IMPACT OF DIFFERENT RADIATION FORMS ON BEECH WOOD DISCOLOURATION

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ABSTRACT

This study analyses beech wood surface discolouration induced through UV radiation during an accelerated ageing process and with radiation emitted from a CO₂ laser beam operating under specific settings.

The results show that the extent of beech wood surface discolouration was dependent on the amount and the type of the energy delivered and on the absorption performance of the main wood components. It was observed that increasing irradiation dose caused decreasing wood surface lightness in both UV radiation and CO₂ laser-produced radiation scenarios. In most cases, the values of colour coordinates $a^*$ and $b^*$ increased, and the wood surface was gradually turning dark brown. At high irradiation doses from the CO₂ laser, there were recorded decreasing trends in $a^*$ and $b^*$, and the beech surface darkened substantially (up to black).

To attain purpose-oriented wood surface discolouration under specific modification modes, there is necessary to carry out thorough chemical analyses of the treated wood surface and to express quantitatively the dependence between the energy supplied, colour, adsorption capacity of the main wood components and the ongoing chemical changes.

KEYWORDS: Beech wood, electromagnetic radiation, laser, colour space CIE $L^*a^*b^*$

INTRODUCTION

Colour is a representative feature of wood’s surface. Wood’s surface colour is important for wood species identification, and it also serves as a benchmark for wood quality assessment (Babiak et al. 2004, Hříčka 2008). At the same time, this feature is important for purpose-oriented wood surface modification with different radiation forms and for assessment of stability of changes induced in this way (Kubovský and Kačík, 2013).

Under the influence of various types of radiation, a wood surface is subject to degradation, the major external manifestation of which is discolouration (Persze and Tolvaj 2012, Kúdela and Kubovský 2016, Kúdela and Andor 2018). The discolouration is the result of chemical
bond splitting, primarily in the main wood components (lignin, hemicelluloses and cellulose). Changes take place to the structure of chromophores that absorb electromagnetic radiation with characteristic wave lengths. These substances are the background for the wood surface's colour patterns (Srinivas and Pandey 2012, Yildiz et al. 2013). Wood colour is primarily affected by chromophores in lignin and to some extent by organometallic complexes in extractive substances (Falkehag et al. 1966, Hon and Minemura 1991).

The wood colour modification process not only depends on the irradiation source (CO\textsubscript{2} laser, UV, IR), but also on the wood species because wood's chemical structure is species-specific (Pandey and Vuorinen 2008, Fan et al. 2010, Chen et al. 2012, Zborowska et al. 2016, Reinprecht 2016, Oberhofnerová et al. 2017).

Chemical reactions in lignin cause wood darkening, especially in light-coloured wood species. Another important aspect is extractives that are sensitive to UV radiation. Extractive substances can react with carbohydrates or products of hydrolysed lignin and create lignin-like compounds (Tolvaj and Faix 1995, Persze and Tolvaj 2012, Chang et al. 2010, Výbohová et al. 2018).


The purpose-oriented discolouration in particular wood species induced with a CO\textsubscript{2} laser, infrared (IR) or ultraviolet (UV) radiation is frequently performed on an empirical basis only. This issue can be approached through quantification of the relation between the discolouration obtained and the energy supplied. An appropriate approach to delivering energy onto the wood surface is using a laser beam. From the absorption coefficient values and the values of radiation intensity affecting the surface of the treated wood, it is possible to derive the relation between the irradiation dose and the resulting discolouration intensity (Kačík and Kubovský 2011, Kubovský and Kačík 2014, Li et al. 2018). These authors show that the change of the energy amount supplied with the aid of a CO\textsubscript{2} laser beam has significant impact on wood surface discolouration, in close connection with the chemical changes described above.

The aim of this work was to study beech wood surface discolouration induced through UV radiation at an accelerated ageing process and through irradiation with a CO\textsubscript{2} laser beam operating under specific settings.

**MATERIALS AND METHODS**

The experiments were carried out on four testing series of beech wood (*Fagus sylvatica* L.) specimens with dimensions of 100 x 50 x 15 mm (Fig. 1). The first series was exposed to UV radiation in a Xenotest Q–SUN Xe–3–H for 600 hours.

![Fig. 1: Specimen shape and dimensions.](image_url)
The ageing conditions in the Xenotest followed the Standard ASTM G155 (Tab. 1). Our choice was a so-called dry regimen simulating outdoor conditions without protection against UV effects but with protection against rain (Tab. 1).

Tab. 1: Ambient conditions and irradiation during the accelerated ageing process (ASTM G155).

<table>
<thead>
<tr>
<th>Step</th>
<th>Function</th>
<th>Radiation intensity (W·m⁻²)</th>
<th>Black panel temperature (°C)</th>
<th>Air temperature (°C)</th>
<th>Relative humidity (%)</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Irradiation</td>
<td>0.35</td>
<td>63</td>
<td>48</td>
<td>30</td>
<td>102</td>
</tr>
<tr>
<td>2</td>
<td>Without irradiation</td>
<td>–</td>
<td>–</td>
<td>38</td>
<td>–</td>
<td>18</td>
</tr>
</tbody>
</table>

According to the standard, the radiation intensity was set to a value of 0.35 W·m⁻² under a wave length of \( \lambda = 340 \) nm. This value represents the average annual radiation intensity in the temperate zone. The temperature controlled on the black panel represented the maximum temperature on the surface. The chosen air temperature had to accelerate the changes to the wood surface. The discolouration was observed after 100, 200, 400 and 600 hours.

The specimens in the second series were irradiated with a power CO₂ laser LCS 400, with a maximum power of 400 W. The specimen was placed at a distance of 230 mm under the focusing lens (the same for all specimens). The laser head moved over the surface, perpendicular to the grain (Fig. 2). The irradiation dose \( H \) was controlled through adjusting the laser head speed within 10–40 mm·s⁻². This dose was calculated according to the equation

\[
H = \frac{P_e \cdot \tau}{A} = \frac{P_e \cdot x}{A \cdot v}
\]

where:
- \( P_e \) - is the effective laser beam power on the specimen's surface,
- \( \tau \) - irradiation time during a passage (the ratio between the specimen's dimension \( x \) and the velocity \( v \)),
- \( A \) - the area irradiated during one passage of the beam.

Fig. 2: Irradiation of a specimen with a CO₂ laser LCS 400.

Fig. 3: Wood surface engraved with a laser CM-1309.

The third and fourth specimen series were irradiated with a CO₂ laser CM-1309 specified for cutting and engraving (Fig. 3) and operating with a maximum power of 135 W.

The specimens were placed at a distance of 17 mm below the focus of the focusing lens (again, the distance was the same in all cases). The speed of the laser head moving parallel to the grain was constant (350 mm·s⁻¹). The discolouration was controlled under the engraving regimen by adjusting the raster density of the laser head perpendicular to the grain within a range from 1 to 20 (the number of parallel laser tracks per width of 1 mm). One specimen series was
irradiated under 4% of the maximum power, and the other one under 8%. Each set consisted of 18 specimens.

The colour space CIE $L^*a^*b^*$ of all specimens was determined before and after irradiation, and the values were compared to the referential ones (untreated). The measuring tool was a spectrometer Spectro-guide 45/0 gloss by BYK–GARDNER GmbH. The discoloration extent was expressed through the total colour difference $\Delta E$, calculated according to the Eq. 2-5:

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2},$$

with

$$\Delta L^* = L_T - L_R$$
$$\Delta a^* = a_T - a_R$$
$$\Delta b^* = b_T - b_R$$

Note: The index „$T$“ expresses discoloration after the treatment, and index „$R$“ is the so-called referential (REF) value measured on untreated wood surface.

**RESULTS AND DISCUSSION**

During the accelerated ageing, the wood surface was affected by solar radiation spectrum (primarily UV radiation) and by heat. This resulted in the wood darkening during the whole process (Tab. 2).

Tab. 2: Values of colour coordinates of beech wood surface irradiated during ageing process. The values in the parentheses represent standard deviations.

<table>
<thead>
<tr>
<th>Colour coordinate</th>
<th>Irradiation time (hours)</th>
<th>REF</th>
<th>100</th>
<th>200</th>
<th>400</th>
<th>600</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L^*$</td>
<td>74.71 (2.99)</td>
<td>65.23 (2.03)</td>
<td>65.05 (2.21)</td>
<td>65.02 (2.42)</td>
<td>64.56 (2.30)</td>
<td></td>
</tr>
<tr>
<td>$a^*$</td>
<td>6.91 (0.57)</td>
<td>8.92 (0.64)</td>
<td>9.39 (0.57)</td>
<td>9.83 (0.61)</td>
<td>10.44 (0.67)</td>
<td></td>
</tr>
<tr>
<td>$b^*$</td>
<td>19.16 (0.91)</td>
<td>26.81 (1.36)</td>
<td>27.92 (1.47)</td>
<td>28.30 (1.57)</td>
<td>28.68 (1.68)</td>
<td></td>
</tr>
</tbody>
</table>

Number of measurements $n = 75$

The lightness $L^*$ decreased continually over the whole accelerated ageing period. The major decrease was recorded during the first 100 ageing hours. The next one was much less obvious. The difference between the lightness values corresponding to 100 and 600 ageing hours was confirmed significant at a 95% significance level; from the practical viewpoint, however, this cannot be considered a substantial change.

Contrarily, the values of coordinates $a^*$ and $b^*$, representing the chromaticity level, exhibited a permanent increase. Value $a^*$ was shifting towards red and value $b^*$ towards yellow, resulting
in progressive surface colour modification towards saturated dark brown. The most conspicuous changes were again obtained after the first 100 ageing hours (Tab. 2). The subsequent changes in these coordinates were much smaller.

The colour differences corresponding to the particular coordinates $\Delta L^*$, $\Delta a^*$ and $\Delta b^*$, together with the total colour difference $\Delta E$ during the ageing process, are demonstrated in Fig. 4. The total difference exceeded the value of 12 as early as after the first 100 ageing hours. This, according to Allegretti et al. (2009), represents the top of the 6-degree evaluation scale, meaning an entirely new colour compared to the original one. With advancing ageing process, the $\Delta E$ values increased continually, but with an evidently lower rate (Fig. 4).

Fig. 4: Discolouration of beech wood surface irradiated during ageing process.

The darkening of the wood surface was the result of photo-chemical reactions accompanying the degradation of lignin, hemicelluloses and cellulose. UV radiation’s impact on a wood surface induces dissociation of chemical bonds, especially in lignin macromolecules, that is accompanied by creation of new chromophore structures. The photo-oxidation reactions produce carbonyl chromophores that back up the wood surface discolouration (Pandey and Vuorinen 2008).

The results of the second experiment revealed that with increasing irradiation doses from the CO$_2$ laser LCS 400, there were also changes to all three colour space coordinates $L^*a^*b^*$ (Tab. 3). With the irradiation dose increasing from 0-47.8 J∙cm$^{-2}$, lightness was decreasing. At the beginning, the wood surface modification did not exhibit carbonisation symptoms. This proves that the surface layer temperature did not exceed 200°C (Haller et al. 2014). At the irradiation dose of about 25-30 J∙cm$^{-2}$, the surface turned darker due to ongoing carbonisation. Kačík and Kubovský (2011) observed a dramatic reduction of saccharides starting at 25 J∙cm$^{-2}$ up, primarily as the result of degradation of hemicelluloses and a certain portion of the amorphous cellulose fraction. Increasing the irradiation dose beyond 48 J∙cm$^{-2}$ caused considerable surface carbonisation, consequently, and the irradiation was stopped. The irradiation doses beyond 48 J∙cm$^{-2}$, however, did not cause additional decrease in lightness. Contrarily, the opposite trend was discernible due to the wood surface’s carbonisation. The carbonised surface was more predisposed to reflect the light, so there was no decrease in the lightness values.

The coordinate $a^*$ values moderately increased, i.e. shifted to red, with the irradiation dose increasing up to 24 J∙cm$^{-2}$. Beyond this value, there followed a decrease as the result of
carbonisation. The $b^*$ exhibited initially a moderate decrease, followed by a steeper one at higher irradiation doses (Tab. 3).

**Tab. 3: Discolouration of beech specimen surface with increasing irradiation dose $H$. The values in parentheses represent standard deviations.**

<table>
<thead>
<tr>
<th>Colour coordinate</th>
<th>Irradiation dose $H$ (J·cm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>REF 14.3 17.9 20.5 23.9 26.1 28.7 31.8 35.8 40.9 47.8</td>
</tr>
<tr>
<td>$L^*$</td>
<td>78.55 (1.57) 77.22 (0.59) 74.87 (0.81) 71.71 (1.62) 65.43 (2.37) 62.58 (2.34) 62.58 (1.57) 47.63 (2.31) 40.29 (2.64) 33.30 (1.51) 30.72 (0.94)</td>
</tr>
<tr>
<td>$a^*$</td>
<td>6.25 (0.61) 6.43 (0.23) 6.78 (0.23) 7.06 (0.40) 7.21 (0.36) 7.16 (0.25) 7.14 (0.38) 6.59 (0.43) 5.42 (0.49) 3.84 (0.59) 1.74 (0.67)</td>
</tr>
<tr>
<td>$b^*$</td>
<td>16.70 (0.48) 15.90 (0.37) 15.61 (0.31) 15.15 (0.38) 15.35 (0.46) 15.13 (0.40) 14.40 (0.54) 13.11 (0.70) 10.47 (1.20) 6.41 (1.19) 2.62 (1.17)</td>
</tr>
</tbody>
</table>

Number of measurements $n = 80$

The surface colour was changing gradually from brown to dark brown or even black. The colour differences in the particular coordinates $\Delta L^*$, $\Delta a^*$ and $\Delta b^*$ related to the irradiation dose are illustrated in Fig. 5.

![Graphs showing colour changes](image)

**Fig. 5: Beech wood surface discolouration induced through irradiation from a CO\(_2\) laser LCS 400.**

The increasing irradiation dose also notably increased the total colour difference $\Delta E$. Having assessed the total colour difference according to Allegretti et al. (2009), we can declare that as early as at an irradiation dose of 20 J·cm\(^{-2}\) from CO\(_2\) laser LCS 400 according the methods reported, there already takes place a distinct wood surface discolouration and that with further dose increases, a completely new colour hue is obtained compared to the original one. The
distance between the specimen’s surface and the laser beam’s focus was sufficient to prevent engraving and eroding the wood substance from the specimen’s surface. These results are in a good accord with the results attained by Kačík and Kubovský (2011) and Vidholdová et al. (2017). Comparing our results with the results of these authors, we can suppose an important role of the direction of the laser beam movements (parallel or perpendicular to the grain).

The laser CM-1309 exhibited different effects, both in terms of quality and quantity, compared to the former experiment. In this experiment, increasing the laser power and the scanning density caused progressive wood substance degradation and removal from the specimen’s surface. The removed layer thickness increased proportionally with the laser’s power increase and scanning unit refinement. This was also responded by qualitative differences in discoloration of the irradiated beech specimens (Tabs. 4 and 5). The two-way variance analysis confirmed the important influence of the laser power and pixel size as well as the influence of interactions between these two factors on the beech wood discoloration.

Increasing the scanning density at a 4% power induced lowering the lightness $L^*$ values and increasing the colour coordinates values $a^*$ and $b^*$ with shifts towards red and yellow, respectively, thus causing the wood colour saturation (Tab. 4). The total colour difference $\Delta E$ ranged from the degree two to six on the six-degree evaluation scale (Fig. 6). Thus, the visual colour changes varied from just discernible up to a completely new colour.

At 8% laser power, the lightness decline due to increasing scanning density was much more obvious. The changes in the colour coordinates $\Delta a^*$ and $\Delta b^*$ were different by quality (Tab. 5, Fig. 6). Just from the minimal scanning density (1 mm$^{-1}$), the total colour difference $\Delta E$ was much more than 12, which means a completely new colour. This colour difference corresponded to the colour difference attained with 4% laser power and the finest raster (20 mm$^{-1}$). By refining the scanning density, the difference $\Delta E$ was increasing up to its up most value of 60 (Fig. 6).

**Tab. 4: Discolouration of beech specimens surface irradiated with a CO$_2$ laser CM-1309, with varied scanning density (power 4%).** The values in parentheses are standard deviations.

<table>
<thead>
<tr>
<th>Colour coordinate</th>
<th>Raster density (mm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>REF</td>
</tr>
<tr>
<td>$L^*$</td>
<td>80.09</td>
</tr>
<tr>
<td>$a^*$</td>
<td>5.33</td>
</tr>
<tr>
<td>$b^*$</td>
<td>16.59</td>
</tr>
</tbody>
</table>

Number of measurements $n = 60$
Tab. 5: Discolouration of beech specimens surface irradiated with a CO₂ laser CM-1309, with varied scanning density (power 8%). The values in brackets are standard deviations.

<table>
<thead>
<tr>
<th>Colour coordinate</th>
<th>Raster density (mm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>REF</td>
</tr>
<tr>
<td>L*</td>
<td>80.09</td>
</tr>
<tr>
<td>(1.59)</td>
<td>(1.32)</td>
</tr>
<tr>
<td>a*</td>
<td>5.33</td>
</tr>
<tr>
<td>(0.32)</td>
<td>(0.25)</td>
</tr>
<tr>
<td>b*</td>
<td>16.59</td>
</tr>
<tr>
<td>(0.43)</td>
<td>(0.42)</td>
</tr>
</tbody>
</table>

Number of measurements n = 60

Each specimen series was irradiated uniformly over the whole length and width. Because the distance between the specimen’s surface and the lens’ focus was by one order shorter than in the preceding experiment, the wood substance was decomposed and removed from the specimen surface. This indicates a temperature of more than 220°C on the surface. The removed layer thickness increased proportionally with the irradiation power and with the raster density, and this was also reflected in the specimens’ surface geometry. The same has been confirmed by Gurau et al. (2018). The specimens’ surface discolouration was more homogeneous than in the former experiment, although with certain differences between the early and the late wood.

Fig. 6: Changes in colour coordinates and in the total colour difference ΔE dependent on the raster density (for two power values at the engraving mode).
The microscopy observations also revealed that the discolouration inhomogeneity was, apart from early and late wood, due to pith rays that represent in beech wood a share of 20-25%. These rays consist of thin parenchyma cells (Kúdela and Čunderlík 2012). With increasing irradiation doses, the pith rays darkened faster than the libriform fibres. The microscopic photos also showed ongoing surface carbonisation.

The results of a Fourier transformed infrared spectroscopy (FTIR) and gas chromatography indicate (Dolan 2014) that beech wood surface irradiation with a CO$_2$ laser reduces amounts of polysaccharides depending on the amount of energy delivered. Surface irradiation with energy below about 20 J cm$^{-2}$ did not cause substantial degradation of polysaccharides, and the wood surface modification was not accompanied with carbonisation. This suggests that the temperature of surface layers did not exceed a value of about 200°C. The irradiation dose over 25 J cm$^{-2}$ initiated a dramatic loss of saccharides due to degradation of hemicelluloses and a portion of amorphous cellulose. There was also a noticeable increase in the ratio between cellulose and hemicelluloses (Kačík and Kubovský 2011). These specimens exhibited gradual carbonisation of the surface layers.

The XPS results also demonstrate changes to the lignin structure (Dolan 2014). Chemical reactions in lignin cause darkening primarily in the case of light-coloured wood species, including beech. Important agents are also extractives (Chang et al. 2010, Tolvaj et al. 2011) that are sensitive to UV radiation but may also respond sensitively to IR radiation effects.

Our results show, in accordance with other authors (Gurau et al. 2018, Li et al. 2018), that the energy amount delivered onto a wood surface with a laser beam and transformation of this energy into heat depend on the laser operating power, speed of the laser head displacement, focal distance and the scanning density. The wood capacity to absorb this energy into the main wood components is closely related to the changes to the wood chemistry. To attain a specific wood surface discolouration, it is necessary to quantify precisely the discolouration extent depending on the energy delivered from the laser and on the wood surface’s capacity to absorb this energy.

**CONCLUSIONS**

During beech wood surface modification with specific irradiation types, the surface was supplied with energy and subsequently, in contact with surface, this energy was transformed to heat.

The beech wood’s surface colour modification depended on the amount and method of the energy provision, on the absorbance capacity of the main beech wood components and on the chemical changes occurring in them.

The increasing irradiation dose always caused decreasing lightness of the beech wood’s surface and, in most cases, also increasing values of colour coordinates $a^*$ and $b^*$. This resulted in colouring the wood’s surface a darker brown. At high irradiation doses from CO$_2$ laser, the coordinate $a^*$ and $b^*$ decreased and the beech wood’s surface darkened (up to black).

The question of the nature of the changes induced by specific irradiation forms is multifaceted. To answer, it is necessary to investigate the surfaces treated in this way by detailed chemical analyses.
ACKNOWLEDGMENTS

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