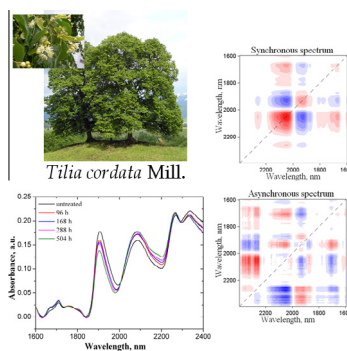# A near infrared spectroscopic study of the structural modifications of lime (*Tilia cordata* Mill.) wood during hydro-thermal treatment

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HIGHLIGHTS

- Characterization of untreated and hydro-thermal treated lime wood.
- Methods used are NIR spectroscopy, principal component analysis and 2D NIR correlation spectroscopy.
- Changes in the carbohydrate and lignin structure during treatment.
- Increased amount of hydroxyl groups with treatment time increases.
- 2D NIR correlation spectroscopy estimated the sequential order of the group variations.

GRAPHICAL ABSTRACT

ABSTRACT

The modifications and/or degradation of lime (*Tillia cordata*) wood components during wood heat treatment under low temperature at about 140 °C and 10% percentage of relative humidity were evaluated. The aim of this study was to obtain results by simple NIR coupled with second derivative, principal component analysis and two dimensional correlation spectroscopy in order to better understand how these techniques are able to evaluate structural differences resulted under hydro-thermal treatment of the wood over a period of 504 h. The NIR spectra of treated samples were compared with the reference one. Due to the broad bands in the NIR spectra, the assignment and modifications occurring during treatment is difficult, therefore the second derivative principal component analysis were applied. Principal component analysis by first two components was able to differentiate the samples series, PC1 being considered as the time axis, and PC2 as the axis representing the structural modification of wood components.

2D NIR correlation spectroscopy was able to estimate the sequential order of the groups variations under the hydro-thermal treatment time as external perturbation, indicating as first moment changes the OH and C—O groups from carbohydrates and lignin, followed by C_{ar}—H, C—H and CH_2 groups from lignin, cellulose and hemicelluloses.

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Introduction

Even wood is widely used in many applications (buildings, furniture, domestic and ecclesial objects, paper pulp production, etc.), due to its structure, the resistance to different environmental factors (biodegradation, weathering conditions) sometimes is limited. In order to understand the degradation mechanisms, researchers tried to simulate the natural environmental conditions with accelerated ones. Thus, different biodegradation agents, like soft, brown and white rot fungi or termites [1–6], thermal conditions [7], weathering or UV light exposure [8–10] were used in the last period in many research studies in order to simulate in laboratory the natural environmental conditions and to understand their degradation

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mechanisms. Apart of the environmental factors, another major factor is the chemical structure of wood. This is composed mainly from cellulose, hemicelluloses and lignin, and some low amounts of extractives and/or resins, depending on the wood species.

Thermal treatments are often used in order to improve some physical properties of wood such us: dimensional stability, durability, hydrophobicity [11], but in the same time thermal treatment can be used in order to simulate the natural degradation of wood [12]. During thermal degradation wooden structure undergo dehydration, decarboxylation and oxidation reactions, coupled with heat and mass transfer. If during thermal degradation an amount of relative humidity is used, the reactions develop faster due to the fact that water act as a reaction catalyst. Further wood undergo also hydrolysis reactions and the crystallization of wood cellulose is affected [13].

Near infrared (NIR) spectroscopy, because of its low cost instrumentation and little or no sample preparation is applicable to process monitoring and quality control evaluations. Changes in chemical composition, morphology or physico-chemical properties of materials such as wood will therefore cause spectral changes in diffusely reflected near infrared radiation. Multiple chemical absorptions considerably affect the shape of NIR spectra and lead to effects such as shifts and baseline offset. NIR spectroscopy has been shown to be versatile in the non-destructive evaluation of various wood species stiffness [14] and structural changes during thermal treatment [15] and/or biodegradation [16].

The principal component analysis (PCA) is a well-established technique in statistics and chemometrics, which gives a precise mathematical estimation of changes along the object and variable vectors. PCA is the data mining method which reduces data dimensionality by redefining the axes, so that 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. 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 loadings matrix defines the new axes of the dimensionally reduced data set, while the scores matrix describes the samples in the PC space. The use of a multivariate analysis with polymer systems has been limited. With PCA, the most important features of the NIR spectra can be identified, and the peak shifts and non-symmetries in the peaks between the samples can be quickly determined.

Two dimensional correlation spectroscopy, which was originally proposed by Noda in 1993 [17–19], is a method based on computation of auto-correlation and cross-correlation between spectra and provides a graphical overview for the analysis of perturbation-induced spectral variations. The external perturbation can be temperature, pressure, moisture, concentration, composition, pH or time change. One of the most important points of 2D correlation analysis lies in the fact that it is applicable to various types of systems as long as an external perturbation is described as a specific function. The method was applied to different techniques such as IR [2,20,21], and NIR [22] spectroscopies.

In the present study, hydro-thermal treated lime (*Tilia cordata* Mill) wood was investigated by NIR, PCA and 2D NIR correlation spectroscopy. The sequential order of changes from the structural modifications as a result of the hydro-thermal treatment was evidenced.

Experimental

Materials

Lime (*Tilia cordata* Mill.) wood samples were kept, in a self designed autoclave, at 140 °C and about 10% relative humidity

conditions for different time periods. The samples were removed at 96, 168, 288 and 504 h.

The hydro-thermal treated samples were compared with the reference (non-treated) one.

Methods

NIR spectra were recorded by means of a PHAZIR Handheld Near-Infrared Analyzer (Thermo Fisher Scientific – Portable Optical Analysis) in the spectral range 1600–2400 nm by diffuse reflectance method. Processing of the spectra was performed using the Grams 9.1 program (Thermo Fisher Scientific).

Principal component analysis (PCA) is a multivariate statistical technique used for extraction and interpretation of the systematic variance in a data set. The underlying idea in PCA modeling is to replace a complex multi-dimensional data set (e.g. spectroscopic data) by a simplified version involving fewer dimensions (principal components (PCs) or factors), but still fitting the original data closely enough to be regarded as a good approximation [23]. 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.

Two-dimensional correlation spectroscopy (2D-COS) enables cross-correlation analysis of spectral series of systems changing with a modulation variable [17]. Two-dimensional wavelength–wavelength correlation analysis provides two different correlation maps. The synchronous map displays correlations between all spectral bands changing in phase in the experiment and shows whether they increase or decrease relative to each other. The asynchronous correlation map, in contrast, relates spectral bands that change at different rates and also contains information about the sequence of the occurring events.

Results and discussion

NIR spectroscopy

The NIR diffuse reflectance spectra in the 1600–2400 nm range of hydro-thermal treated lime (*Tilia cordata* Mill.) wood and their second derivatives are shows in Fig. 1.

The NIR spectra, independently to the treatment, showed similar trends, and typical broad vibration bands associated with chemical components of wood were evidenced. Three spectral regions 1640–1850, 1850–2007, and 2007–2400 nm associated with H-bonded OH groups, carbonyl groups and different C—H linkages were observed. Therefore, the bands in the 1640–1850 nm region correspond to the first overtone of C—H or CH$_2$ stretching vibrations from aromatic groups in lignin and semi-crystalline or crystalline regions in cellulose, whereas the bands in the 1850–2007 nm region are assigned to the combinations of OH stretching and bending vibrations and second overtone of C=O stretching vibrations. The third region (2007–2400 nm) is more difficult to assign due to high number of possibilities for the coupling of vibrations. The changes made by the hydro-thermal treatment in the structure and content of wood components are reflected in the NIR bands intensities and width.

In comparison with infrared (IR) spectroscopy, in NIR spectroscopy it is difficult to assign the bands to specific functional groups because of the peaks overlapping. When there are overlapped bands, the reason of the spectral bands intensity increase or decrease can be due to a shift or a change in the location of the component bands. In order to improve the spectral resolution, second derivative (Savitzky–Golay method with 25 points) was used, and a number of 16 bands were evidenced.