Analysis of Photodegradation Process of *Pinus sylvestris* L. Wood after Treatment with Acid and Alkaline Buffers and Light Irradiation

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The purpose of this investigation was to evaluate the effect of acid and alkaline treatment of pine wood on photodegradation. The work presented here deals with changes in the wood colour and infrared spectrum caused by UV light. The colour changes were monitored with a reflectance spectrophotometer. The analysis of the colour changes in wood surfaces was carried out by measuring CIE *L*a*b** parameters. Infrared spectroscopy was used to study chemical changes occurring on the surface of wood samples caused by light. Wood treated with alkaline buffer was characterized by higher brightness changes than wood treated with acid. The surface of samples treated with alkaline buffer revealed similar resistance to photodegradation against both outdoor and indoor light. Greater changes in colour were detected in the case of samples treated with acid and exposed to outdoor light in comparison to indoor light. FTIR results showed degradation in the lignin structure both in the case of samples treated with acid and alkaline buffer and exposure to outdoor and indoor irradiation. The difference between the samples treated with UV 340 nm and UV 351 nm irradiation was seen in the 1512 cm^{-1} band.

Keywords: Scots pine (Pinus sylvestris L.); Photodegradation; Alkaline and acid reaction; Colorimetry; Infrared spectroscopy

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INTRODUCTION

Wood is prone to changes in surface colour under various factors (Chang and Cheng 2001; Mitsui *et al*. 2001; Tolvaj and Mitsui 2005, Tolvaj *et al*. 2014). The photochemical degradation of wood due to sunlight occurs fairly rapidly on exposed wood surfaces. The initial colour change of wood exposed to sunlight is yellowing or browning, which proceeds to an eventual graying.

The change in wood colour with exposure to light depends on the wood species, and to be more precise, on the wood chemical composition in terms of its quality and quantity (Fiest and Hon 1984). The most important photochemical changes are seen in lignin, with extractives also playing an important role. Lignin and polyphenols absorb light strongly below 200 nm and have a strong peak at 280 nm with absorption down through the visible region. Extractives usually have the ability to absorb light between 300 nm and 400 nm. Consequently, most of the components in wood are capable of absorbing enough visible and UV light to undergo photochemical reactions. This

adsorption leads to discolouration and degradation. Older trees tend to have a higher amount of extractives and a lower pH value (Hernández 2013).

Some researchers have discussed the effect of wavelength on photodegradation of wood. Although visible radiation is characterized by lower energy compared to the energy of UV light, this energy is still high enough to initiate photochemical reactions in wood. The wood species sensitive to visible light are, among others, pine, spruce, mahogany, cedar, oak, cherry, and walnut (Chang *et al* 2000; Suttie 2006; Zborowska *et al.* 2011; Nowaczyk-Organista and Prądzyński 2012). Oltean *et al.* (2010) described wood surface discoloration of selected hardwood samples due to simulated indoor sunlight exposure. According to Kataoka *et al.* (2007), the blue light (434 to 496 nm) causes bleaching without significantly modifying the IR spectra of lignin.

There have been many reports dealing with changes in colour parameters by light irradiation. The lightness (*L**) of almost all wood species decreases while the chromaticity coordinate (*b**), which indicates yellowing, increases upon exposure to light irradiation. Although Park *et al.* (1996) reported that the changes in carbonyl groups at around 1730 cm^{-1} have a close relation to those in the colour of wood, Tolvaj and Faix (1995) noted that the correlation is only statistical. This statistical nature of the correlation is attributed to the carbonyl group at around 1730 cm^{-1} being indicated as unconjugated, and therefore not a chromophoric group.

Moreover colour changes of wood surfaces can appear as a result of finishing (*e.g*. coating, chemical and thermal modification as well as surface impregnation). The influence of wood finishing has been previously described (Jankowska and Szczęsna 2011; Hochmańska *et al.* 2014; Teacă *et al*. 2013). In the furniture industry it is very important to improve aesthetics and protective properties such as resistance to light. With this aim, the wood surface is often coated with a lacquer system characterized by a different pH value. A polyurethane lacquer system has an acid hardener that causes darkening of the wood surface after coating. A water-based lacquer gives a more natural colour to the finished surface. However, it is difficult to determine whether or not the reaction of this coating influences changes in colour. Therefore, the aim of this work is to investigate the influence of pH of pine wood on resistance to light irradiation.

EXPERIMENTAL

Preparation of Samples

The investigated material was softwood of Scots pine (*Pinus sylvestris* L.). Samples with dimension of 40 × 15 × 5 mm (±1 mm) (long. × tang. × rad.) were prepared from the same board. They were cut from sapwood and included both early and late wood. The test samples were polished with sandpaper (400 P) prior to the investigation. Then, they were divided into three groups. The first group was the control sample. The second and third groups were dipped in acid (pH = 4.0) and alkaline (pH = 10.0) buffers, produced by Honeywell Burdick & Jackson. The investigations were performed using three samples from each variant. Three circle measuring points were marked on each sample (diameter 10 mm). The buffer treatment lasted 24 h and was performed under laboratory conditions (23 °C, 45% RH). After dipping, the samples were dried at 40 °C for 24 h. The samples humidity during experiment was constants and amounted 5.8%±0.1.

Light Irradiation

Light irradiation was carried out twice with an ATLAS apparatus. The first test was performed with the use of low-pressure UV radiators with maximum emission at 340 and the second one with 351 nm. The UV-A-340 lamp emitted UV resembling solar light found outdoors (with a wavelength range of 290 to 400 nm), while the UV-A-351 lamp emitted daylight that penetrates window panes and is found indoors (with a wavelength range of 300 to 400 nm) (EN-ISO 4892-3/2006). The distance between the UV light sources and sample surfaces was set to about 4.0 cm. The intensity of light projected onto the tested surfaces was 0.5 W/m^2, and the black panel temperature (BPT) equalled 38 °C. The irradiation under an air atmosphere. The total irradiation time was 100 h in all cases.

Colour Measurements

All the colour measurements were taken from the radial surface of the samples. The samples (control and after treatment in the acid and alkaline buffers) were measured before and after irradiation. The light exposure was interrupted after 1, 5, 10, 25, 50 and 100 h of irradiation to acquire data. The colour coordinates in the CIE *L*a*b** system were recorded with a Datacolour 600 dual-beam d/8° spectrophotometer, using the D_{65} standard illuminant. The wavelength range of spectrophotometer was from 360 nm to 700 nm, reporting at 10 nm intervals. Reflectance of instrument was 0.15 (max), 0.08 (avg.). The sensor head diameter was 10 mm. The measurement of colour coordinates *L**, *a**, *b**, and evaluation of colour changes were performed on three samples per each variant. Calibration of the instrument was performed before testing using the white tile, green tile, and black trap standards provided with the spectrophotometer. Three points of fixed locations were measured on each sample.

Data listed in this work are the average of nine replicated measurements. The colour sphere (*L**, *a**, *b**) is described as a tridimensional system of colour co-ordinates (axes *L**, *a**, and *b**). Axis *a** depicts the share of green or red colour within the analysed colour; hues of green take on negative values and hues of red, positive values. Axis *b** depicts the share of blue or yellow colour within the analysed colour; hues of blue take on negative values and hues of yellow, positive values. Axis *L** describes colour brightness within the value range from 0 to 100. *L**=100 means that a given colour is close to white, and L*= 0 that a colour is close to black.

Colour change in the CIE *L*a*b** system was calculated according to the following formula:

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

where ΔE^* is the total colour change, *L** is the achromatic coordinate (brightness), and *a** and *b** are chromatic coordinates.

Colour coordinates of pine surface before and after 24 h of treatment with the acid and alkaline buffers, as well as before and after the light irradiation, were referred to the white standard (*L** = 96.29, *a** = - 0.34, *b** = 1.25).

FTIR Measurement

The control samples, and samples after treatment with the acid and alkaline buffers were analysed after the UV light irradiation using a FTIR spectrometer produced by Bruker Optics GmbH. This spectrophotometer was equipped with an attenuated total

reflectance (ATR with germanium crystal) accessory Alpha Spectrometer. The spectral range was measured between 4000 cm^{-1} and 600 cm^{-1}. The spectral resolution of the spectrophotometer was 4 cm^{-1}. Each spectrum was computed as an average of 32 successive measurements to minimize the measurement error. Five measurements were performed on each sample. The bands in the FTIR spectra of the sample were assigned with the aid of data from the literature (Wang and Ren 2008).

RESULTS AND DISCUSSION

Colour Measurement

Colour changes due to acid and alkaline buffer treatment

Figure 1 shows the change in colour coordinates (ΔL^*, Δa^*, Δb^*) and colour (ΔE^*) of the pine wood samples after treatment with acid and alkaline buffers as compared to the control samples. Treatment with the acid and alkaline buffers caused minor darkening, yellowing, and reddening of the wood surface as compared to the control sample. Greater changes in colour (ΔE^*) and colour coordinates (ΔL^*, Δa^*, Δb^*) were observed in the case of pine wood treated with the alkaline buffer. The total colour change ΔE^* of the alkaline-treated surface amounted to 2.83 units. ΔE^* values of the alkaline-treated wood were caused primarily by the brightness coordinate (ΔL^*). Wood treatment with acid buffer produced a moderate change in colour (ΔE^*). The total colour change ΔE^* of acid-treated samples amounted to 0.52 units. The detected changes of ΔE^* parameters were lower than $\Delta E^*=3$ therefore were invisible to the human eye (Hon and Shiraishi 2001).

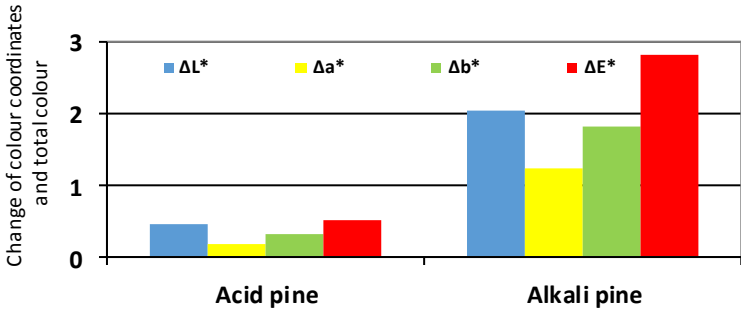

Fig. 1. Change in colour and colour coordinates of pine samples after treatment with acid and alkaline buffers

Colour changes due to irradiation

Greater changes in the colour coordinates (ΔL^*, Δa^*, Δb^*) were caused by the action of the light. Progress of the above parameters during 1, 5, 10, 25, 50, and 100 h of light exposure under two types of UV lamps, with wood samples treated with acid and alkaline buffers are presented as a function of irradiation time in Fig. 2. Figure 3 shows differences between ΔL^*, Δa^*, Δb^*, and ΔE^* values of wood treated with buffers and surfaces after 100 h of irradiation using two types of lamps, UV-A 340 and UV-A 351.

Based on the curve for ΔL^*, it was seen that the lightness in all sample variations changed rapidly in the first 25 h of exposure to light (Fig. 2). Later, between 25 and 100 h

of light exposure, the changes were not so intensive. Irrespective of type of light used in a test performance (UV-A 340 nm and UV-A 351 nm), the parameter Δ*L** of wood treated with the acid and alkaline buffers had an increasing negative value, which indicates that their surface darkened. Noticeable differences were found between values of Δ*L** of acid- and alkaline-treated wood samples. The results indicated that the surfaces of the wood samples treated with the alkaline buffer were darker after light irradiation in comparison to samples treated with acid buffer. Figure 3 shows that the changes in lightness values in the samples treated with acid buffer and exposed to light irradiation were smaller than the changes observed in samples treated with the alkaline buffer.

The irradiated surface showed a tendency, as indicated by an increase in the chromaticity parameters Δ*a** and Δ*b**, to turn red and yellow. The intensification of these changes followed throughout the duration of irradiation. The greatest changes occurred in the first 25 h of irradiation (Fig. 2). Taking into account the changes in parameter Δ*a**, there were not any noticeable differences between values obtained for the acid- and alkaline-treated wood samples with the same irradiation parameters. The wood samples preliminarily treated by acid and alkaline buffers were slightly more red after exposure to a UV-A 340 lamp as compared to samples exposed to a UV-A 351 lamp. Figure 3 shows that samples treated with acid buffer are slightly more prone to changes in the red direction compared to samples treated with the alkaline buffer.

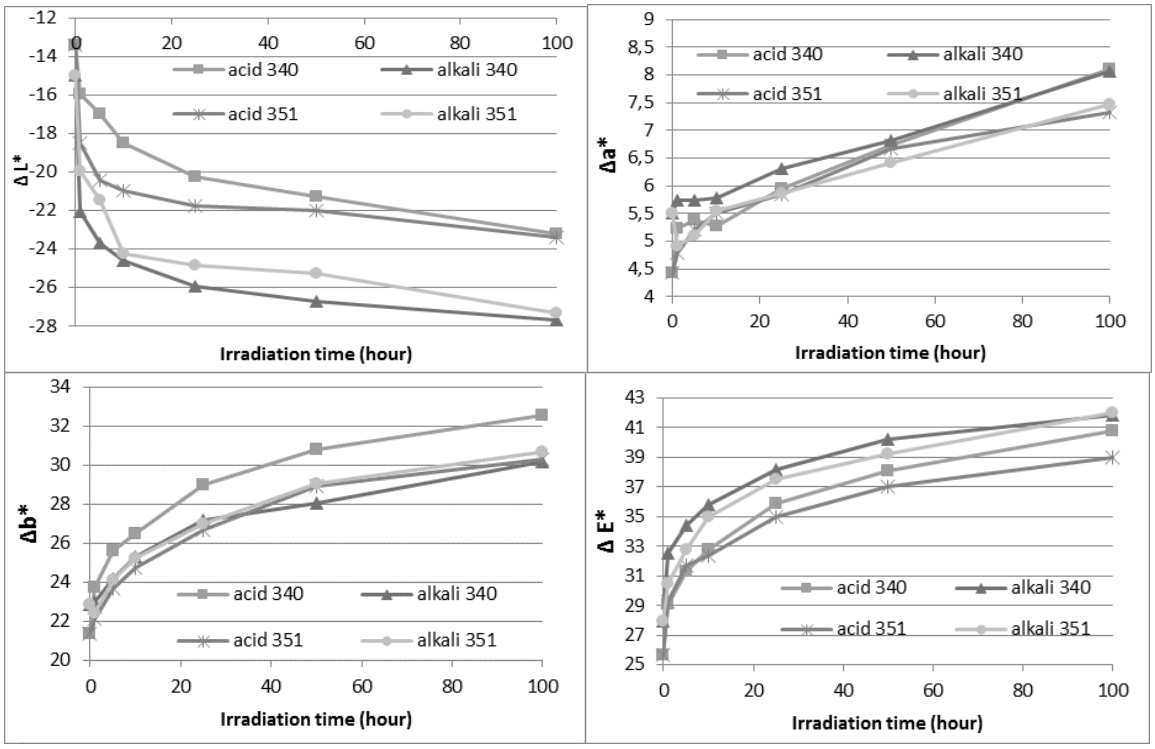

Fig. 2. Changes in colour (Δ*E**) and colour coordinates (Δ*L**, Δ*a**, Δ*b**) in pine samples during treatment with acid and alkali buffer caused by 1, 5, 10, 25, 50, and 100 h of UVA irradiation with light of wavelengths 340 and 351 nm

In the case of the pine wood samples treated with acid and alkaline buffer, yellowing of the surface under light exposure was the primary colour change caused by the photodegradation. The changes in this coordinate indicate alternation of lignin and

hemicellulose with the occurrence of unstable products (Müller *et al*. 2003; Teacă *et al*. 2013). Samples treated with acid buffer and then exposed to 340 nm light were the yellowest (Fig. 2). The remaining samples were characterised by lower values of Δ*b**, and their values were similar to each other. Figure 3 shows that, in the case of the wood samples treated with alkaline buffer, the chromaticity coordinate Δ*b** was more stable and changed in a smaller range in comparison to samples treated with the acid buffer.

The total colour change (Δ*E**) of all samples during 100 h of irradiation is presented in Fig. 2. The highest total colour changes in all variations of sample rates were observed during the first 25 h of elapsed experiment time. Finally, after 100 h of irradiation, higher values of Δ*E** were achieved in the case of the samples treated with the alkaline buffer. Figure 3 shows that the greatest changes in colour occurred in the case of wood samples treated with acid buffer and exposed to UV light at 340 nm.

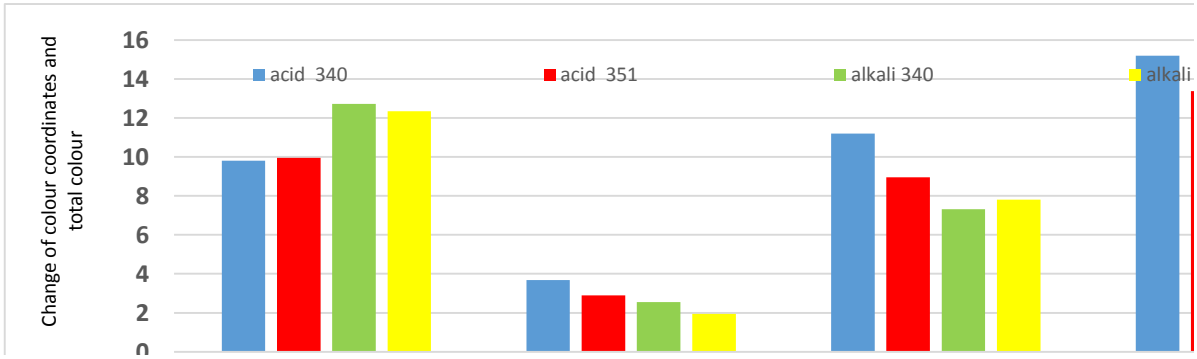

Fig. 3. Changes in colour (Δ*E**) and coordinates (Δ*L**, Δ*a**, Δ*b**) of pine samples after treatment with acid and alkali buffers caused by 100 h of UVA irradiation with light of wavelengths 340 and 351 nm

FTIR Analysis

Figures 4 and 5 show the FTIR spectra of acid- and alkaline-treated pine samples exposed to 100 h of irradiation from UV-A 340 nm and 351 nm lamps. These lamps emit UV light resembling solar light found outdoors and light resembling daylight found indoors that penetrates window panes, respectively. The differences between the spectra of the control samples and the samples treated with acid (without irradiation) were not so noticeable (Fig. 4). The 24-h treatment with the acid buffer did not change the chemical structure of the wood components on the surface of the samples. However, visible changes were seen in samples treated with acid buffer and then light irradiation.

The primary differences were observed in regions assigned to both carbohydrates and lignin structures. In the spectra of samples exposed to irradiation with UV light at 340 nm and UV light at 351 nm, the intensity of the absorption bands related to lignin at 1600 cm^{-1} (7) (aromatic skeletal vibration) and 1262 cm^{-1} (4) (guaiacyl ring breathing with C-O stretch) decreased in comparison to the spectra of the untreated samples. These differences confirmed that lignin underwent structural changes during photodegradation and that these changes were similar in the case of samples exposed to indoor and outdoor irradiation.

Another band at 1512 cm^{-1} (6) decreased after light treatment with UV light at 340 nm and disappeared in the case of exposure at 351 nm. According to the literature, absorption in this range of wavelengths is indicative of aromatic skeletal vibrations in lignin (Wang and Ren 2008).

The opposite situation is observed at 1462 cm^{-1} (5), which is also attributed to the asymmetric bending of lignin structure. This peak is found in the spectra of the sample exposed to light at 340 nm, but does not occur in the spectra of the sample exposed to light at 351 nm. It is likely that indoor and outdoor light irradiation causes different changes in the aromatic skeletal and aliphatic structure of lignin. The bands associated with carbohydrates showed a tendency to increase. That change was observed in the case of peaks at 1735 cm^{-1} (8) connected with non-conjugated bond of C=O structures in hemicellulose and 1157 cm^{-1} (3) resulting from vibration of C–O–C linkages in cellulose and hemicellulose. Intensification of absorption is also observed in other bands, *i.e.*, 1105 cm^{-1} (2) and 1056 cm^{-1} (1), which are specific for carbohydrate components of wood connected with stretching vibrations of C–O linkages in cellulose and hemicellulose. This phenomenon occurs because of changes in the relationship between the concentration of the primary components of wood, carbohydrates, and lignin. Light irradiation with UV light at both 340 nm and 351 nm caused degradation of lignin, *e.g.*, oxidation and depolymerisation of this polymer structure and loss or change of moieties. Finally, the concentration of aromatic structures in wood after light irradiation was smaller and that of carbohydrates was higher.

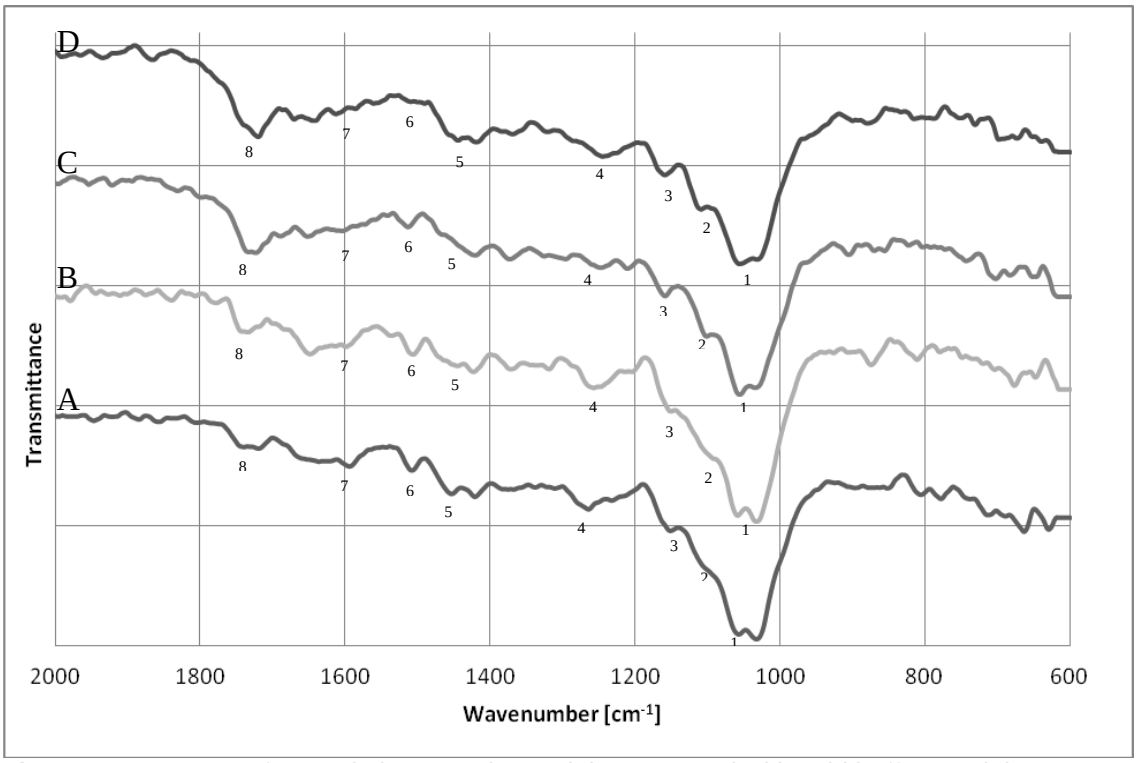

Fig. 4. FTIR spectra of control pine samples and those treated with acid buffers and then exposed to 100 h of photodegradation by UV-A 340 and UV-A 351 lamps. A - control, B - after buffer treatment, C - after buffer and UVA 340 nm treatment, D - after buffer and UVA 351 nm treatment

Analysis of the spectra of control samples and samples treated with alkaline buffer (Fig. 5) demonstrated differences in absorption bands at 1655 cm^{-1} (9) related to the stretching of conjugated or aromatic ketones and at 1260 cm^{-1} (4), which is assigned to the C–O structure of a guaiacyl unit in lignin. A decrease in absorption was found at

peaks 1600 cm^{-1} (7) and 1512 cm^{-1} (6) (aromatic skeletal vibration) on the basis of the change in the spectra after 340 and 351 nm light irradiation. The changes at 1512 cm^{-1} are similar to those observed in the spectra of samples treated with acid, *e.g*., after exposure with light at 340 nm. This peak decreased and disappeared after irradiation at 351 nm. It can be expected that the influence of this outdoor light is stronger. The bands that are characteristic for carbohydrates, 1157 cm^{-1} (3), 1105 cm^{-1} (2), and 1056 cm^{-1} (1), increased after treatment with light irradiation and present the same trend as the case of the samples treated with acid buffer.

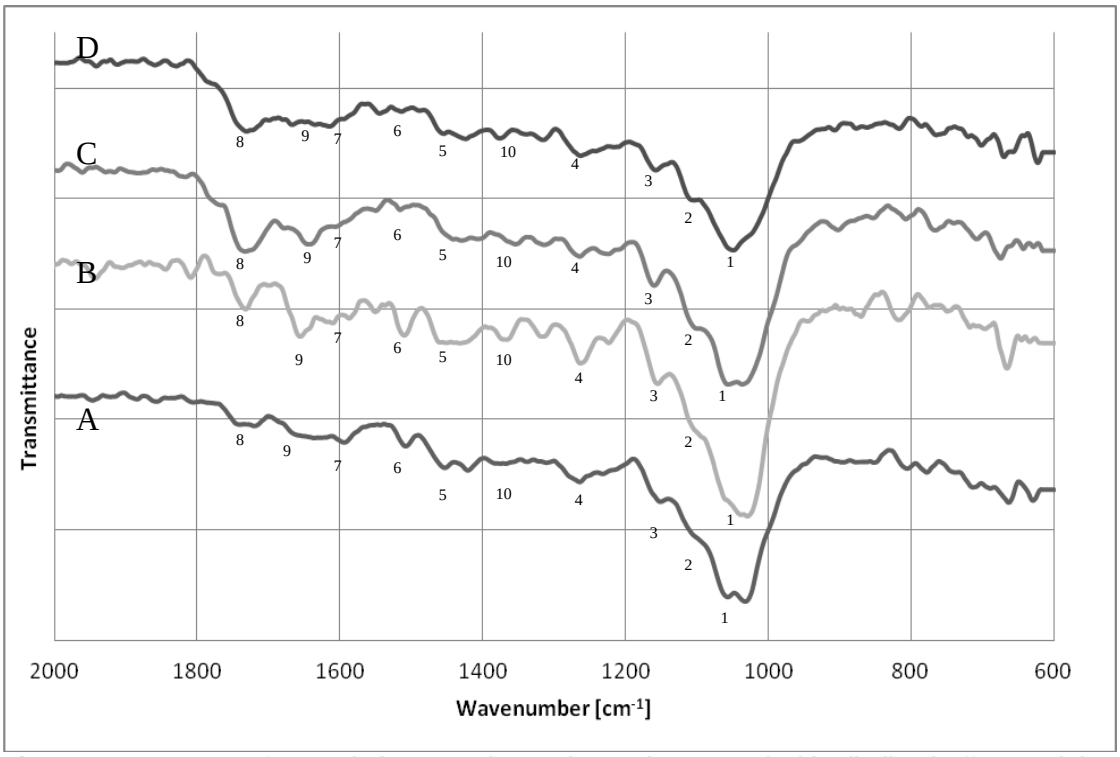

Fig. 5. FTIR spectra of control pine samples and samples treated with alkaline buffers and then exposed to 100 h of photo-degradation with UV-A 340 and UV-A 351 lamps. A - control, B - after buffer treatment, C - after buffer and UVA 340 nm treatment, D - after buffer and UVA 351 nm treatment

CONCLUSIONS

1. Treatment with acid and alkaline buffers, without photodegradation, caused minor darkening, yellowing, and reddening of the wood surface. More pronounced changes were observed in the case of samples subjected to the alkaline solution.
2. Samples treated with acid and alkaline buffers have different susceptibilities to photodegradation, resulting in changes in colour coordinates.
3. Samples treated with acid buffer are less susceptible to lightness changes in comparison to samples treated with alkaline buffer. The samples treated with acid reveal a higher tendency to redden and yellow.
4. Samples treated with alkaline buffer show similar discolouration (ΔE^*) under the influence of UV-A 340 nm and UV-A 351 nm light irradiation.

5. Samples treated with acid buffer are more resistant to UV-A 351 nm light irradiation in comparison to UV-A 340 nm.
6. The photodegradation caused by UV 340 nm and UV 351 nm lamps altered the chemical structure of wood components, and these changes were manifested in the degradation of lignin. On the basis of the absorption at 1512 cm^{-1}, differences between chemical changes of the lignin structure of the samples treated with the acid and alkaline buffers due to 340 and 351 nm light irradiation were found.

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