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MODIFICATIONS IN SPRUCE WOOD STRUCTURE FOLLOWING HYDRO-THERMAL TREATMENT EVALUATED BY NIR SPECTROSCOPY

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Abstract:

Sitka spruce wood samples were subjected to different conditions of hydrothermal treatment at 140^{o}C by varying the relative humidity and period of exposure. The control/reference and treated wood samples were evaluated using near infrared spectroscopy (NIRS), principal component analysis (PCA) and two dimensional correlation spectroscopy (2DCOS) in order to identify the structural modifications appearing during the treatment. Following this, the changes were reflected by the shifting of the bands position, modifications in bands intensities and width, as well as baseline offset. Higher modifications were identified in the 7400-6000 and 5100-4100 cm^{-1} regions assigned mainly to hemicelluloses and extractives, indicating that these components were the most susceptible to degradation in the present treatment conditions. Further, by PCA was possible to differentiate the modifications in the wood samples according to the time of treatment and relative humidity, while by 2DCOS was possible to identify the sequential order of modifications.

Key words: *sitka spruce wood; hydrothermal treatment; near infrared spectroscopy; principal component analysis, two dimensional correlation spectroscopy.*

INTRODUCTION

Wood is a material used in many applications (from construction to furniture and different objects), but due to its structural features and depending on the environmental conditions (humidity, temperature and biological agents), can be easily degraded by different factors.

Three major components, cellulose, lignin and hemicellulose are composing the structure of wood, along with other low molecular compounds. Cellulose is a linear polymer composed by anhydro–D–gluco–pyranose units which are linked via β(1–4) glycosidic linkages. On the other side, lignin is a three dimensional crosslinked aromatic polymer formed from phenyl propane units, with/without methoxyl groups bonded to the aromatic ring (guaiacyl, syringyl and p-hydroxyphenyl units), and linked together by β–O–4 aryl ether or carbon-carbon linkages, while hemicelluloses are mainly composed of glucose, mannose, galactose, xylose and arabinose, and are branched polymers with a significantly lower molecular mass comparing to cellulose (Chang et al. 2010; Assor et al. 2009).

To understand the mechanisms of degradation of wood during natural conditions, many researchers tried to simulate the natural environmental conditions with accelerated controlled ones. In this context,

biodegradation agents, like soft, brown and white rot fungi or termites (Fackler and Schwanninger 2011; Lekounougou and Kocaefe 2012; Popescu et al. 2016); thermal and hydrothermal ageing (Popescu et al. 2018; Zeniya et al. 2019a; Zeniya et al. 2019b) or weathering and UV light eposure (Popescu et al. 2011; Tolvaj et al. 2016) were investigated in the last years in research studies in order to simulate by accelerated controlled conditions the natural occurring ones and to understand the mechanisms of degradation.

Thermal and hydrothermal treatments are often used to improve some of the wood material properties (i.e. durability, dimensional stability of hydrophobicity) (Esteves and Pereira 2009), but also, as mentioned above, at the same time can be used to simulate the natural degradation of wood (Popescu et al. 2018; Zeniya et al. 2019a; Zeniya et al. 2019b; Candelier et al. 2011). During dry thermal degradation, wood undergoes combined dehydration, decarboxylation and oxidation reactions coupled with heat and mass transfer. If certain amounts of water vapours are present in the medium during the treatment, other than the above-mentioned reactions, wood undergoes hydrolysis reactions and the crystallization of wood cellulose might be affected (Akgul et al. 2007; Popescu et al. 2018). In this context, the degradation of wood components is reached mainly by means of hydronium catalysed reactions. In a first stage, these ions are generated from the water molecules autohydrolysis, followed by the generation of the acetic acid (by the hydrolysis of the acetyl groups from the wood structure). Further ionization provides most of the catalytic species involved in the degradation process (Conner 1984). Therefore, the susceptibility of a certain wood species to hydro thermolysis depends on its ability to generate acetic acid in the reaction media, although the neutralizing ability of the wood plays a role in the presence of hyronium ions (Garrote et al. 2001).

Spectral techniques, and in particular near infrared spectroscopy (NIRS), gives exceptional combination of speed, little or no sample preparation, easy use, non-destructiveness and good reproducibility and low cost instrumentation, thus can be applied to process monitoring and quality control evaluation (Schwanninger et al. 2011; Popescu and Popescu 2013). Small changes in the chemical composition or physico-chemical properties of materials will cause spectral changes in diffusely reflected near infrared radiation, the multiple chemical absorptions considerably affecting the shape of the near infrared spectra leading to sifts of the position of the maxima, increased or reduced bands' intensities and/or baseline offset (Schwanninger et al. 2011; Popescu et al. 2016; Popescu et al. 2018). In the case of wood material, near infrared spectroscopy can be successfully used for the non-destructive evaluation of various wood species stiffness (i.e. Meder et al. 2002) and structural changes during thermal treatment (Schwanninger et al. 2004; Popescu and Popescu 2013; Popescu et al. 2018) etc.

Principal component analysis (PCA) is a well-established statistical procedure, which gives a precise mathematical estimation of the changes taking place along the object and variable vectors. By PCA data dimensionality is reduced by redefining the axes, therefore they correspond with the directions of most variances, where these new axes or principal components (PCs) correspond with the eigenvectors of the original data's covariance matrix (Via et al. 2014; dos Santos Grasel et al. 2016). By converting the data into the dimensionally reduced PCA space, the input data set is decomposed into two matrices of interest: scores and loadings (Via et al. 2014). The loadings matrix defines the new axes of the dimensionally reduced data set, while the scores matrix describes the samples in the PC space. With PCA, the most important features of the NIR spectra can be identified, and the band shifts and non-symmetries in the bands between the samples can be quickly determined (Via et al. 2014; Popescu and Popescu 2013; Popescu et al. 2018).

Two dimensional correlation spectroscopy (2DCOS), a technique established by Noda in 1993 (Noda 1993), is based on computation of auto-correlation and cross-correlation between spectra and provides a graphical overview for the analysis of external perturbation induced variations. This external perturbation can be related to temperature, pressure, moisture, concentration, composition, pH or time change (Noda 1993; Czarnecki 1998; Noda and Ozaki 2004). 2D correlation analysis can be applied to various types of systems, once the external perturbation is described as a specific function. The method was widely applied in wood science to mid infrared spectroscopy (i.e. Popescu et al. 2011; Popescu et al. 2007; Popescu et al. 2016) and near infrared spectroscopy (Fackler and Schwanninger 2010; Wanga et al. 2009; Popescu and Popescu 2013; Popescu et al. 2018).

In previous papers (Zeniya et al. 2019a; Zeniya et al. 2019b) time–temperature–superposition relationship to predict the mass loss of wood after hydrothermal treatment at arbitrary temperature and relative humidity, as well as the mass loss dependencies of vibrational properties and colour parameters were discussed. In the present study, we describe the relation between the applied treatment and the related structural changes taking place by near infrared spectroscopy, principal component analysis and two dimensional correlation spectroscopy.

OBJECTIVE

The purpose of the present research was to evaluate the structural changes which may appear during the hydrothermal treatment of Sitka spruce wood under 140 ^{o}C and different values of RH (0, 60, 75 or 100 %RH) and periods of exposure, by using near infrared spectroscopy (NIRS) and chemometric techniques.

MATERIAL, METHOD, EQUIPMENT

Materials

Sitka spruce (*Picea sitchensis*) wood specimens with an average air-dry density of 439 kg/m^3 and dimensions of 120mm (longitudinal) x 15mm (radial) x 1.6mm (tangential) were used in the present study. In order to remove the hygroscopic history during seasoning, the wood samples were moistened at 25^{o}C and 100%RH for about 5 days, followed by vacuum drying on P_2O_5 at 25^{o}C for about 7 days. On a second step the wood samples were conditioned at 25^{o}C and 0, 60, 75 or 100%RH for more than 30 days prior the hydrothermal treatments.

Hydrothermal treatment

The wood samples, previously conditioned at 25^{o}C and 0, 60, 75 or 100%RH for more than 30 days, were hydrothermally treated in an autoclave at 140^{o}C, different RH values and different periods of time. The autoclave was equipped with a thermocouple and pressure sensor (PHS-B-500KP, Kyowa Dengyo Co.). For each treatment condition were used five sample replicates.

The wood samples were placed in the autoclave along with different amounts of deionized water in order to achieve the desired values of the RH in the chamber, then closed and the temperature was increased to 140^{o}C. Both, temperature and pressure reached the expected levels within 1h. The values of RH in the autoclave were calculated from the water vapour pressure. Detailed information about the specification and performance of the autoclave are given in a previous paper (Endo et al. 2016).

The samples treated at 0 %RH were heated in an oven at 140^{o}C for up to 47 days, in order to obtain a sufficient mass loss comparable with that obtained in moist conditions.

After the treatments, the wood samples were immediately cooled down to room temperature and vacuum dried on P_2O_5. The absolute dry mass was determined according to the following formulae:

$$ML\% = \frac{M_1 - M_0}{M_0} \times 100 \quad (1)$$

where: ML is the mass loss, M_1 and M_0 are the absolute dry mass of the control/unmodified and hydrothermally modified wood samples respectively.

Near infrared spectroscopy (NIRS) measurements

Near infrared spectra were recorded on a NIRFlex N500 instrument with a resolution of 8 cm^{-1}, in the 10000-4000 cm^{-1} spectral range. The data processing was performed using The Unscrambler® X 10.4.1 program (CAMO AS, Trondheim, Norway). Further, in order to get more detailed information, principal component analysis (PCA) and two-dimensional correlation spectroscopy (2DCOS) were applied. For the analysis, the medium spectrum obtained from the three recordings of each sample replicate was retained.

For PCA analysis, the NIR spectra of all the measured samples were used and the processing was performed by The Unscrambler® X 10.4.1 program (CAMO AS, Trondheim, Norway).

Generalized 2D correlation spectra were created using *2Dshige* (c) (developed by Shigeaki Morita, Kwansei-Gakuin University, 2004-2005) and the second derivative of the medium spectrum obtained from the five replicates of the wood NIR spectra.

RESULTS AND DISCUSSION

Hydrothermal treated samples present different values of mass loss depending on the values of relative humidity during the treatment and on the treatment time (see Table 1). As can be observed, the wood samples treated at higher RH values and time present higher values of the mass loss.

Table 1

Hydrothermal conditions and mass loss

Temperature (^{o}C)	RH (%)	Time (days)	average ML (%)
140	0	0	0.23
		12	4.47
		23	7.79
		47	7.78
	60	0	0.11
		1	2.56
		2	3.65
		4	8.54
		7	11.94

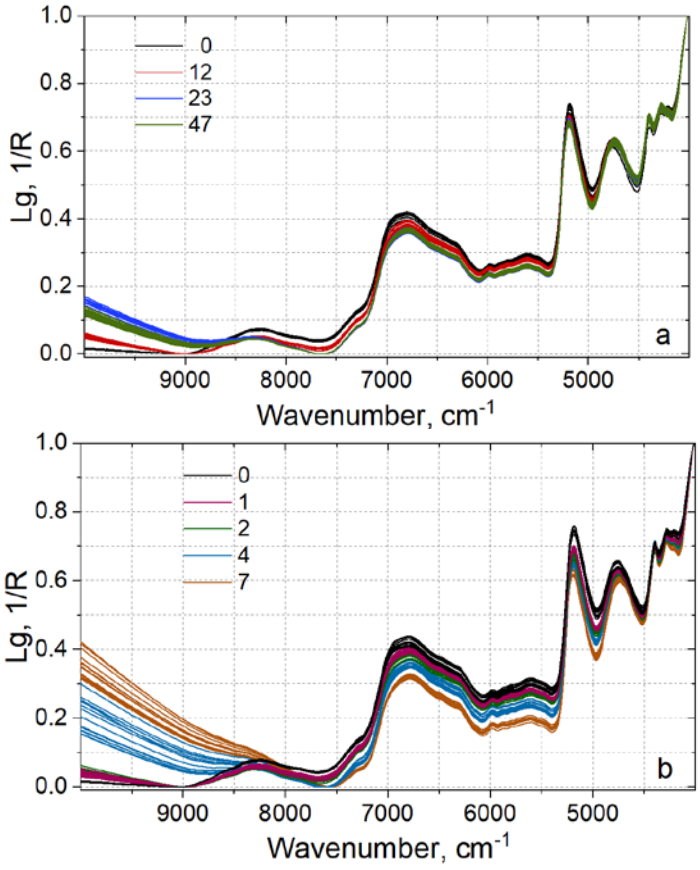
	75	0	0.10
		0.5	2.01
		1	4.74
		1.875	6.23
		4	11.74
	100	0	0.30
		0.125	1.29
		0.25	2.58
		0.5	4.39
		1	6.69

Near infrared spectroscopy

The NIR spectra recorded in the 10000-4000 cm^{-1} region are presented in Figures 1a – d. The spectra present typical absorption bands for wood, consisting in broad signals of highly overllaping individual bands of the overtone and combination modes associated with its chemical components. Generally, the spectra are divided in five main regions, namely: 10000-7000 cm^{-1} assigned to first and second overtones of C-H stretching vibrations in methyl and methylene groups from carbohydrates and lignin (Schwanninger et al. 2011; Popescu et al. 2018); 7000-6000 cm^{-1} assigned to first overtone of the C-H combination bands, and first overtone of different O-H stretching vibrations (Schwanninger et al. 2011; Popescu et al. 2018); 6000-5000 cm^{-1} dominated by the first overtone of the aliphatic and aromatic C-H stretching vibrations and O-H combination bands in all wood components (Schwanninger et al. 2011; Popescu and Popescu 2013; Popescu et al. 2018) and 5000-4000 cm^{-1} assigned mostly to C=O groups, O-H stretching and deformation vibrations, C_{ar}-H and C-H stretching vibrations and also to C-H stretching and C-H deformation vibrations (Schwanninger et al. 2011; Popescu and Popescu 2013; Popescu et al. 2018).

As can be observed from Figure 1, the changes induced in the structure and content of wood components by hydrothermal treatment are reflected in the NIR bands position of the maxima, intensities, width, as well as baseline offset, and they differ according to the applied treatment.

The samples treated in dry conditions, even though the treatment time is longer than for the other samples, present less variations in their spectra (Fig 1a) comparing to the spectra of the samples treated in different humid conditions (Figs 1b, 1c and 1d).



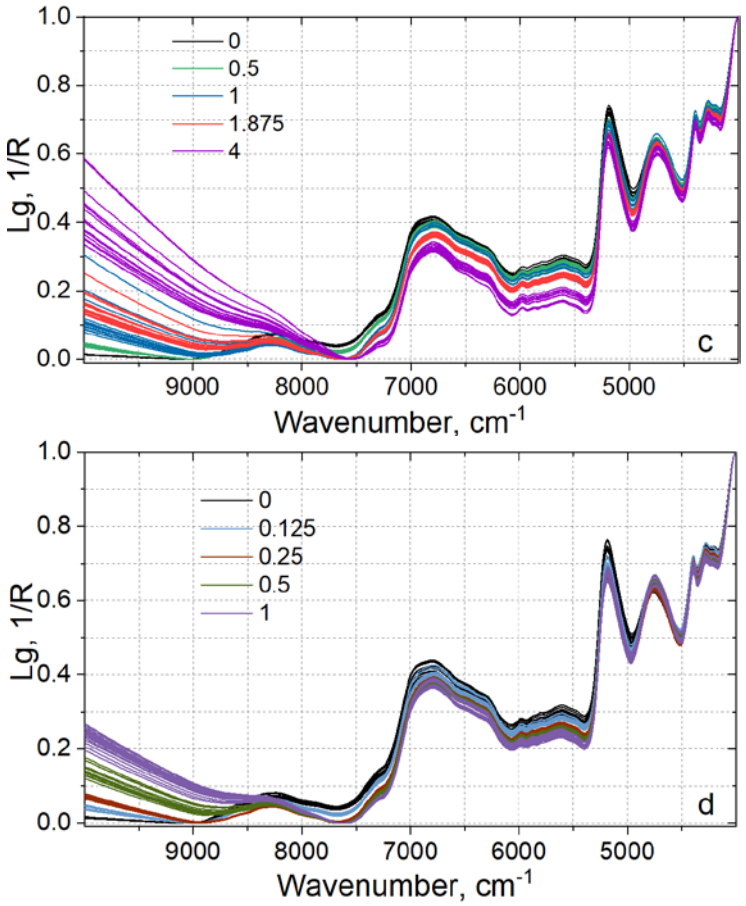


Fig. 1.
NIR spectra of reference and hydrothermally treated wood samples at 0%RH (a); 60%RH (b); 75%RH (c) and 100%RH (d).

In contrast to mid infrared spectroscopy, in NIRS it is more difficult to assign the bands to a certain functional group and to identify the specific individual signal due to their overlapping. Also, the reason of intensity decrease or increase or position shift may be due to only one component band modification. Therefore, to improve the spectral resolution, the second derivative (Savitzky-Golay method) spectra were obtained. In Fig. 2 are presented the second derivative spectra of the hydrothermally treated samples in 100% RH conditions (as an example). The strongest differences were observed in the 7400-6000cm^{-1} and 5100-4100cm^{-1} (regions highlighted in Fig. 2).

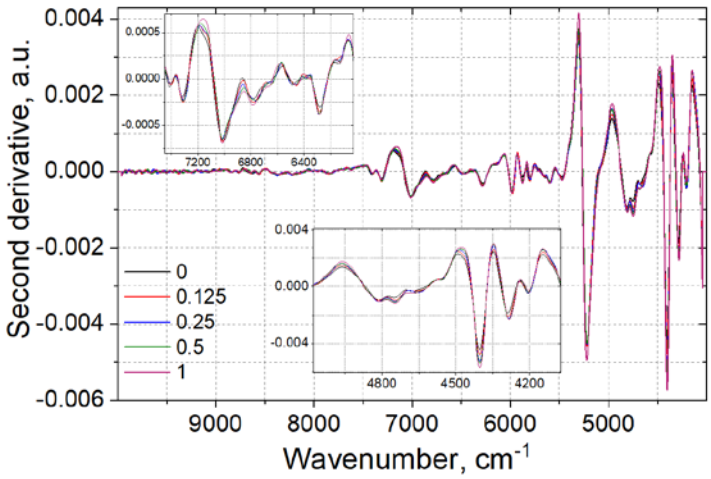


Fig. 2.
Second derivative of the NIR spectra of reference and hydrothermally treated wood samples 100%RH.

In the first region, the bands from 7412, 7315 and 6490cm^{-1} are shifting to lower wavenumber to 7402, 7309 and 6470cm^{-1}, respectively. These bands are assigned to first overtone of the combination band of C-H stretching vibration and C-H deformation vibration from methyl groups in hemicelluloses, and to first overtone of O-H stretching vibration from intramolecular H-bonds in cellulose (Schwanninger et al. 2011). The bands from 6782, 6647, and 6280cm^{-1} increase in intensity with the increase of the treatment time. These are assigned to first overtone of O-H stretching vibration from semi crystalline regions and O(6)-H6…O(3)' intermolecular H-bonds in cellulose (Schwanninger et al. 2011). The last band is also shifted to higher wavenumber, at 6290 cm^{-1}. The modification in these bands is due to the modifications induced in the wood structure due to partial removal of low molecular compounds and hemicelluloses during the treatment, as well as formation of new compounds.

The second region, 5100-4100cm^{-1}, indicate modifications of the bands from 4746, 4673, 4403 and 4287cm^{-1}. The bands from 4746, 4403 and 4287cm^{-1} assigned to combination band of O-H deformation and O-H stretching vibration in carbohydrates, and to C-H stretching and deformation vibration in cellulose and hemicelluloses increase in intensity with the increase of the treatment time, while the band from 4673cm^{-1} assigned to combination of C-H and C=O stretching vibration of the acetyl groups is shifted to lower wavenumber, at 4650cm^{-1}.

Principal component analysis differentiated the groups of treated samples according to the relative humidity involved during the treatment, as well as according to the time of treatment, while by 2DCOS synchronous and asynchronous maps was possible to identify the auto and cross-peaks, as well as the sequential order of bands' modification under the applied hydrothermal treatments. Thus, firstly modify the bands related to O-H and C-H groups from hemicelluloses, followed by the O-H and C=O groups from extractives and lignin as well as the bands related to C-H and O-H groups in cellulose.

CONCLUSIONS

The structural modifications occurring during hydrothermal treatment at 140^{o}C and different values of RH and time of exposure were evaluated by near infrared spectroscopy and chemometric methods (principal component analysis and two dimensional correlation spectroscopy). It has been observed that during treatment, hemicelluloses and extractives are the most susceptible, but also the lignin and cellulose presented bands variations. Moreover, these methods indicate a different degradation pattern of the wood samples related to the relative humidity values presented in the environment.

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