

Steaming-caused chemical changes of sugi (*Cryptomeria japonica*) wood monitored by NIR spectroscopy

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Abstract. Mahdiyanti SH, Tsuchikawa S, Mitsui K, Tolvaj L. 2020. Steaming-caused chemical changes of sugi (*Cryptomeria japonica*) wood monitored by NIR spectroscopy. *Asian J For* 4: 6-9. Steaming is a common method to change the color of wood to enhance attractiveness. This study aimed to investigate time-dependence of chemical changes of sugi (*Cryptomeria japonica* D. Don) wood steamed with temperature of 90 and 110°C and monitored up to 20 days using NIR spectroscopy. The difference spectrum method was applied to find the absorption increases and decreases. Before the subtraction, the spectra were normalized to one unit at 1739 nm to eliminate the parallel shift of the spectra. The results showed that steam-induced chemical changes in the wavelength range of 1300-2100 nm were related to the absorption of water and the absorption of extractives, especially phenolic contents. These chemical changes were suspected to be strongly related to color changes in steamed wood. Longer duration of steaming caused phenolic compounds to change into similar contents in all wood tissues, which cause their color to change more uniformly. Steaming caused a water bounding capacity loss of the cell wall. This change was much faster at 110°C than at 90°C.

Keywords: Color change, hydroxyl groups, steaming, sugi wood, NIR spectroscopy

Abbreviations: NIR: near infra-red, E: earlywood, L: latewood, H: heartwood, S: sapwood, nm: nanometre

INTRODUCTION

Steaming is a useful method for color modification of wood materials. Some wood species have a white-greyish color without a distinct texture (e.g., poplar, beech, hornbeam, etc.), while some other species have a strikingly inhomogeneous color (e.g., black locust, Turkey oak, beech having red heart, etc.). Disadvantageous wood texture might be turned to a more favorable appearance using steam treatment. The color modification effect of steaming is a widely investigated phenomenon (e.g., Varga and van der Zee 2008; Straze and Gorisek 2008; Tolvaj et al. 2009, 2010, 2012; Milic et al. 2015; Geffert et al. 2017; Dzurenda 2017, 2018a, 2018b; Banadics and Tolvaj 2019).

The color of a material is determined by the presence of conjugated double bond chemical systems. In natural wood material, these systems are located in lignin and in extractives with the color of wood species is primarily determined by the extractive content. Extractives are highly sensitive to heat and this is exploited as the main basis of color modification by steaming where wood material is subjected to the simultaneous effect of heat and moisture. Generally, the maximum steaming temperature is 120°C in industrial practice. This is the upper temperature limit because of the high steam pressure above this temperature. Most of the main chemical substances of wood (cellulose, hemicelluloses, and lignin) are stable below 120°C. It is

well known that mainly the thermally less stable polyoses are decomposed due to the influence of heat (Fengel and Wegener 1984). Acetic acid is released by the scission of acetyl groups linked as an ester group to the hemicelluloses (Tjeerdsmas and Militz 2005; Windeisen et al. 2007). The degradation products of hemicelluloses modify the initial color of wood. This phenomenon is the second-order producer of color changes during steaming. The main creators of this color change are the extractives, yet the chemical changes of extractives cannot be traced by middle IR spectroscopy because of their low-level quantity (Tolvaj et al. 2013).

The NIR wavenumber range from 12800 to 7000 cm⁻¹ is considered to be influenced by particle size and especially by visible color change, and it has proven to be useful for qualitative purposes (Schwanninger et al. 2011). The NIR wavenumbers related to extractives, 7092 and 6913 cm⁻¹ assigned to first overtone of O-H stretching, is due to the presence of phenolic hydroxyl groups (Schwanninger et al. 2011). Phenolic compounds are suspected to be responsible for wood discoloration related to extractives (Torres et al. 2010). The change in acetyl ester in hemicellulose due to thermal degradation related to color change can be observed in the NIR second-derivative spectra between 8650-8450 cm⁻¹ (Schwanninger et al. 2011). The NIR wavenumber, which is adjacent to the visible-light range, is supposed to be sensitive to trace

visual color change, and is more suitable for the observation of chemical change related to the color in wood.

The aim of this study was to investigate the chemical changes of sugi (*Cryptomeria japonica* D. Don) wood generated by the steaming temperature of 90 and 110°C. The time-dependence of the chemical changes of sugi wood was monitored up to 20 days of steaming using NIR spectroscopy.

MATERIALS AND METHODS

Preparation of materials

Sugi (*Cryptomeria japonica* D. Don) samples were prepared for steaming. The specimen size was 150x20x10 (mm). The largest surface contained only earlywood or latewood (tangential surface). Half part of the specimens was sapwood and the other half part was heartwood. The average moisture content of the samples was 9.1% before the steaming process.

Steaming treatment

Steaming was carried out at 90 and at 110°C. Wood specimens were placed in a large pot with distilled water beneath for conditioning the air to generate 100% relative humidity. Even at 110°C the pot was able to maintain overpressure. The pot was heated in a drying chamber to the indicated temperatures. The steaming process started with a four-hour pre-heating period. The temperature was regulated automatically around the pre-set values with a tolerance of 0.5°C. Specimens were removed after 5, 9, 14 or 20 days of steaming, respectively. The wood specimens were conditioned for one month both before and after steaming at room temperature before the NIR measurement.

Color changes monitoring

For NIR measurement the sample size was 20x20x10 (mm). The measured surface contained only earlywood or latewood. Three samples were prepared for each NIR measurement (earlywood of sapwood and heartwood, latewood of sapwood and heartwood, before steaming and after each steaming period). Altogether 96 samples were prepared for NIR measurement. The samples of steaming schedule 90°C and 5 days were ignored for NIR measurement, because the color change was small in this case.

The NIR device used to measure the samples was a Fourier transform (FT) NIR spectrometer, Matrix-F (Bruker Optics, Germany), with instrument settings as follows: wavenumber resolution of 8 cm⁻¹, 32 scans of samples and references, and a wavenumber range of 10000-4000 cm⁻¹. After the measurement, wavenumbers were transformed into wavelengths. The measured three NIR spectra were averaged for further evaluation. All NIR spectra were parallel with the horizontal axis in the 1700-1800 nm range. Spectra show that there is no absorption in this region. But the spectra were slightly shifted from each other in the vertical direction. This parallel shift was generated by the different scattering properties of the individual samples. The effect of scattering was eliminated by the normalization of the spectra. All data of the

individual spectrum were multiplied with a proper constant to get the unit value at 1739 nm. The normalization eliminated the parallel shift of the spectra. The effect of steaming was presented by the different spectra. The spectrum of the initial (unsteamed) sample was subtracted from the spectrum of steamed sample. In this case, positive and negative bands represent absorption increases and absorption decreases, respectively. Details of spectrum manipulations are explained in previous work (Csanady et al. 2015).

RESULTS AND DISCUSSION

The results showed that chemical changes related to color in the NIR spectra observed in wood samples treated at 110°C were more obvious than in those treated at 90°C, especially at the wavelength of 1410 nm (7092 cm⁻¹) and 1447 nm (6913 cm⁻¹). These wavelength ranges are assigned to phenolic hydroxyl compounds (Schwanninger et al. 2011). The values of difference NIR spectra of latewood in both heartwood and sapwood showed a decrease at these wavelengths from day-5 to 14 of treatments, but then increased by the 20th day (Figure 1 and 2). Meanwhile, the values NIR spectra of earlywood in both heartwood and sapwood (Figures 3 and 4) at 110°C increased from 5 to 14 days of treatment, then decreased by the 20th day. Heartwood and sapwood contain different amounts of phenolic extractives (Fengel and Wegener 1984). This showed in the different changes of phenolic compounds in heartwood and sapwood during steaming, where heartwood had higher extractive contents than sapwood (Figures 1 and 3). There is no clear distinction between latewood and earlywood extractive contents, but in the study of *Pinus radiata*, latewood in the heartwood, especially in the inner heartwood, higher extractive contents were found than in earlywood (Lloyd 1978). This explains the different changes of phenolic extractive contents in the latewood and earlywood of heartwood.

In latewood, the increasing amount of phenolic compounds by the 20th day of treatment indicated the contribution of other wood cell wall components degradation. As explained by Esteves and Pereira (2009), most extractives degrade during heat treatment, but new compounds that can be extracted from wood appear as a result of the degradation of cell wall structural components. Hemicellulose degradation is suspected to contribute to the chemical changes related to color in steamed wood, as it is the least stable cell wall component even at low temperatures (Esteves and Pereira 2009). Latewood appears to have higher hemicellulose contents than earlywood, according to Kurata et al. (2018) in their report on sugi. Steaming causes partial degradation to hemicellulose (Geffert et al. 2017) and sometimes it is accompanied by the relative increase of total extractive contents (Sikora et al. 2018).

A report by Torres et al. (2010) explains that in heartwood, the brown color is primarily related to the oxidation of phenolic compounds. In this experiment, latewood in both heartwood and sapwood tissues had

darker color than earlywood in both heartwood and sapwood, indicating higher content of phenolic compounds in latewood. It explained the change of phenolic compounds in latewood, which was greater than in earlywood during steaming. By the 14th to 20th days of treatment, yellowness (b^*) showed small change and resulted in an almost uniform yellow color level of all wood tissues (Figure 5). This result is in accordance with the report by Sundqvist (2002) in heat-treated wood, where heat treatment produced similar contents of phenolic

compounds in wood tissues, and led to a more uniform color.

The evaluation of color change showed that both yellowness and redness changes were mostly completed before the fifth day of steaming (See the yellowness change presented in Figure 5). At the same time, absorption decrease around 1930 nm occurred during the first five days of steaming at 110°C (Figures 1-4). In contrast, the absorption decrease around 1930 nm continued during the full 20 days of steaming at 90°C (Figure 6).

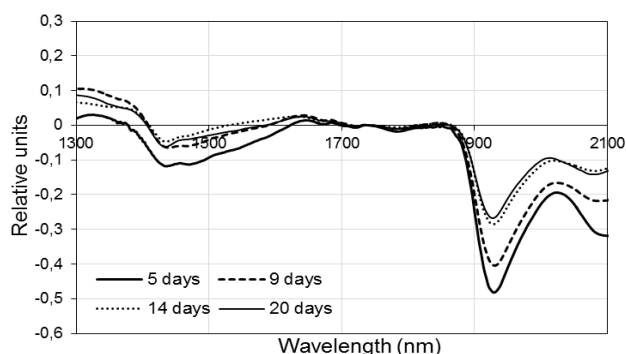


Figure 1. Difference NIR spectra of the latewood in heartwood of sugi steamed at 110°C

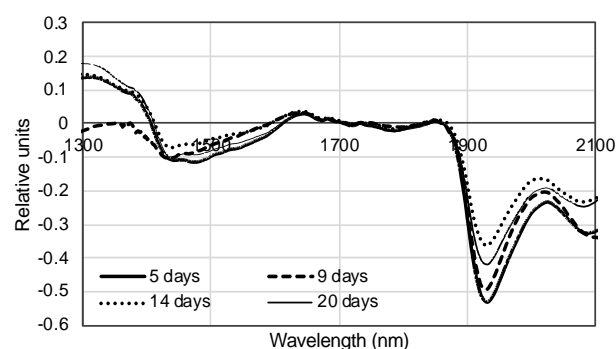


Figure 2. Difference NIR spectra of the latewood in sapwood of sugi steamed at 110°C.

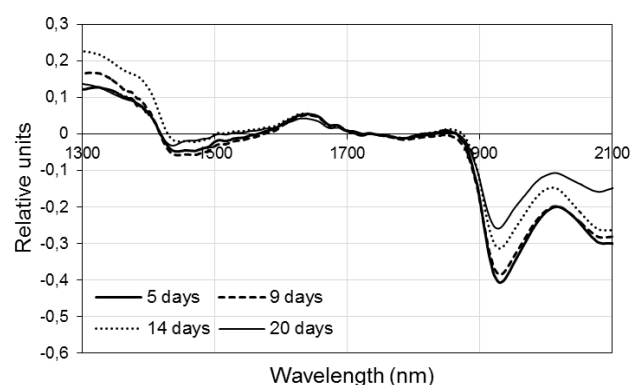


Figure 3. Difference NIR spectra of the earlywood in heartwood of sugi steamed at 110°C.

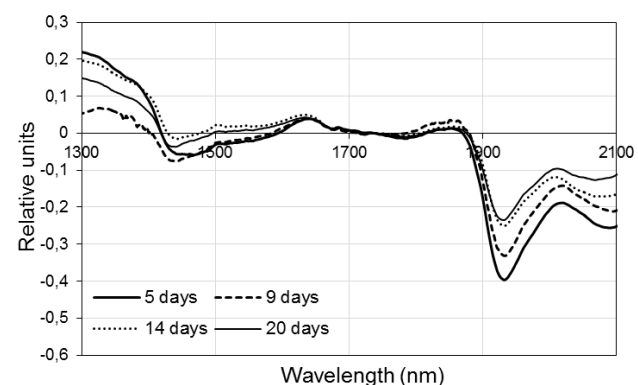


Figure 4. Difference NIR spectra of the earlywood in sapwood of sugi steamed at 110°C.

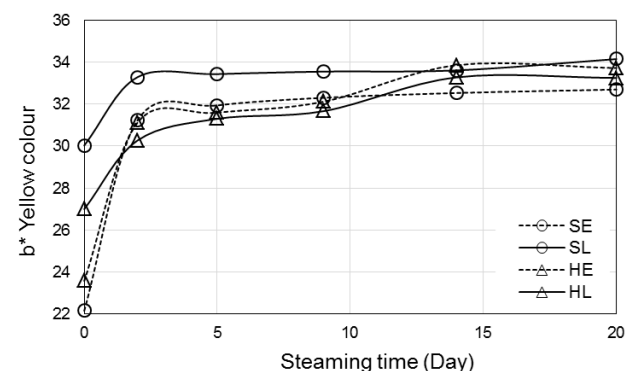


Figure 5. The yellowness changes in different tissues during steaming at 110°C. (S: sapwood, H: heartwood, E: earlywood, L: latewood) (Tolvaj et al. 2019)

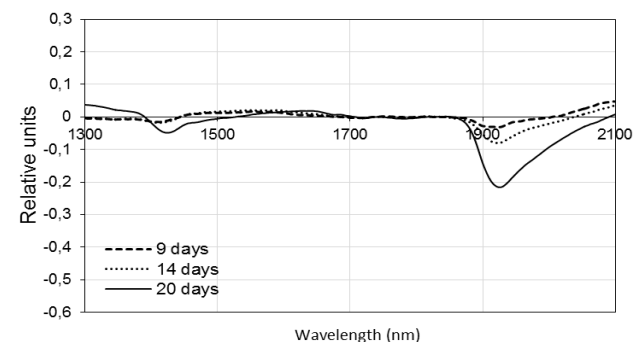


Figure 6. Difference NIR spectra of the latewood in heartwood of sugi steamed at 90°C.

This absorption band around 1930 nm is the typical band of bound water located in the cell wall. (Schwanninger et al. 2011). Figures 1-4 show that steaming reduced the water bounding capacity of sugi wood. As the NIR spectra were measured three months after the steaming, results demonstrate that this water bounding capacity loss was stable. The steaming time dependence of water bounding capacity loss showed a minimum at the fifth day of steaming at 110°C. Our results demonstrated that five days of steaming at 110°C generated the optimum of both color change and water bounding capacity loss. The consequence of decreased water bounding capacity is an increase in dimensional stability. The dimensional stability increase is an important advantage of steaming.

Figure 6 demonstrates that the water bounding capacity loss at 90°C was much slower than at 110°C. The water bounding capacity loss continued during the full 20 days of steaming at this lower temperature.

In conclusion, chemical changes in sugi wood steamed at 90 and 110°C and observed using NIR spectroscopy in the wavelength range of 1300-2100 nm are related to water contents and extractives, especially phenolic contents. These chemical changes are suspected to be strongly related to color changes in steamed wood. Longer duration and higher temperatures of steaming "equalize" the amount of phenolic compounds in all wood tissues, which caused their color to change more uniformly. Phenolic compounds are suspected to show initial changes at steaming temperatures of 90°C. Hemicellulose is also suspected to contribute to the color changes of steamed wood. Steaming generated a water bounding capacity loss in the cell wall. This change was much faster at 110°C than at 90°C.

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