Wavelength-dependent photodegradation of wood and its effects on fluorescence

Authors: Frank B. Peters (corresponding author)
Institut für Berufswissenschaften im Bauwesen (IBW),
Leibniz-Universität Hannover
peters@ibw.uni-hannover.de

Prof. Dr. rer. nat. Andreas O. Rapp
Institut für Berufswissenschaften im Bauwesen (IBW)
Leibniz-Universität Hannover

This is a repository version of the original article.
The original article was published online on 16.11.2021 by De Gruyter Publishers under the following link:

Please Cite as:

Abstract
Apart from some strongly fluorescent wood species, the general fluorescence of wood has long been ignored. Recent studies suggest that each species has a distinct fluorescence, originating from both basic components and characteristic extractives. However, wood colour and fluorescence rapidly change upon exposure to sunlight. In this study, 288 samples of *Acer pseudoplatanus, Quercus robur, Picea abies* and *Juglans nigra* were irradiated with different bands of ultraviolet (UV) and visible (VIS) light. Photosensitivity was examined in regards of colour, infrared absorbance (FTIR), and fluorescence imaging. UV light caused strong yellowing in all examined species, mostly correlating with lignin degradation, carbonyl formation and the appearance of a broad banded fluorescence emission. VIS light above 420 nm, however, caused different, partly contradicting effects in colour and fluorescence, and did not affect lignin. *Juglans nigra* proved to be most sensitive towards VIS-induced yellowing and bleaching. The main new finding of this study is that the native long wave fluorescence of wood was strongly decreased by VIS-irradiation above 510 nm wavelength in all samples. This effect was not species-specific, probably originating from a cross-species wood component. The results have potential impacts on non-destructive image-based evaluation methods and wood identification.

Keywords: discolouration, fluorescence imaging, FTIR, longwave fluorescence decrease, photodegradation
1. Introduction

Wood is subject to photochemical degradation when irradiated with light, leading to changes in colour and chemical composition of the surface (Evans 2013; Fengel and Wegener 2003; Hon and Minemura 2001; Kataoka et al. 2007; Prieto and Kiene 2019; Rabek 1996). Photosensitivity and discoloration are undesired effects not only in the use of solid wood, but as well in industrial processing of lignocellulose-based materials. The photodegradation process is dependent on temperature (Derbyshire et al. 1997), moisture (Turkulin et al. 2004), and irradiation wavelength, the latter having a decisive influence on the penetration depth (Kataoka et al. 2007; Živković et al. 2014) and chemical changes (Chang et al. 2000; Hon and Minemura 2001). The UV and violet portions of light cause the largest changes, most prominently degradation of lignin, leading to microcracks, checking (Evans et al. 2008) and reduction of tensile strength (Derbyshire and Miller 1981; Turkulin and Živković 2018). The most prominent discoloration process is yellowing, which is commonly attributed to lignin degradation (Bonifazi et al. 2015; Kataoka et al. 2007; Müller et al. 2003), accompanied by quinone and stilbene formation.

Visible light causes bleaching of characteristic chromophores in many dark woods (Prieto and Kiene 2019). Although blue light seems to be unable to degrade lignin, it can bleach wood (Baur and Easteal 2014; Kataoka et al. 2007). Hon and Minemura (2001) state that light of up to 580 nm causes lightening of Japanese larch (Larix kaempferi) and Passauer et al. (2015) report colour changes on thermically modified spruce wood by irradiation of up to 700 nm. However, the effect of visible (VIS) light on wood has received little attention. Together with the enormous heterogeneity of wood, these effects make it hard to develop non-destructive image-based evaluation applications for lignocellulosic materials.

Fluorescence imaging is a highly sensitive method that can reveal slight changes in chemistry below the detection limit of other methods. It is affordable, fast, and non-destructive and has become a popular tool in the analysis of material properties in many areas of live sciences (Miyawaki and Sakurai 2020), aquatic analysis (Coble et al. 2014), food sciences (Firouzjaei et al. 2018; Kalkan et al. 2014), forensics, and industrial quality control. The characteristic fluorescence of certain wood species is used as means of identification (Avella et al. 1988; Moya et al. 2013) and differentiation between CITES listed and closely related non-listed species (Miller and Wiemann 2006), partially also in form of fluorescing extracts (Miller 1976; Wheeler et al. 1989). Apart from that, fluorescence analysis methods are rarely used in wood science and technology. However, in the last years, fluorescence imaging methods have been applied to wood and other building materials as part of the emerging field of optical building-forensics (Rapp 2018). Although it is not as precise as fluorescence spectroscopy, the imaging component is an advantage when observing heterogeneous materials like wood (e.g. wood rays, decayed areas etc).
Promising approaches like automatic fluorescence-based wood classification systems (Antikainen et al. 2012; Camorani et al. 2008; Piuri and Scotti 2010), single board durability sorting, and industrial quality control applications need an in-depth knowledge of the optical properties of wood and its compounds. Moreover, the understanding of discoloration processes by VIS light can help in the development of individual light protection solutions for precious woods. Therefore, the aim of this study was to find correlations between irradiation wavelength, photodegradation, discolouration, and fluorescence changes in different wood types.

2. Material and methods

Samples of four different wood species (*Acer pseudoplatanus, Quercus robur* heartwood, *Picea abies, Juglans nigra* heartwood) were examined. The dice-shaped samples with an edge length of 15 mm were irradiated for 336 hours with mercury vapour lamps (OSRAM ultra vitalux 300W), covered by seven different edge filter glasses, an additional reference sample set being covered by light tight material. The long pass filters had edge wavelengths of \( \lambda_{T50\%} = 270; 280; 360; 380; 420; 460; \) and 510 nm. Edge filter glasses absorb light of lower wavelength and transmit light of higher wavelength. Consequently, the edge wavelength describes the type of light that is 50 % transmitted by the filter. Each species was examined in nine parallel samples per irradiation mode. The irradiated surface was radial, except for spruce, where the tangential surface was irradiated to analyse earlywood. Axially matched samples were taken to minimize natural variation. The test chamber was ventilated, and the air temperature above the samples did not exceed 30 °C. The moisture of the samples was between 5 and 12 % during irradiation.

After irradiation, infrared absorbance was measured with an FTIR-spectrometer (Thermo Scientific, Nicolet iZ10) by ATR at three different spots per sample. The number of multiple scans was 16, the resolution was 4 cm\(^{-1}\). The spectra were recorded and processed with the software OMNIC 9 and interpreted based on literature (Müller et al. 2003; Temiz et al. 2007; Tolvaj and Faix 1995; Ximenes and Evans 2006). To determine the degradation of lignin and the formation of aliphatic carbonyls, the peak heights at 1511 (skeletal vibration in the aromatic ring) and 1720–1740 cm\(^{-1}\) (C=O vibration in aliphatic carbonyls) were measured with the peak height tool of the software and divided by a reference peak at 898 cm\(^{-1}\). This peak is attributed to C1-vibrations in hexoses and was chosen due to its high stability against irradiation.

The colour of all irradiated samples was measured according to the CIE L*a*b* colour system, using a BYK-GARDNER (Geretsried, Germany) tool, type "spectro-guide sphere gloss". After three parallel measurements, the average values of each sample were recorded.

To measure the fluorescence, photographs were taken with a modified Canon EOS 6D forensic camera under use of narrow band Lumatec M05 forensic LED light sources and excitation/camera
light filters. The spectral range of the camera unit was $\lambda \approx 320–1050$ nm.

Figure 1 is a schematic representation of the fluorescence photography setting. Table 1 shows the light source/filter combinations of the different settings. All samples of one species were recorded in one shot to ensure comparability of the specimens. Exposure time, ISO number and excitation intensity were individually optimized for each setting.

![Figure 1: Experiment setting for fluorescence photography.](image)

Table 1: Light sources and filters according to fluorescence photography setting.

<table>
<thead>
<tr>
<th>Designation of setting</th>
<th>$\lambda_{\text{Peak}}$ of light source [nm]</th>
<th>$\lambda_{T50%}$ of excitation filter [nm]</th>
<th>$\lambda_{T50%}$ of camera filter [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV induced VIS-NIR fluorescence</td>
<td>365</td>
<td>Band pass 340-610</td>
<td>430</td>
</tr>
<tr>
<td>UV induced NIR fluorescence</td>
<td>365</td>
<td>Band pass 340-610</td>
<td>430</td>
</tr>
<tr>
<td>Blue induced VIS+NIR fluorescence</td>
<td>445</td>
<td>Band pass 410-510</td>
<td>540</td>
</tr>
<tr>
<td>Green induced VIS+NIR fluorescence</td>
<td>530</td>
<td>Band pass 410-510</td>
<td>640</td>
</tr>
<tr>
<td>Red induced NIR fluorescence</td>
<td>620</td>
<td>Band pass 340-610</td>
<td>850</td>
</tr>
</tbody>
</table>

$\lambda_{T50\%} = \text{edge wavelength of light filter}; \ UV = \text{ultraviolet}; \ VIS = \text{visible}; \ NIR = \text{near infrared}$

Two reference samples – PTFE and raw cotton fabric – were placed next to the samples in every setting. PTFE completely reflects almost all wavelengths and is non-fluorescent. Therefore, it was used as dark reference to rule out stray light. Unbleached cotton fabric served as bright reference due
to its relatively constant fluorescence emission over a broad wavelength range and its structural similarity to cellulose in wood. The white balance of all images was made on cotton fabric. RGB-values of the fluorescence images were read out and transferred into the CIE L*a*b* colour system.

3. Results and discussion

The FTIR examinations showed the degradation of the aromatic ring in lignin and the production of aliphatic carbonyls upon irradiation below $\lambda_{T50\%} = 420$ nm. This effect occurred in all wood species and the loss of aromaticity was almost complete at full irradiation ($\lambda_{T50\%} = 270$ nm). However, both lignin and carbonyl reference peaks (1510 and 1730 cm$^{-1}$, respectively) were not changed by irradiation above $\lambda_{T50\%} = 420$ nm. Hence, lignin was not degraded above $\lambda_{T50\%} = 420$ nm. This matches with literature (Evans et al. 2008; Evans 2013; Fengel and Wegener 2003; Mitsui 2010). Figure 2 shows the relative peak heights at 1510 and 1730 cm$^{-1}$ at different irradiation wavelengths, relative to the signal at 898 cm$^{-1}$.

Colour analysis showed yellowing and reddening of all species, darkening of light-coloured wood (Picea, Acer), and bleaching of dark wood (Juglans). Figure 3a–c depict the mean L*, a* and b*-values of the irradiated samples. However, yellowing proved to be a non-linear and multicausal effect, dependent of the wood species. Acer and Picea showed yellowing upon violet and UV-irradiation ($\lambda_{T50\%} = 420$ nm and below), approximately correlating with carbonyl formation (Figure 4). For
Quercus, this correlation was weaker. Bonifazi et al. (2015) found a similar correlation between colour change and lignin degradation in beech wood (Fagus sylvatica L.). Yellowing of Juglans, however, appeared almost exclusively upon irradiation above 420 nm (Figure 3c), whereas lignin degradation mainly occurred below 420 nm. Hence, yellowing of Juglans cannot be explained by lignin degradation but is dominated by chromophores vulnerable to visible light. This matches with results of Beyer et al. (2012) and Passauer et al. (2015), who emphasize the high susceptibility of many dark woods against visible light due to their photosensitive chromophores.

Figure 3: Mean colour values of species plotted against edge wavelength of irradiation filter. (a) Lightness values L* (b) red values a* (c) yellow values b*.

Brightness values (L*) of Juglans rose upon irradiation with \( \lambda_{50\%} = 460 \) and 420 nm, indicating a bleaching effect by blue light. Obviously, dark chromophores of Juglans are transformed to yellow degradation products by visible light, regardless of the yellow degradation products of lignin. The dark chromophores in Juglans heartwood mostly consist of ellagic acid derivatives, juglone.
derivatives, and other phenolic compounds (Bianco et al. 1998; Burtin et al. 1998). Many of them are known for their antioxidant activity (Ho et al. 2020) and form colourless, yellow, or black charge-transfer complexes or derivatives in different oxidation and condensation stages (Burtin et al. 2000; Dehon et al. 2002; Prieto and Kiene 2019; Tokutomi et al. 2018). The free radical generation in wood by visible light (Baur and Easteal 2014) could lead to a selective degradation of those chromophores. However, an abrupt slope between $\lambda_{T50\%} = 360$ and 280 nm indicates that UV light between 280 and 360 nm has a darkening effect, probably due to lignin degradation products. Passauer et al. (2015) found similar effects, stating that treatment with conventional UV-absorbers can have a negative effect on dark woods, resulting in increased bleaching compared to the untreated wood surface.

![Figure 4: Yellow values of samples in relation to carbonyl index, calculated from absorbance at 1730/898 cm$^{-1}$ in FTIR.](image)

All samples irradiated with light of $\lambda_{T50\%} = 460$ and 510 nm showed reduced red values ($a^*$), compared to the unirradiated samples. Lower irradiation wavelengths ($\lambda_{T50\%} = 420$ and below) reversed that effect, causing an increase in red values. *Quercus* and *Picea* showed a surprising colour difference between $\lambda_{T50\%} = 460$ nm and 510 nm irradiation modes. Irradiation of $\lambda_{T50\%} = 510$ nm caused significant yellowing, whereas yellow values were smaller for the samples irradiated with $\lambda_{T50\%} = 460$ nm (Figure 3). Reduction of yellow values upon $\lambda_{T50\%} = 460$ nm-irradiation were also observed for *Acer*, but without a yellowing effect at longer wavelengths.

Since the 460 nm-filter transmits all wavelengths above 460 nm – including light transmitted by the 510 nm-filter – it can be concluded that exposure to blue light ($\lambda \approx 440–500$ nm) has an anti-yellowing effect on *Quercus, Picea* and *Acer*, and exposure to green light ($\lambda \approx 490–575$ nm) has an anti-reddening effect on all observed species. This is also indicated by results of Hon and Minemura (2001)
and Beyer et al. (2012), who report a blue shift after irradiation with blue light and a green shift after irradiation with green light, respectively. This might be due to the selective degradation of blue/green absorbing chromophores in wood, respectively, leading to less blue/green absorption and therefore smaller yellow/red values. These substances might be especially unstable in blue/green light, because absorption is the uptake of energy by molecules and a requirement for photodegradation. Chang et al. (2000) report increased a* (red) values of Cryptomeria japonica heartwood after red irradiation (\(\lambda > 600\) nm), which supports this hypothesis. Although the VIS-induced colour shifts were comparably small, the error probability according to Student’s t-test was below 1 % for all above-mentioned discoloration effects, indicating a high significance of the results. Apparently, yellowing and colour change of wood is a multi-causal effect and cannot be ascribed to lignin degradation alone – not even for light coloured wood species.

Fluorescence photography

In the unirradiated state, light coloured woods (Picea and Acer) showed a UV-induced blue autofluorescence (\(\bullet\) in Figure 5a and b). Pandey and Chandrashekar (2005) reported blue fluorescence of unirradiated Pinus roxburghii, which is also a light-coloured species. Lignin is fluorescent in this area (Donaldson 2020). However, the UV-induced VIS+NIR fluorescence of Quercus was weaker (\(\circ\) in Figure 5c) and the emission of Juglans was red and NIR in colour (\(\ast\) in Figure 5d). Possibly, unirradiated light coloured wood species generally show emission spectra similar to lignin, while this emission is superimposed or reabsorbed in species with higher chromophore content.

Violet and ultraviolet irradiation below \(\lambda_{T50\%} = 420\) nm led to a strong broad-banded fluorescence, identifiable by its striking lightness under fluorescence photography (\(\bigcirc\) in Figure 5a–d). This effect occurred in all examined wood types and all excitation wavelengths (365–620 nm) and correlated with carbonyl production and lignin degradation (Figure 6a and b, respectively). In conclusion, the degradation products of lignin contain aliphatic carbonyl groups and have a strong fluorescence with broad excitation and emission bands, reaching beyond the visible area (\(\bigcirc\) in Figure 5a–d). The large stokes-shift and bandwidth are characteristic and might be used for the distinct measurement of lignin degradation products in wood, paper, and other lignocellulose-based products. For example, fluorescence could be an effective tool in monitoring the photodegradation process, complementary to other methods like microtensile testing (Turkulin and Živković 2018).

Irradiation with \(\lambda_{T50\%} = 380, 420, 460\) and 510 nm caused fluorescence decrease in all examined species. Most prominently at longer excitation wavelengths (\(\bigcirc\) in Figure 5a–d), a significant loss of emission was observed. For shorter irradiation wavelengths (\(\bigcirc\) in Figure 5a–d), these changes were weak or non-existent, possibly because this effect was superimposed with the fluorescence of lignin.
degradation products (as described above). Therefore, there were chemical changes caused by visible light ($\lambda > 500$ nm) even in those species where FTIR-analysis did not reveal changes.

Figure 5: Compilation of fluorescence photographs of (a) Acer (b) Picea (c) Quercus (d) Juglans. Lines represent excitation/emission setting according to Table 1; columns represent irradiation modes. (1) Native blue fluorescence of Acer and Picea (2) weak native fluorescence of Quercus (3) red and NIR native fluorescence of Juglans (4) broad banded emission of lignin degradation products in all observed species, excited by UV and (5) VIS light (6) loss of VIS-excited NIR emission after VIS irradiation. Note: Only specimens in the same line can be semi-quantitatively compared, because they were recorded in the same shot.

Since the observed fluorescence decrease affected all examined species at comparable scale, it is unlikely that the substances in question are wood type-specific extractives. In contrary, they seem to be basic components of wood in general. Based on literature research, an overview of eligible VIS-
sensitive fluorophores and quenching effects is given below:

Pfanz et al. (2002) and Mishra et al. (2018) report chlorophylls in sapwood of diverse species, which have broad band fluorescence with an emission peak between 645–670 nm. However, there are no indications that chlorophyll residues are present in heartwood, nor that chlorophyll is degraded by visible light. Cellulose of different origins (Castellan et al. 2007; Grönroos et al. 2018) and degrees of purity (Tylli et al. 1996) is fluorescent in the visible range, with emission peaks in the blue to yellow area (Khalid et al. 2019).

The origin of cellulose fluorescence is assumed to be in trace compounds, cellulose functioning as a focalizer and exciton-donor (Castellan et al. 2007; Grönroos et al. 2018). Energy-transfer processes in cellulose have also been assumed by Fengel and Wegener (2003), and cellulose derivatives are systematically used to form charge-transfer-complexes for diverse applications (Mao and Ritcey 1996; Nagai et al. 2015). These hypotheses are supported by the findings of Ding et al. (2020), who

![Figure 6: Yellow fluorescence of the irradiated samples plotted against (a) carbonyl and (b) lignin indices. Yellow values (b*) were digitally read out of the UV-induced VIS and NIR fluorescence images.](image-url)
report a proportional correlation between the degree of polymerisation of nanocelluloses and their fluorescence emission at $\lambda = 574$ nm. Although it is known that the degree of polymerisation of cellulose rapidly reduces upon UV-irradiation (Desai and Shields 1969; Ou and Huang 2003), visible light does not seem to have a measurable effect (Buschle-Diller and Zeronian 1993). Tylli et al. (1996) describe the photochromic behaviour of pure cotton cellulose and found that the fluorescence emission was quenched upon irradiation at 350 nm. Since degradation of cellulose alone is not fully convincing, further studies are needed to explain the NIR fluorescence of native wood and its reduction by visible light. If the longwave fluorescence decrease can be attributed to other material properties (degree of polymerisation, crystallinity, cross-linking etc.), potential monitoring applications lie in the fields of pulp and paper industry, biobased polymers, and other lignocellulosics.

4. Conclusions
To observe photodegradation products of lignin, fluorescence is more useful than colour, because it is independent of the native wood colour. Lignin degradation products contain aliphatic carbonyl groups and are easily identifiable by their strong fluorescence emission in a wide range from yellow to near infrared at any excitation wavelength (Figure 5).

The observed NIR-fluorescence of untreated wood seems to be present in all species, although further research is needed to extend this hypothesis to other species. It strongly decreases upon irradiation with visible light of wavelength above 500 nm. Since the longest edge wavelength of filters in this study was 510 nm, conclusions about even longer wavelengths could not be made. Theoretically, the longwave fluorescence decrease could also be an effect of longer irradiation wavelengths in the green, yellow, or red wavelength band. The underlying mechanisms need to be further examined to make full use of the findings in potential monitoring applications.

Due to its high sensitivity, fluorescence is a good indicator for changes in the chemistry and composition of complex polymers like wood. Possible applications are in timber identification, the evaluation of wood degradation, and process control in wood polymers and composite materials. Although it is not as precise as spectroscopy, fluorescence photography with its advantage of spatial resolution proved to be an appropriate method of examining surface photodegradation and shows effects which are not measurable in FTIR spectroscopy and colour analysis. To make full use of the potential of this method, the underlying mechanisms need to be further examined.

Conflicts of interest:
The authors declare no conflicts of interest regarding this article.
References


Evans, P.D., Urban, K., Chowdhury, M.J.A. (2008) Surface checking of wood is increased by photodegradation caused by ultraviolet and visible light. Wood science and technology : journal
of the International Academy of Wood Science; research journal 42:251.


