

THE EFFECT OF UV IRRADIATION ON THE COLOUR CHANGE OF THE SPRUCE WOOD

Jarmila Geffertová – Anton Geffert – Eva Výbohová

ABSTRACT

The effect of UV irradiation on the colour changes of the surface of spruce wood was evaluated in relation to the chemical changes of the main wood components. The colour changes were carried out by measuring CIELab characteristics (L^* , a^* , b^* and ΔE^*). ATR-FTIR spectroscopy was used to study chemical changes caused by irradiations.

UV irradiation resulted in rapid colour changes of the surface of spruce wood that are mostly related to lignin photodegradation and increased content of new chromophoric groups. FTIR analysis confirms the wood sensitivity to UV irradiation. In consequence of UV irradiation the characteristic bands of lignin decreased significantly. The intensity of the bands associated mainly with carbohydrates is not significantly affected by UV irradiation. A combined analysis of FTIR ratio with colour changes showed an increasing trend of b^* coordinate, indicating by yellowing. The yellowness increased while the relative ratio lignin/carbohydrates decreased and the relative ratio carbonyl/carbohydrates increased.

Key words: spruce wood, UV irradiation, colour changes, ATR-FTIR spectroscopy, CIELab colour space, lignin degradation.

INTRODUCTION

Spruce wood is a material often used in the exterior exposed to external conditions for a long time causing wood aging and associated colour change. One of the most negative influences is solar radiation, the UV component of which causes photochemical reactions of the individual wood components (REINPRECHT *et al.* 2011).

Lignocellulosic materials undergo degradation reactions indicated by light, which are reflected by changing their mechanical and physicochemical properties (change of initial colour, loss of gloss, roughening and cracking). The resulting colour shade of wood is the result of complex chemical changes of extractives, polysaccharides and lignin. The main cause of these changes is the interaction of polysaccharides and lignin with light, especially with its close UV-A component combined with humidity, temperature and oxidizing agents (ANDRADY *et al.* 1998, KUBOVSKÝ and KAČÍK 2009, MIKULA *et al.* 2001, ROSU *et al.* 2010).

The polysaccharides and UV light component interact and cause mass loss, depolymerization and also the reduction of the α -cellulose content in cellulose. It is assumed that the chromophore group in the cellulose interaction with electromagnetic radiation is a grouping of oxygen atoms on the C1 carbon of the glucopyranose unit (FENGEL and WEGENER 1984).

Lignin plays an important role in the degradation of polysaccharides, because it indicates secondary photodegradation reactions of the other components by energy transfer from excited α -carbonyl groups to the environment. The aldehyde and primary alcoholic groups of reducing cellulose terminal units are simultaneously oxidized by the action of light on wood in the presence of oxygen. Lignin undergoes the interaction with its UV component (λ 180–300 nm) at light exposure. A particular site of absorption of UV radiation is phenolic hydroxyl groups, aromatic nuclei, unsaturated bonds and carbonyl groups. α -carbonyls and π -bonds in the side chains of phenyl propane units have the ability to transmit absorbed energy quantum (photon) to less stable bonds in the immediate vicinity and cause them homolytic cleavage (FENGEL and WEGENER 1984, HON 2001, TIMAR *et al.* 2016).

Due to the low ability of UV and the visible component of daylight to penetrate heavy materials, primary changes occur only to a depth of several tens of nanometers. Secondary changes to wood components continue to distant areas up to a depth of 0.15 mm (FENGEL and WEGENER 1984).

The aim of the paper was to evaluate the colour changes on the surface of spruce wood caused by UV radiation and to characterize them in relation to the chemical changes of the main components of wood.

MATERIAL AND METHODS

The untreated spruce 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: cellulose content by the Kürschner-Hoffer and Seifert method, holocellulose content according to Wise, lignin content by the Klason method (KAČÍK and SOLÁR 2000, MELCER *et al.* 1976), and the content of extractives with ethanol-toluene (T 204 os-76).

Samples of spruce wood with dimension of $100 \times 100 \times 20$ mm were used to monitor colour changes depending on the time of exposure to UV radiation.

The stability of selected wood characteristics on light was monitored by modified method STN 50 0376 (Paper Testing. Light Fastness of Paper). The distance of samples from the UV radiation source was 20 ± 2 cm.

Wood samples were exposed to intense UV radiation for 2.5 hours. To monitor the rate of change, the UV irradiation time was changed to 30, 60, 90, 120 and 150 minutes. Brightness of irradiated wood samples was determined by a device Leukometer and surface colour was determined using the colour reader CR-10 defined by the coordinates of the CIELab colour space (L^* , a^* , b^*) and is evenly perceptible over a wide range of colours (ISO 11664-4:2008 en, HRČKA 2013, DZURENDA 2018). Colour parameters (L^* , a^* , b^* and brightness) of each sample were measured 10-times and total colour difference ΔE^* 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 spruce 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 cm^{-1} , 32 scans were recorded for each analysis and the wavenumber range was from 4000 cm^{-1} to 650 cm^{-1} . Six analyses were performed on six 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

The chemical composition values of the investigated spruce wood compliant with the data reported by the authors (BLAŽEJ *et al.* 1975, FENGEL and WEGENER 1984) are shown in Table 1. The observed differences can be explained by differences in the procedures used in the chemical composition of the analysed samples as well.

Tab. 1 Chemical composition of spruce wood.

Content	Sawdust (%)	Fengel and Wegener 1984 (%)	Blažej <i>et al.</i> 1975 (%)
Extractives	1.0	2.0	1.6
Holocellulose	77.8	80.9	73.2
Cellulose Kürschner-Hoffer	50.0	46.0	-
Seifert	45.7	-	(45.6)
Lignin	26.5	27.3	26.1

The colour changes on the spruce wood surface by UV irradiation are shown in Fig. 1.



Fig. 1 Colour changes on the spruce wood surface during the exposure to UV irradiation (a - exposed surface, b - unexposed surface).

Course changes in brightness on the spruce wood surface by UV irradiation is shown in Fig. 2. The decrease in brightness values is evident from 8.4% to 15.1%, depending on irradiation time.

Brightness values measured on the surface of original spruce wood samples ranged from 55.5% to 53.9% MgO. During the exposure to UV irradiation, the brightness of the spruce wood surface was unevenly reduced. The rate of decrease in brightness was highest in the first 30 minutes of irradiation (8.4% MgO). During 150 minutes of wood irradiation, the average rate of decline of brightness was only 3% of MgO in 30 minutes.

Reduction in the brightness, the colour change of the spruce wood surface can be characterized more objectively by the coordinates of the CIELab colour space.

Darkening of the spruce wood surface by the influence of UV irradiation and the acquisition of yellowish orange shades of the different intensity is associated with a shift of coordinates L^* , a^* and b^* in the colour space, wherein the lightness L^* is black and white coordinate, a^* is the red and green coordinate and b^* is blue and yellow coordinate of the colour space.

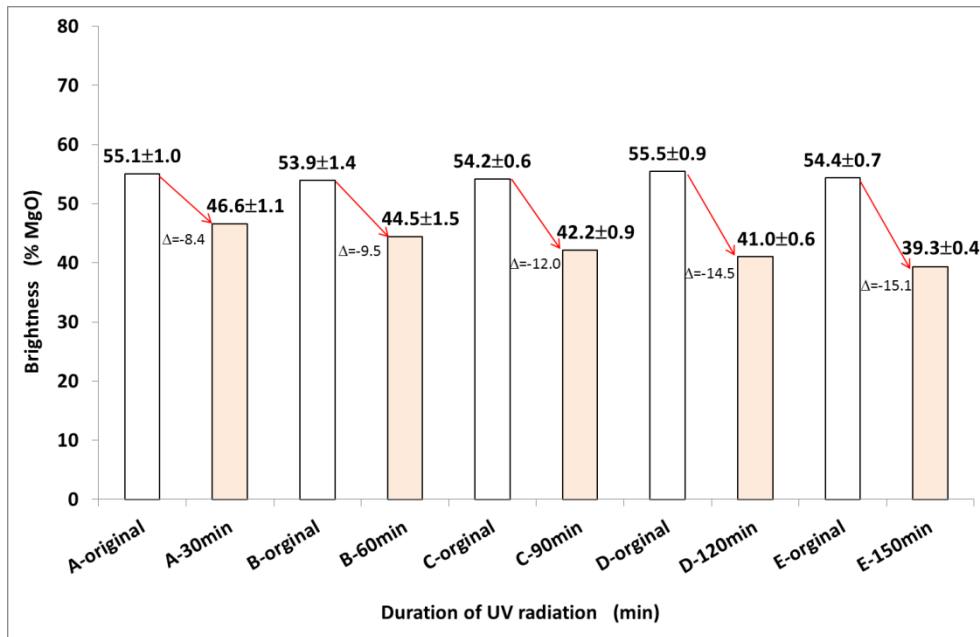


Fig. 2 Changes of the brightness and its fastness on the spruce wood surface by UV irradiation.

Fig. 3 shows the change of coordinates a^* and b^* under the action of UV radiation.

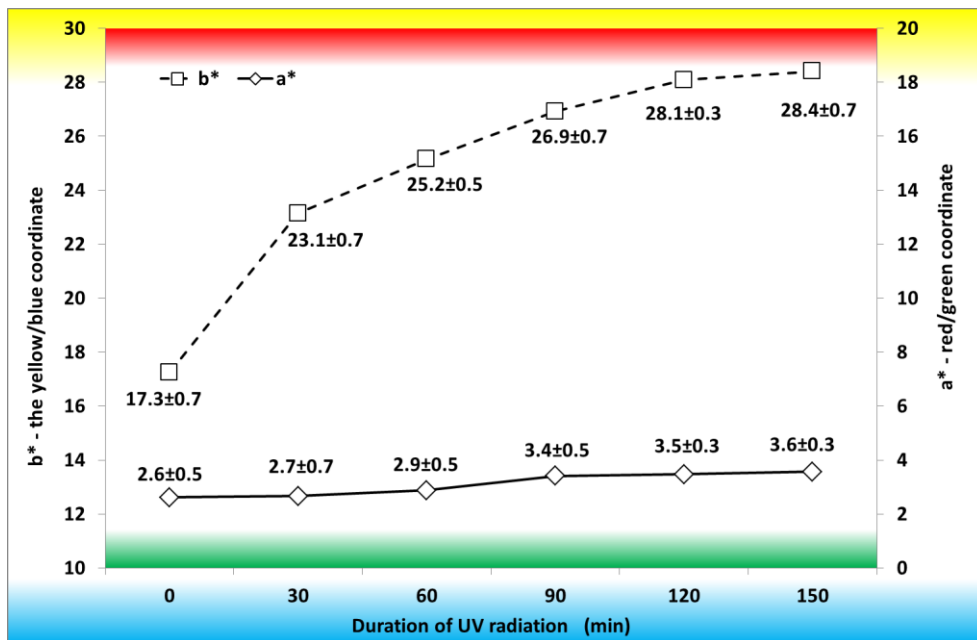


Fig. 3 Changes of colour characteristics a^* , b^* of the colour space by UV irradiation.

It can be concluded that coordinate a^* under the impact of UV irradiation in the whole the monitored range shifted slightly to the red region of the colour space. This shift represents an increase of its original value from 2.6 to 3.6.

The blue-yellow coordinate b^* moved to the yellow of the colour space during UV irradiation. It moved from the original average value of 17.3 to 28.4 after 150 minutes of UV irradiation, which is more than 1.6 times of the original value of this coordinate. The biggest change in b^* coordinate was recorded after the first time interval (30 minutes) and represented the whole shift more than 52%.

The yellowing of lignocellulosic materials and wood surfaces indicates the modification of lignin and holocellulose (HON 2001, MÜLLER *et al.* 2003, KUBOVSKÝ *et al.* 2016).

According to TIMAR *et al.* (2016), the combined analysis of ATR-FTIR results with CIELab measurements showed only slight trend in case of yellowness, which was associated with lignin degradation, but none for redness, associated mostly with wood extractives (TIMAR *et al.* 2016).

The role of extractives in determining of natural wood colour and highly influencing the light fastness of wood were demonstrated by CHANG *et al.* (2010a, b). Wood extractives can act as UV absorbers, scavenge free radicals and undergo photooxidation reactions retarding photodegradation of lignin/wood. Experiments on non-extracted and extracted wood samples showed that on extracted wood the derivatives responsible for colour change were mainly derived from lignin, whereas extractives were the major component responsible for the generation of such derivatives non- extracted wood surface (CHANG *et al.* 2010a, b).

The three-dimensional diagram in Fig. 4 demonstrates the changes and shifting in colour coordinates L^* , a^* and b^* of the spruce wood surface due to UV irradiation more clearly.

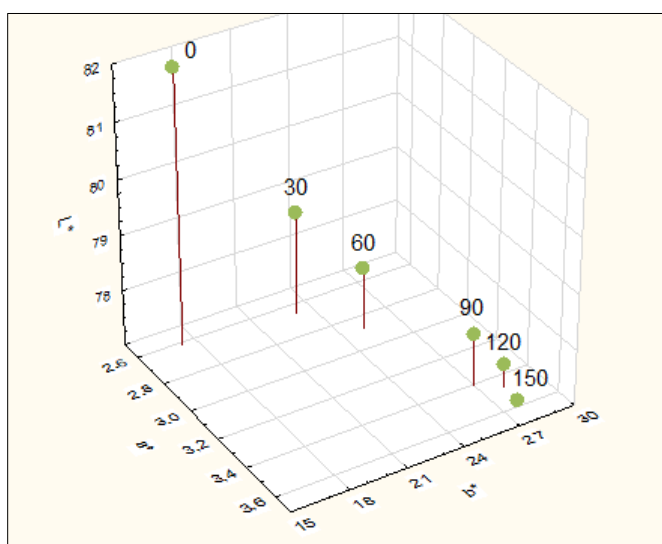


Fig. 4 Changes of colour characteristics L^* , a^* , b^* of the colour space by UV irradiation.

The third coordinate of the CIELab colour space is the lightness - L^* . The average value of lightness L of the original spruce wood surface was 82.0 and during 150 minutes of UV irradiation it decreased to 77.0, which represented 9.1% decrease in this characteristic. The largest reduction in L^* was observed after the first time interval (30 minutes) of UV irradiation and from the overall change in lightness it amounted 62.0%. The measured values of the colour coordinates L^* , a^* and b^* are well in line with the values given by ŠOMŠÁK *et al.* (2015).

KUBOVSKÝ and URGELA (2004) consider the colour difference ΔE^* to be a parameter of the fundamental importance, because the total colour difference reflects the changes in all three coordinates of the colour space due to the colour of the original sample.

Fig. 5 shows the overall colour differences after individual time intervals of UV irradiation, moreover it is also showed that highest change ΔE^* is in the first 30 minutes of UV radiation.

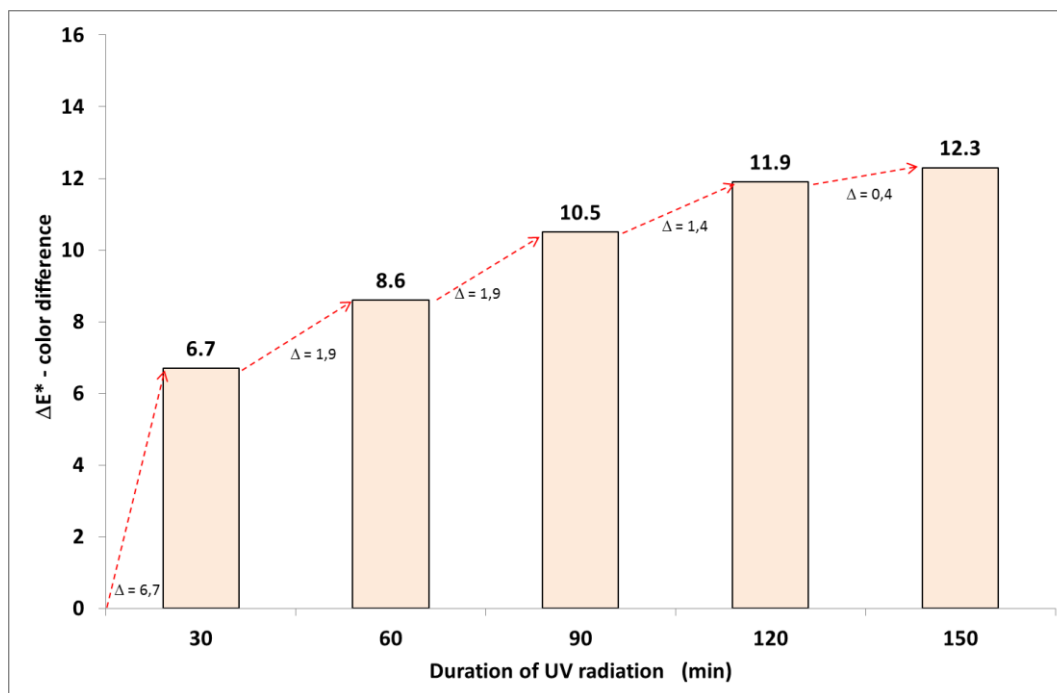


Fig. 5 Changes of the colour difference ΔE^* by UV irradiation.

The degree of colouring of the spruce wood surface may be evaluated on the basis of the following scale (ALLEGRETTI *et al.* 2009):

- | | | |
|----|------------------------|--|
| 1. | $0.2 < \Delta E^*$ | not visible difference |
| 2. | $0.2 < \Delta E^* < 2$ | small difference |
| 3. | $2 < \Delta E^* < 3$ | colour difference visible with high quality screen |
| 4. | $3 < \Delta E^* < 6$ | colour difference visible with medium quality screen |
| 5. | $6 < \Delta E^* < 12$ | high colour difference |
| 6. | $\Delta E^* > 12$ | difference colours |

A colour difference ΔE^* reached the value of 12.3 after UV irradiation for 150 minutes, while the values of the colour difference above the value of 12 can be described as different colours. In the first time interval it was observed a high colour difference ($\Delta E^* = 6.7$), next changes of ΔE^* ranged from 0.4 to 1.9 between individual time intervals and they fit into the range $0.2 < \Delta E^* < 2$, which is defined as small difference.

FTIR analysis confirms the wood sensitivity to UV irradiation. Since the change caused by UV irradiation appears in a thin surface layer, the ATR technique is a very appropriate method for its study. The most specific chemical changes associated with the UV irradiation were visible in the “fingerprint region” ($1800\text{--}800\text{ cm}^{-1}$). The ATR-FTIR spectra of original and irradiated spruce wood in this wavenumber range are shown in Fig. 6.

The wavenumbers of the most representative bands are marked. Band assignment was made according to the references (COLOM *et al.* 2003, HON 2001, MÜLLER *et al.* 2003, PANDEY and PITMAN 2003). The absorption band at 1736 cm^{-1} is the C=O stretch in non-conjugated ketones, acetyl or carboxylic acid and in ester groups. The C=O stretch of conjugated or aromatic ketones absorbs below 1700 cm^{-1} and can be seen as shoulders in the spectra. Following three bands are characteristic for lignin: 1605 cm^{-1} (aromatic skeletal vibration of lignin plus C=O stretching), 1509 cm^{-1} (aromatic skeletal vibration of lignin), 1461 cm^{-1} (aromatic CH deformation and asymmetric bending of CH_3 in lignin). Lignin contributes also to other peaks identifiable in the spectra, as follows:

1422 cm^{-1} (C–H deformation in lignin and carbohydrates; CH_2 bending in cellulose), 1263 cm^{-1} (C–O stretch in lignin ring in guaiacyl units), and 1104 cm^{-1} (aromatic skeletal vibration and C–O stretch). Other bands are assigned to polysaccharides: 1369 cm^{-1} (C–H in-plane deformation for polysaccharides), 1334 cm^{-1} (OH in plane bending in cellulose), 1316 cm^{-1} (CH_2 wagging in cellulose), 1156 cm^{-1} (C–O–C asymmetric bridge in cellulose and hemicellulose), 1051 cm^{-1} (C–O vibration in cellulose and hemicellulose), 1028 cm^{-1} (C–O vibration in cellulose and hemicellulose), and 897 cm^{-1} (C–H deformation in cellulose).

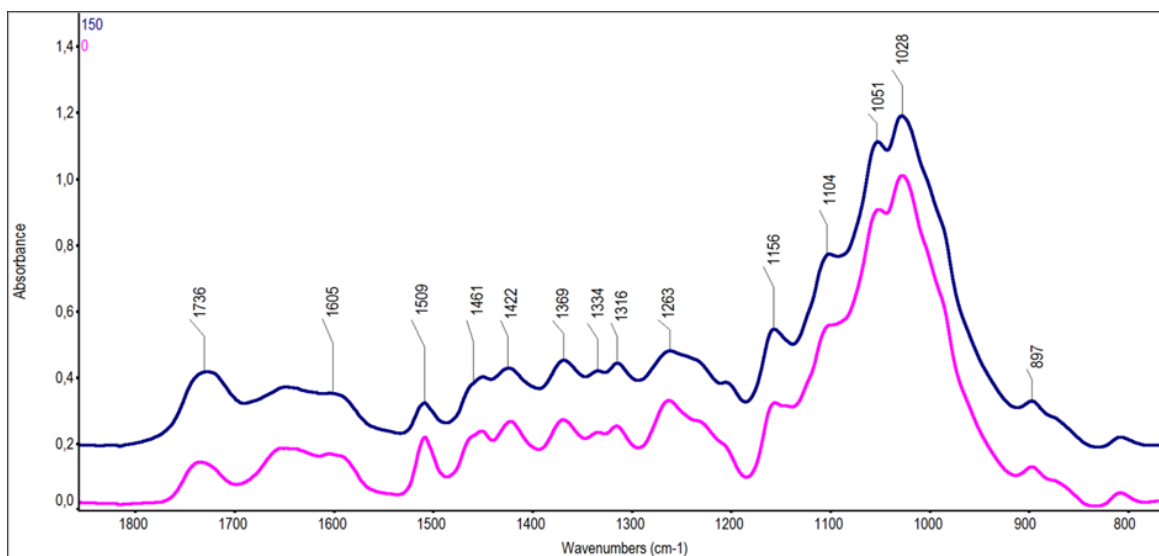


Fig. 6 Comparative FTIR spectra of the surface of UV irradiated (150 min) and original spruce wood in the “fingerprint region”.

Clear differences can be detected in the intensity of several absorption bands. In consequence of UV irradiation the characteristic bands of lignin (1605, 1509, 1461 and 1263 cm^{-1}) significantly decreased. The degradation of lignin is evident already for 30 minutes of irradiation. According to COLOM *et al.* (2003), the evolution of the lignin loss depending on irradiation time is best followed by the absorbance ratio A_{1509}/A_{1316} (Fig. 7).

Following UV irradiation for 150 minutes, the ratio of intensities A_{1509}/A_{1316} decreased down to 56% of its original value. According to Liu *et al.* (2016), a slight increase and better differentiation of the absorption band at 1156 cm^{-1} (C–O–C asymmetric bridge stretching vibration in cellulose and hemicelluloses) is also possibly explained by surface delignification. The increasing of absorbance at 1736 cm^{-1} and simultaneous broadening of this band indicate that during the UV irradiation new and different carbonyl-containing chromophores are formed (LIU *et al.* 2016). COLOM *et al.* (2003) reported that they are derived mainly from lignin. The formation of carbonyl bands proves the photoinduced oxidation of the wood surfaces (MÜLLER *et al.* 2003).

In contrast to lignin, the intensities of the bands associated mainly with carbohydrates (1369, 1334, 1316 cm^{-1}) are not significantly affected by UV irradiation. In addition, the ratio of intensities A_{1334}/A_{1316} , which can be used to monitor the degradation process, does not show significant changes.

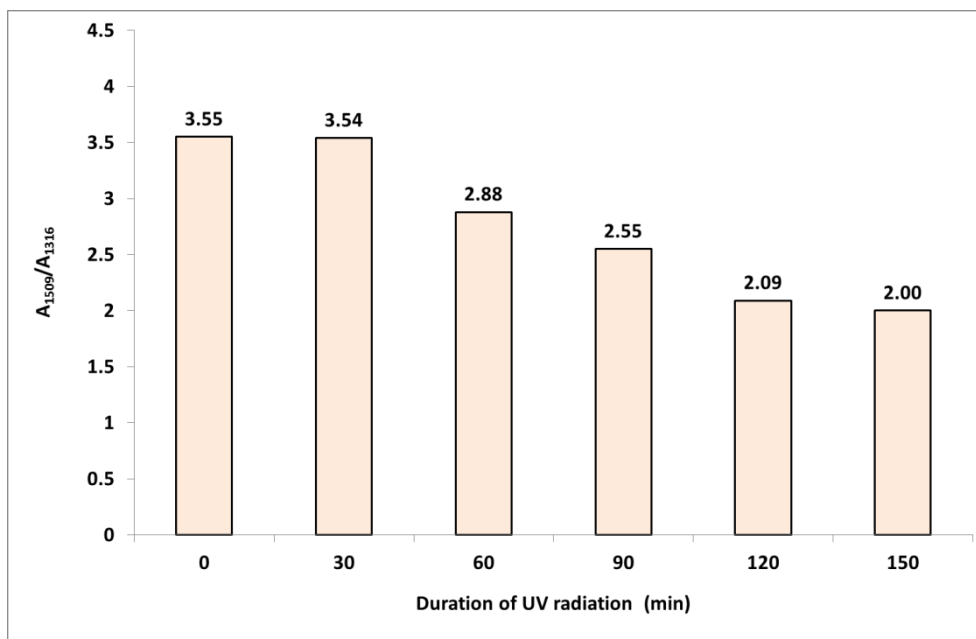


Fig. 7 The lignin loss depending on irradiation time expressed as the ratio of absorbances A_{1509}/A_{1316} .

CONCLUSION

The highest changes of colour characteristics L^* and b^* were observed in the first 30 minutes of the UV exposure. Coordinate a^* in the whole the monitored range shifted slightly to the red region of the colour space. A colour difference ΔE^* reached the value of 12.3 after UV irradiation for 150 minutes can be described as different colours.

FTIR analysis confirms the wood sensitivity to UV irradiation. In consequence of UV irradiation the characteristic bands of lignin decreased significantly. The degradation of lignin is evident already for 30 minutes of irradiation. The intensities of the bands associated mainly with carbohydrates are not significantly affected by UV irradiation.

A combined analysis of FTIR ratio with colour changes showed an increasing trend of b^* coordinate indicating the yellowing mostly related to lignin photodegradation. The yellowness increased while the relative ratio lignin/carbohydrates decreased and the relative ratio carbonyl/carbohydrates increased.

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ADDRESSES OF THE AUTHORS

doc. Ing. Jarmila Geffertová, PhD.

doc. Ing. Anton Geffert, CSc.

Ing. Eva Výbohová, PhD.

Technical University in Zvolen

Faculty of Wood Sciences and Technology

Department of Chemistry and Chemical Technologies

T.G.Masaryka 24

Slovakia

geffertova@tuzvo.sk

geffert@tuzvo.sk

vybohova@tuzvo.sk