a^*$  and  $b^*$  during irradiation.

The average values of the  $b^*$  coordinate, characterizing the blue-yellow area of the color space, were higher for the original pine wood and also in the entire observed irradiation time range. A shift to the yellow area was noted for both trees. The shift was higher for pine wood by 11.1 (50%), for beech by 8.4 (44%).

According to several authors, yellowing of the wood surface due to UV radiation is associated with the degradation of lignin and the formation of new structures - quinones, quinonemides, stilbenes and diphenyls (HON and GLASSER 1979, GIERER and LIN 1972, GELLERSTEDT and PETTERSSON 1977, MÜLLER *et al.* 2003, KUBOVSKÝ *et al.* 2016). However, some authors also attribute the yellowing to the formation of chromophore groups (carbonyls, carboxyls and hydroperoxides) during cellulose irradiation (KLEINERT and MARRACCINI 1966 a,b, KLEINERT 1969, HON 1979).

It could be concluded from the measured values of the coordinates  $a^*$  and  $b^*$  that the blue-yellow coordinate  $b^*$  shows larger changes comparing to green-red coordinate  $a^*$  and also more significant changes of both coordinates in the pine wood. In Fig. 4, a gradual increase in the intensity of the yellow-red hues with a prolonged exposure time to UV radiation can be seen on the beech and pine wood samples.



**Fig. 4** Color changes on the pine and beech wood surface during the exposure to UV radiation.

The evaluation of the color coordinates  $L^*$ ,  $a^*$ ,  $b^*$ , expressed in terms of the total color difference ( $\Delta E^*$ ), showed that the largest change in the wood surface color in both trees was recorded in the first 30 minutes of irradiation (Fig. 5). This conclusion is in accordance with the views of many authors who state that photodegradation effects of UV radiation occurs rapidly at the beginning of exposure and slows down with the time (BAAR and GRYC 2012, TOLVAJ and FAIX 1995, TOLVAJ and MITSUI 2010, AGRESTI *et al.* 2001, CALIENNO *et al.* 2014, GEFFERTO VÁ *et al.* 2016, KÚDELA and KUBOVSKÝ 2016, TIMAR *et al.* 2016, GEFFERTO VÁ *et al.* 2018).

The total color difference  $\Delta E^*$  reached a value of 7.2 for pine wood after 30 minutes of irradiation, and due to the commonly used color change scale (ALLEGRETTI *et al.* 2009), the change can be classified up to level 5, which is defined as "high color difference" for  $6 < \Delta E^* < 12$ . The total color difference increased with increasing irradiation time and after 150 minutes reached the value of 15.0, which according to the given scale is "difference colors". The largest change  $\Delta E^*$  for pine wood in the photodegradation of six woods is also reported by TIMAR *et al.* (2016).

$\Delta E^*$  of beech wood after 30 minutes of irradiation reached a value of 5.4 and classification into the 4th degree of color change, which is characterized for  $3 < \Delta E^* < 6$  as "color difference visible with medium quality screen" and after 150 minutes of irradiation reached color difference value 11.3 (high color difference).

The effect of UV radiation was manifested by a visible darkening and a change in the shade of the surface of the samples of pine and beech wood (Fig. 4), which is related to the chemical composition of the wood (Table 1) and changes in its chemical components. This fact was also reflected in the values of the total color difference  $\Delta E^*$ , where e.g. a value of 7.2 was reached for pine wood after only 30 minutes of exposure to UV radiation, while beech wood has reached the given value of color change until after 60 minutes of irradiation.

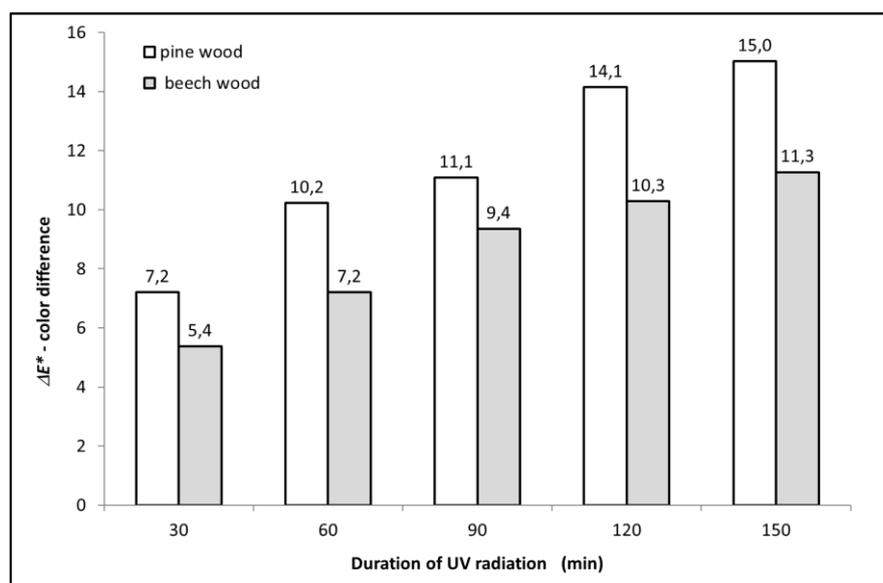
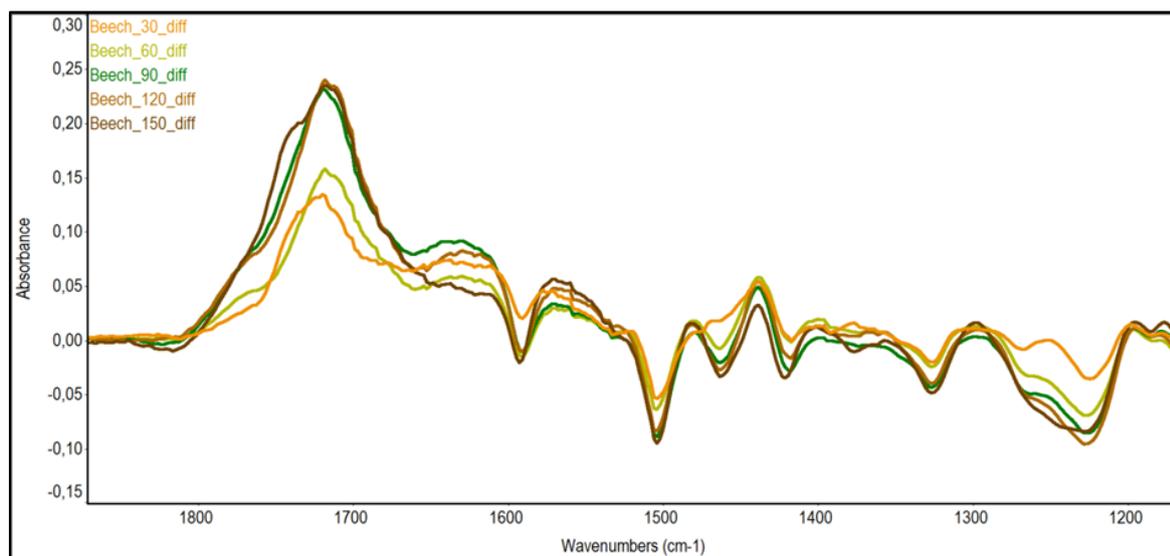


Fig. 5 Changes of the color difference  $\Delta E^*$  by UV radiation.

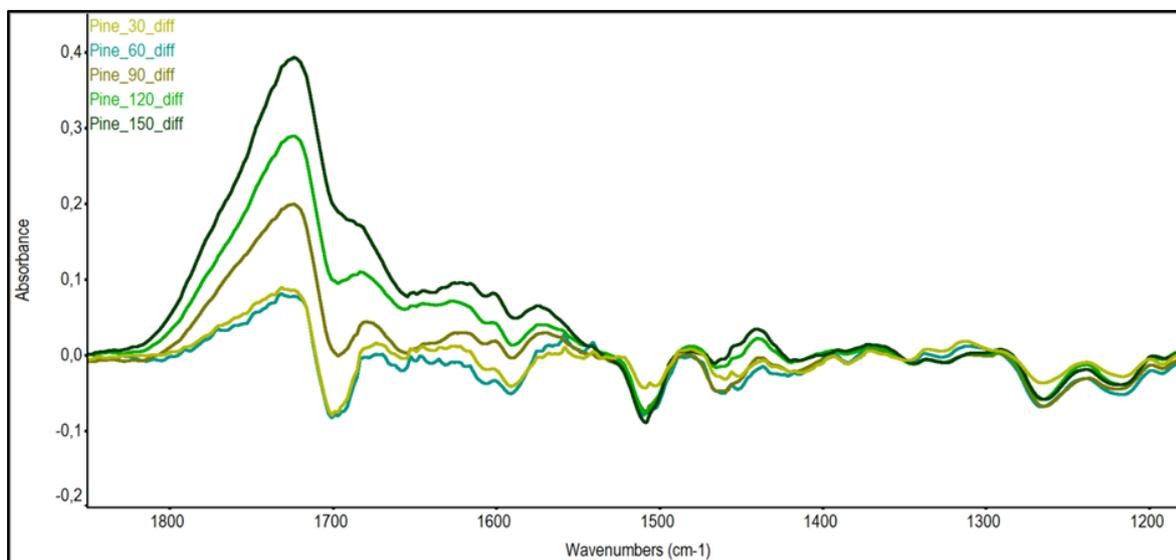
Originally lighter pine wood with  $L^* = 81.9$ , darkened more due to irradiation ( $\Delta L^*$  pine = 9.2) than the original beech wood with  $L^* = 72.0$  ( $\Delta L^*$  beech = 7.0). More lignin (25.6%) and extractives (5.2%) were determined in pine wood than in beech wood (22.7% and 1.8%). Lignin and phenolic extractives act as absorbers of UV radiation due to their chemical structure. Their aromatic rings, unsaturated bonds and carbonyl groups interact with UV radiation, resulting in homolytic cleavage to form a variety of radicals. The

absorbed energy quantum is then transferred to the surrounding, less stable chemical bonds, and causes secondary photodegradation reactions of the other components of the wood. In addition to degradation reactions, condensation reactions also take place and result to the formation of new chromophoric structures that visually manifest by darkening of the wood surface (FENGEL and WEGENER 1984, SOLÁR 2004).

Thin samples of  $10 \times 10$  mm in size were taken from the surface of irradiated beech and pine wood samples after color measurement in order to assess chemical changes by FTIR spectroscopy. The observed differential FTIR spectra are presented in Figures 6 and 7.



**Fig. 6 Differential FTIR spectra of beech wood.**



**Fig. 7 Differential FTIR spectra of pine wood.**

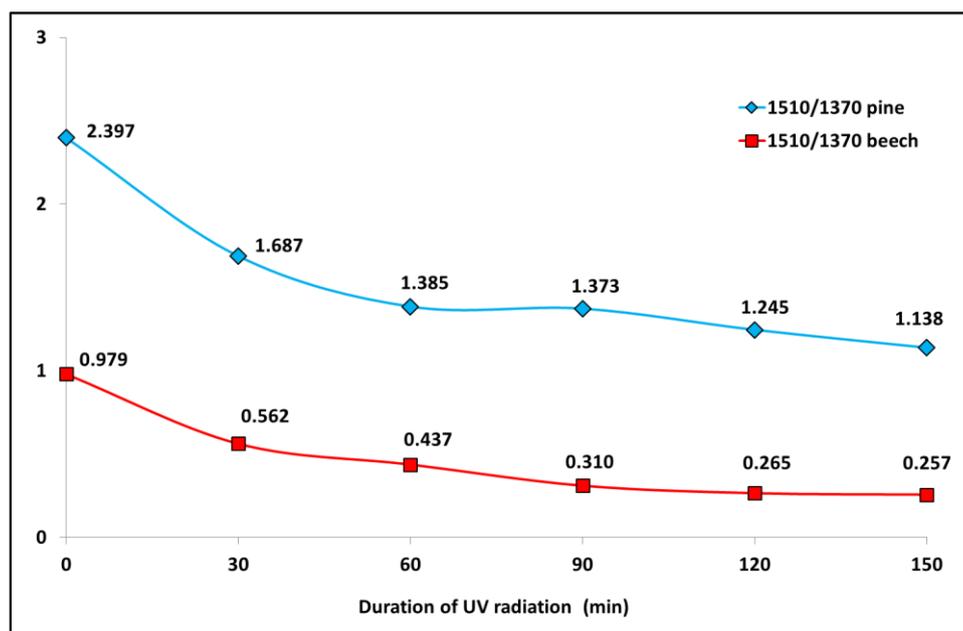
They show changes in chemical components in the upper region of the so-called "fingerprint" ( $1200\text{--}1800\text{ cm}^{-1}$ ) that occurred in the surface layers of the wood due to UV radiation, compared to the original wood.

The differential spectra of both tree species show the decrease in absorption within the range of  $1200\text{--}1300\text{ cm}^{-1}$ . In the case of pine, the decrease is more intensive at  $1267\text{ cm}^{-1}$ . This fact indicates degradation of guaiacyl ring, which is the main structural component in the

lignin macromolecule of conifers. In the case of beech, the decrease is more intensive at  $1229\text{ cm}^{-1}$ . This band is characteristic for syringyl ring in hardwoods lignin and xylan (HON 2001). The decrease in absorption around  $1462\text{ cm}^{-1}$  also indicated the degradation of lignin and hemicelluloses. Hemicelluloses and amorphous cellulose also degraded by UV radiation, but less than lignin (COGULET *et al.* 2016).

A visible decrease in the absorbance of the aromatic lignin band at  $1510\text{ cm}^{-1}$ , in combination with an increase in the carbonyl bands in the range between  $1660$  and  $1800\text{ cm}^{-1}$ , proves the course of the light-induced oxidation reactions. Significant formation of new conjugated and aromatic carbonyls as well as quinones can be observed in the region of  $1660\text{--}1700\text{ cm}^{-1}$  and the formation of unconjugated aliphatic carbonyls in the region of  $1700\text{--}1800\text{ cm}^{-1}$  (PANDEY 2005, LIU *et al.* 2016). Production of unsaturated carbonyl compounds (quinones) is related to wood discoloration. According to FEIST and HON (1984) the oxidation of cellulose also contributed to increment of carbonyl groups.

The progress of the chemical changes on the surface of the monitored samples of beech and pine wood was observed on the absorption bands A1510 (for lignin) and A1730 (for unconjugated aliphatic carbonyls) in relation to the duration of UV radiation - Figures 8 and 9. The intensity of the chemical changes was expressed as the ratio of the absorbance of the selected chemical component and the relatively stable carbohydrate band at  $1370\text{ cm}^{-1}$ , which was used as a reference.



**Fig. 8 Change of A1510/1370 ratio during irradiation.**

Fig. 8 shows the changes in the A1510/1370 ratio during irradiation for both monitored trees determined from the difference graphs. The trend in the decrease in lignin content in the wood surface layers was similar in both wood species, while the picture also shows a higher content of lignin in pine wood.

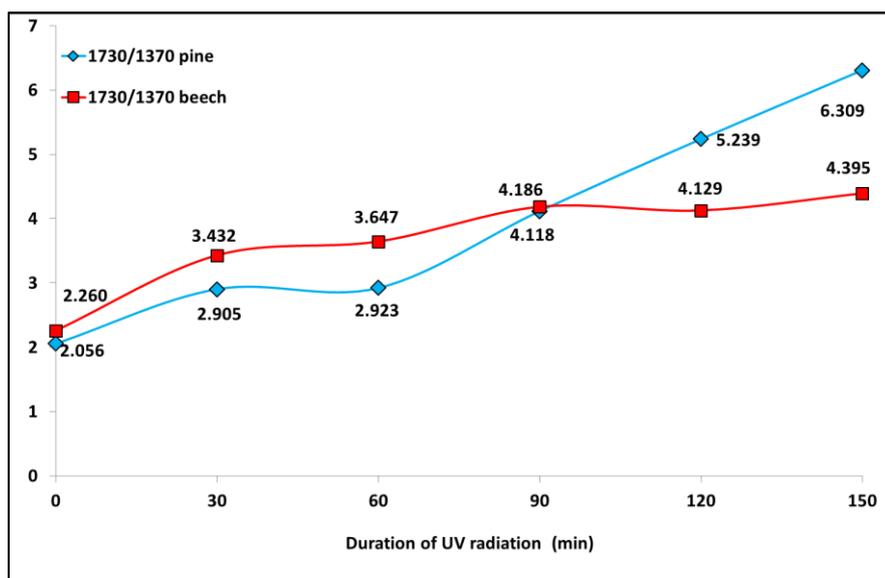


Fig. 9 Change of A1730/A1370 during irradiation.

Fig. 9 shows changes in the A1730/1370 ratio during irradiation of both monitored trees. The increasing trend of the content of unconjugated carbonyls in the wood surface layers was much more significant in pine, where the increase in the proportion of A1730/1370 was 3 times higher than the original value, while in beech the increase was only 2-fold.

The chemical changes of lignin and unconjugated carbonyls during UV exposure, which caused color changes in the wood surface, are shown in Figures 10 and 11.

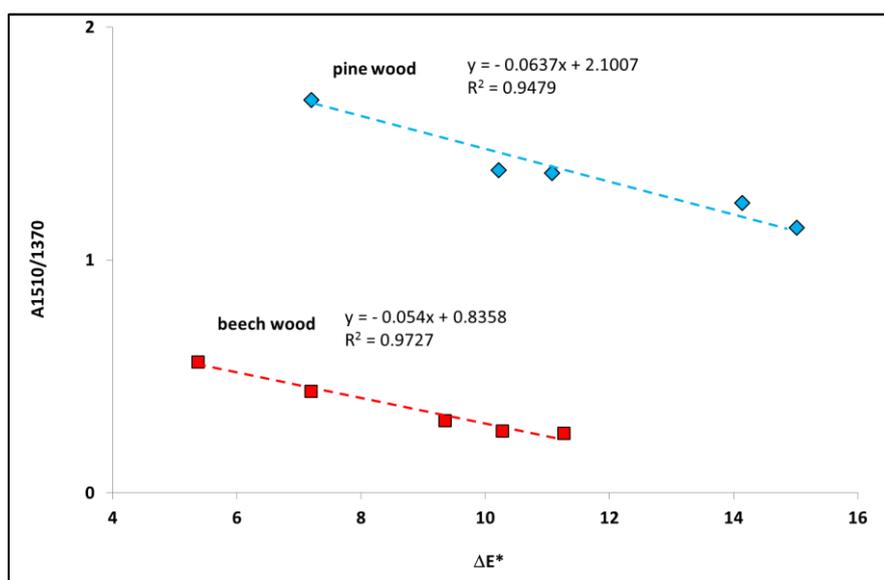


Fig. 10 Dependence of the A1510/1370 ratio on the total color difference  $\Delta E^*$ .

The relationship between the total color difference  $\Delta E^*$  and the values that characterize the lignin relative content (A1510/1370) is shown in Fig. 10. The course of dependence showed a decreasing trend of (A1510/1370) ratio related to decomposition of lignin due to photodegradation. It could be concluded that for both wood species it is a linear dependence.

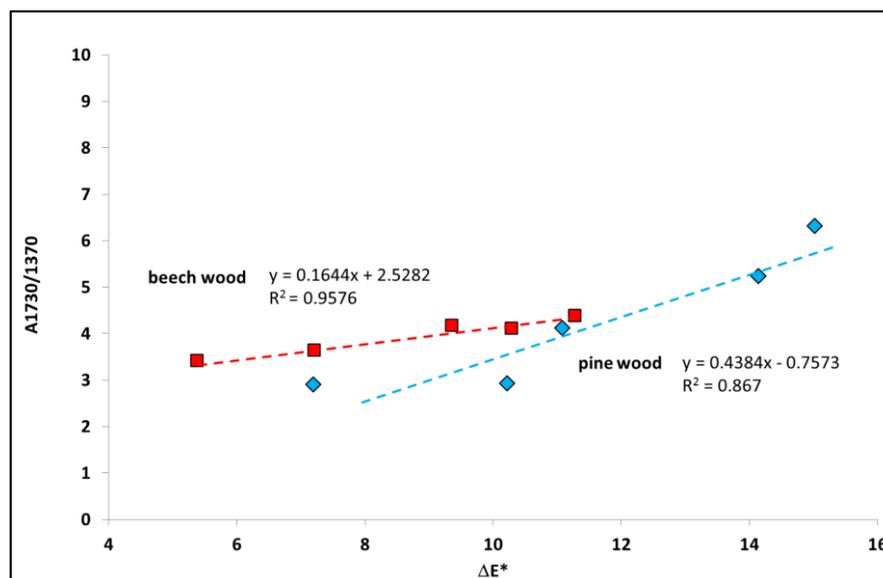


Fig. 11 Dependence of the A1730/1370 ratio on the total color difference  $\Delta E^*$ .

Figure 11 is showing that the total color difference  $\Delta E^*$  of the two woods is linearly correlated with the ratios of the corrected area of the relevant absorption bands A1730/A1370. The course of dependencies showed an increase in unconjugated carbonyl groups (A1730/A1370) as a result of photooxidation reactions, which is consistent with the conclusions of TIMAR *et al.* (2016).

The differences between the monitored trees (beech, pine) are resulting from the differences in their chemical composition. This applies to the content of lignin, hemicelluloses and also to the content of extractives, which are significantly higher in pine wood than in beech wood. The faster and uneven increase in the carbonyl content can be attributed to the effect of UV radiation on the non-lignin components of the wood (polysaccharides and extractives), as well as the heterogeneity of the wood. Similar conclusions were reached in their work by TIMAR *et al.* (2016) and MÜLLER *et al.* (2003), that tried to express the relationship between carbonyls and  $\Delta E^*$  by nonlinear polynomial dependence.

## CONCLUSION

Chemical analysis of the monitored samples of beech and pine wood confirmed higher content of cellulose, lignin and extractives in pine wood than in beech wood. At the same time, an overall lower content of holocellulose and also hemicelluloses was determined in pine wood.

Although the chemical composition of the original wood of the two monitored woods was different, the trends of changes in color characteristics due to radiation were similar - decrease in brightness and lightness, increase in green-red coordinate  $a^*$ , blue-yellow coordinate  $b^*$  and total color difference  $\Delta E^*$ , whereas the changes were more significant in pine wood.

The largest changes of color characteristics were recorded after the first 30 minutes of irradiation. The changes of color characteristics in other time intervals were less significant. While the lightness values  $L^*$  were decreasing, the coordinate values  $a^*$  and  $b^*$  increased. It was observed a shift to the red and yellow areas of the color space with more significant

increase in the values of the  $b^*$  coordinate than the increase in the values of the  $a^*$  coordinates.

The total color difference  $\Delta E^*$  showed a steady increase with prolonging irradiation time, whereas the  $b^*$  coordinate contributing the most to its change.

Changes in the FTIR spectra of the surface of the irradiated wood showed that UV radiation caused lignin degradation and the formation of conjugated and unconjugated carbonyls and quinoid structures due to the photooxidation reactions of the wood components responsible for yellowing of the wood surface.

The decrease in lignin content in the surface layers of wood due to UV radiation was similar in both woods, but the increase in carbonyl content was more significant in pine compared to beech.

The dependence of the ratio of "relative" absorbances of lignin and carbonyls on the total color difference  $\Delta E^*$  in both monitored woods showed a linear increasing trend in the case of carbonyls and a slightly decreasing trend in the case of lignin.

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