



# Structural changes of wood during hydro-thermal and thermal treatments evaluated through NIR spectroscopy and principal component analysis



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## ABSTRACT

Spruce wood samples were subjected to different conditions of thermal and hydro-thermal treatment by varying the temperature, relative humidity and period of exposure. The obtained treated samples were evaluated using near infrared spectroscopy (NIR), principal component analysis (PCA) and hierarchical cluster analysis (HCA) in order to evidence the structural changes which may occur during the applied treatment conditions.

Following this, modification in all wood components were observed, modifications which were dependent on the temperature, amount of relative humidity and also the treatment time. Therefore, higher variations were evidenced for samples treated at higher temperatures and for longer periods. At the same time, the increase in the amount of water vapours in the medium induced a reduced rate of side chains and condensation reactions occurring in the wood structure.

Further, by PCA and HCA was possible to discriminate the modifications in the wood samples according to treatment time and amount of relative humidity.

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## 1. Introduction

Due to its advantages, wood is used in many different applications, but because of its structure and depending on the environmental conditions (humidity, temperature and biological agents), may not be a very durable material. Wood is composed mainly from three major components, such as cellulose (a linear polymer built up of anhydro-D-glucopyranose units linked by  $\beta(1-4)$  glycosidic linkages), lignin (a three dimensional crosslinked aromatic polymer formed from phenyl propane units, with/without methoxyl groups bonded to the aromatic ring, and linked together by  $\beta-0-4$  aryl ether or carbon-carbon linkages) and hemicelluloses (mainly composed of glucose, mannose, galactose, xylose and arabinose, which are branched polymers with a significantly lower molecular mass comparing to cellulose) [1,2].

Different attempts have been made in order to improve wood durability and its mechanical and physical properties, by thermal, hydro-thermal, and chemical modification treatments [2–7]. It is known that, thermal modification treatment of wood may improve some of its properties, such as: dimensional stability, durability, and hydrophobicity [3].

At the same time, simple thermal modification or hydro-thermal modification (in which a certain amount of relative humidity is involved) can be used to simulate the ageing of wood in accelerated conditions [8,9] in order to identify the degradation mechanisms which may take place during the natural degradation process.

During thermal degradation, wood components undergo oxidation, dehydration and decarboxylation reactions, coupled with heat and mass transfer. When certain amount of relative humidity is involved, the degradation reactions take place faster and hydrolysis reactions may occur due to the fact that water act as a reaction catalyst [10,11]. It also should be noted that the presence of water vapours during the treatment process can prevent the oxidative processes [4]. The structural modifications strongly depend on the applied temperature, relative humidity, treatment time and also by the nature of the wood species taken into consideration [10,12].

Spectral techniques, due to the low cost instrumentation and little or no sample preparation, are easy applicable to process monitoring and quality control evaluations. Particularly, near infrared (NIR) spectroscopy can evidence changes in chemical and structural composition, or physico-chemical properties of materials, such as wood. Multiple chemical absorptions considerably affect the shape of NIR spectra and lead to effects such as shifts and baseline offset. Therefore, NIR spectroscopy has been shown to be a versatile tool

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for the non-destructive evaluation of the stiffness of various wood species [13] and structural changes during thermal treatment [14, 15], or biodegradation [16].

Further data processing – principal component analysis (PCA) – gives precise mathematical estimations of changes along the object and variable vectors, and reduces data dimensionality by redefining the axes. It can be used to give detailed information extracted from a dataset, therefore, can be used to control and process monitoring and classification of products origin [17]. By converting the data into the dimensionally reduced PCA space, the input data set is decomposed into two matrices of interest: scores and loadings. The scores matrix describes the samples in the PC space, while the loadings matrix defines the new axes of the dimensionally reduced data set. With PCA, the most important features of the NIR spectra can be identified, and the bands shifts and non-symmetries in the bands between the samples can be quickly determined [15,18].

Hierarchical cluster analysis (HCA) present the data as a dendrogram which emphasize the natural grouping in a data set. This method group the data and present the relationships among different groups [19,20], being used successfully to discriminate between same wood specie grown in different regions [19], between soft and hardwoods [20] and identify the nature of the polyphenolic extracts [17].

The present study summarize the evaluation of the chemical and structural changes occurring during the thermal and hydro-thermal treatment of spruce wood by near infrared spectroscopy, principal component analysis and hierarchical cluster analysis.

## 2. Materials and Methods

### 2.1. Materials

Spruce wood samples were kept, in a self-designed autoclave, at 130 and 150 °C and 0, 10 and 25% relative humidity conditions for different time periods. The samples were removed at 5, 11 and 26 days. For each treatment type five replicates were used.

To identify the changes occurring in the structure, the thermal and hydro-thermal treated samples were compared with the reference (non-treated) one.

### 2.2. Methods

NIR spectra were recorded by a Frontier FT-NIR Perkin Elmer spectrometer in the spectral range 1100–2600 nm by diffuse reflectance method. Processing of the spectra was performed using the Grams 9.1 program (Thermo Fisher Scientific).

Principal component analysis (PCA), a multivariate statistical technique is used for extraction and interpretation of the systematic variance in a data set. The idea in the PCA modelling is to replace a complex multi-dimensional data set by a simplified one, involving fewer dimensions (principal components (PCs) or factors), but still fitting the original data closely enough to be regarded as a good approximation [17,18]. One of the many outputs from PCA analysis is represented by the “loadings plot”. These are calculated per PC and indicate which variables (wavelength) contribute to the variance explained by that particular PC.

Hierarchical cluster analysis (HCA) present the data in a form of a dendrogram indicating the relation among different groups.

The multivariate analyses were performed by using the R software.

## 3. Results and Discussion

### 3.1. NIR Spectroscopy

Near infrared diffuse reflectance spectra in the 1100–2600 nm range of thermal and hydro-thermal treated spruce wood samples are represented in Fig. 1.

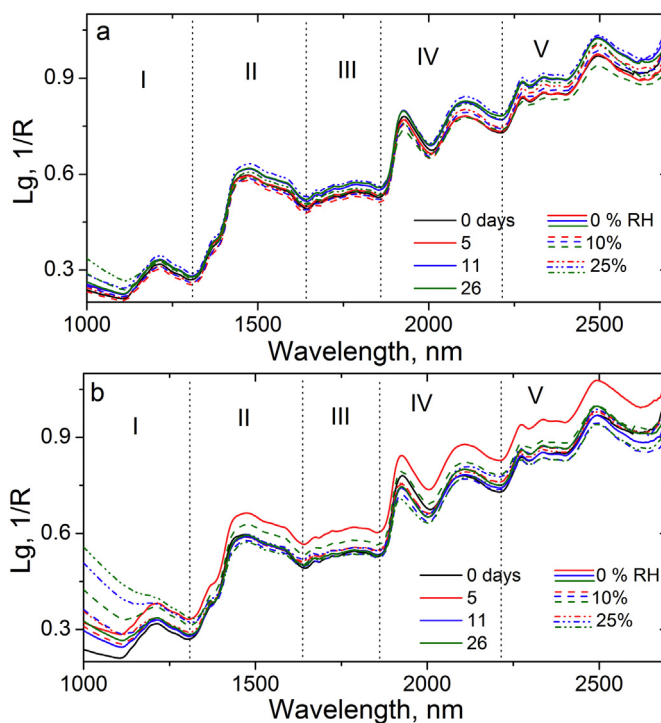


Fig. 1. Raw NIR spectra of the thermal and hydro-thermal treated spruce wood samples at 130 °C (a) and 150 °C (b) for different relative humidity values and periods of time.

Independently to the applied treatment, the spectra showed similar shapes. Typical broad vibration bands associated with chemical components of wood were identified and the spectra were separated in five spectral regions:

- the first region, between 1100 and 1330 nm, is assigned to first and second overtones of C—H stretching vibrations in methyl and methylene groups from carbohydrates and lignin [21] (Fig. 1, I);
- the 1330–1640 nm region is assigned to first overtone of the C—H combination bands, and first overtone of different O—H stretching vibrations [21] (Fig. 1, II);
- the third region, 1640–1850 nm, is dominated by the first overtone of the aliphatic and aromatic C—H stretching vibrations and O—H combination bands in all wood components [15,21] (Fig. 1, III);
- the 1850–2210 nm region is assigned mostly to C=O groups, O—H stretching and deformation vibrations, and also to C<sub>ar</sub>—H and C—H stretching vibrations [15,21], (Fig. 1, IV) and
- the last region (2210–2510 nm) is assigned mostly to C—H stretching and C—H deformation vibrations [15,21] (Fig. 1, V).

The changes induced by the thermal and hydro-thermal treatments in the structure and content of wood components are reflected in the NIR bands intensities, maxima and width according to the applied treatment.

As can be observed in Fig. 1a, for the samples treated at 130 °C, there are several bands intensities modifying with increasing the treatment time. Higher variations in the spectra can be identified for the samples which were kept in higher relative humidity values conditions. In Fig. 1b, the spectra of the untreated and treated samples at 150 °C are represented and, comparing to the previous figure (Fig. 1a), higher differences can be observed.

In contrast to infrared (IR) spectroscopy, in NIR spectroscopy it is more difficult to assign the bands to specific functional groups because of their overlapping. Therefore, the reason of the decrease/increase of the bands intensity can be due to a shift or a change in the location of

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