

Chemical changes of cell wall components of heat-treated wood**Alterações químicas dos componentes da parede celular de madeiras tratadas termicamente**

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ABSTRACT

The wood's cell wall undergoes chemical modifications due to thermal action. The goal of this work was to analyze these changes in the *Pinus caribaea* var. *caribaea* and *Khaya ivorensis*, untreated and heat treated. The thermal treatment temperatures were 160° C, 180° C and 200° C, and the samples were then evaluated by Fourier transform infrared spectroscopy (FTIR). Fourier transform infrared spectroscopy analyzes were performed on samples with and without treatment, using a spectrometer in the Attenuated Total Reflectance (ATR) mode. The results were plotted in the Origin-Pro 8 program, obtaining comparison charts. In treated and untreated samples, the bands at $\sim 1027\text{cm}^{-1}$ and $\sim 3337\text{cm}^{-1}$ were more intense with increasing temperature. It suggests that the structural elements degraded, and small molecules were then obtained. It is concluded that the increase in temperature implied a greater absorption of infrared by the peaks related to cellulose, hemicelluloses, and lignin, indicating that they are undergoing changes.

Keywords: Thermoretification, Pinus, African Mahogany, FTIR, Commercial Wood.

RESUMO

A parede celular da madeira sofre modificações químicas devido à ação térmica. Deste modo, o objetivo deste trabalho foi analisar essas modificações nas madeiras de *Pinus caribaea* var. *caribaea* e Mogno Africano (*Khaya ivorensis*), não tratadas e tratadas termicamente nas temperaturas de 160°C, 180°C e 200°C, e avaliadas por espectroscopia de infravermelho por transformada de Fourier (FTIR). As análises de FTIR foram realizadas nas amostras com e sem tratamento, utilizando espectrômetro no módulo de Reflectância Total Atenuada (ATR). Os resultados foram plotados no programa Origin-Pro 8, obtendo-se os determinados gráficos de comparação. Em ambos os gráficos, os picos $\sim 1027\text{cm}^{-1}$ e $\sim 3337\text{cm}^{-1}$ ficaram mais intensos com o aumento da temperatura, sugerindo que os elementos estruturais estão gerando moléculas menores. Conclui-se que o aumento da temperatura implicou na maior absorção de infravermelho pelos picos referentes a celulose, hemiceluloses e lignina, indicando que estão sofrendo modificações.

Palavras-chave: Termorretificação, Pinus, Mogno Africano, FTIR, Madeira comercial.

1 INTRODUCTION

The demand for Brazilian forest plantations, to supply industries and to meet the population's quality standards, is growing, as the forest sector is constantly expanding (Moreira & Oliveira, 2017; Junior Coelho *et al.*, 2020). The country has the second largest forest cover in the world, with approximately 10 million hectares of forest plantations (SNIF, 2019). This led to the development of a complex productive system, increasing the participation of the Brazilian forest sector in world trade (SNIF, 2020).

Regarding the mentioned plantations, *Pinus caribaea* plantations and their variations stand out. They have proven potential in terms of silvicultural aspects, where it is one of the main crops that nourished the demand for forest crops in Brazil (Moreira & Oliveira, 2017). According to the bulletin of the National Forestry Information System (SNIF, 2019), in 2018, the country had 1,984,333 hectares of Pinus planted area.

African Mahogany is a designation for several species of the genus *Khaya*. It has an important prominence in the forestry market (it is considered a noble wood for use mainly in furniture), since it has adequate behavior to be used in the construction of furniture. It is visually attractive, and it has proper workability (Silva & Vidaure, 2019). In Brazil, there are four species of interest of this genus (Reis *et al.*, 2019) and, despite the differences in the characteristics of the wood, all of them are still used for some purpose in the international market (Ribeiro *et al.*, 2019; Silva & Vidaure, 2019). According to Silva & Vidaure (2019), *Khaya ivorensis* wood, for example, is soft to cut and has excellent dimensional stability. In addition, it has good air-drying performance, being widely used for light residential properties, for finishing and bulkhead, for utility furniture and hardboard.

According to Gérardin (2016), since these woods are commercially important, thermal modification is a valuable alternative for wood preservation, avoiding the use of chemical products. This method provides high resistance to fungi, and high natural durability and dimensional stability. Nonetheless, there are several chemical modifications due to thermal degradation of the wood's cell wall. These modifications limit the availability of substances attractive to xylophagous organisms, and it modifies the colorimetric pattern of the wood according to the treatment temperature (Lima, 2019).

Infrared spectroscopy is widely used to identify modification of functional groups (He *et al.*, 2017; Yin *et al.*, 2018). This technique is used to characterize cellulose and lignin, both qualitatively and quantitatively, in woods submitted to heat treatment (Timar *et al.*, 2016; Özgenç *et al.*, 2017; Lopes *et al.*, 2018). Therefore, the goal of this work is to analyze the chemical changes in the cell wall of *Pinus caribaea* var. *caribaea* and *Khaya ivorensis* samples untreated and thermally treated by Fourier transformed infrared spectroscopy (FTIR).

2 METHODS

The materials (samples) used were obtained from 6 trees, 3 from *Pinus caribaea* var. *caribaea* and 3 from *Khaya ivorensis*, from plantations located on the campus of the Federal Rural University of Rio de Janeiro (UFRRJ), Seropédica-RJ. The trees of *Khaya ivorensis* were approximately 33 years old and were planted in isolation on the campus of Embrapa Agrobiologia and UFRRJ, Seropédica, RJ. *Pinus caribaea* var. *caribaea* came from trees aged approximately 25 years.

The tree stem obtained were split into boards measuring 3.6m x 0.07m x 0.40m. They had been stored in a covered environment until constant weight was achieved. After drying, samples with dimensions of 350 x 60 x 21 mm (length x width x thickness) were obtained, cut transversely, and heated in an environment with an average relative humidity of 65% and controlled temperature (~20 °C).

The samples of both species were heat treated at different temperatures (160 °C, 180 °C and 200 °C) and untreated samples were considered as control. For each treatment, 6 samples of each specie were used per treatment. The heat treatment was carried out in an electric muffle furnace, equipped with a programmable temperature and time control system. It was carried out in four stages: 1) heating the material up to 100 °C, to diminish water content, for 120 minutes; 2) temperature increase, from 100 °C to the desired heat treatment temperature (160, 180 or 200 °C) for 60 minutes; 3) residence time, samples were maintained at the heat treatment temperature for 90 minutes; and 4) cooling of the material. After heat treatment, the samples were reconditioned in a climatic chamber

at 20 °C and 65% relative humidity until they reached constant weight, and they were subsequently packed to avoid moisture exchange with the environment.

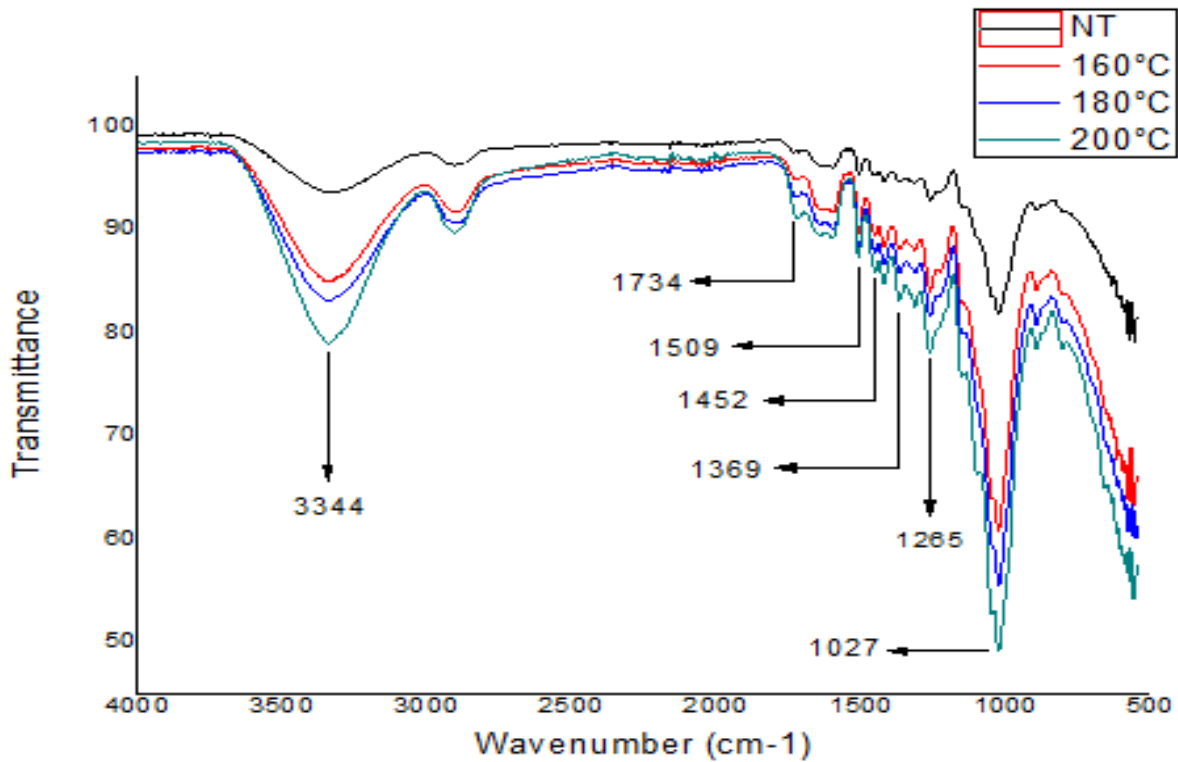
The samples (Untreated, 160°C, 180°C and 200°C) were identified, and the wood was scraped to obtain particulate material for FTIR analysis. The analysis was performed in the Multiuser Lab of PEMM/UFRJ, equipment Perkin Elmer Spectrum 100, using the Attenuated Total Reflectance (ATR) mode, in the range of 4000-500 cm^{-1} , with 32 scans per sample and 4 cm^{-1} of resolution. The results were exported and later plotted in the Origin-Pro 8 program, where it was possible to obtain their spectra for analysis and comparison.

3 RESULTS

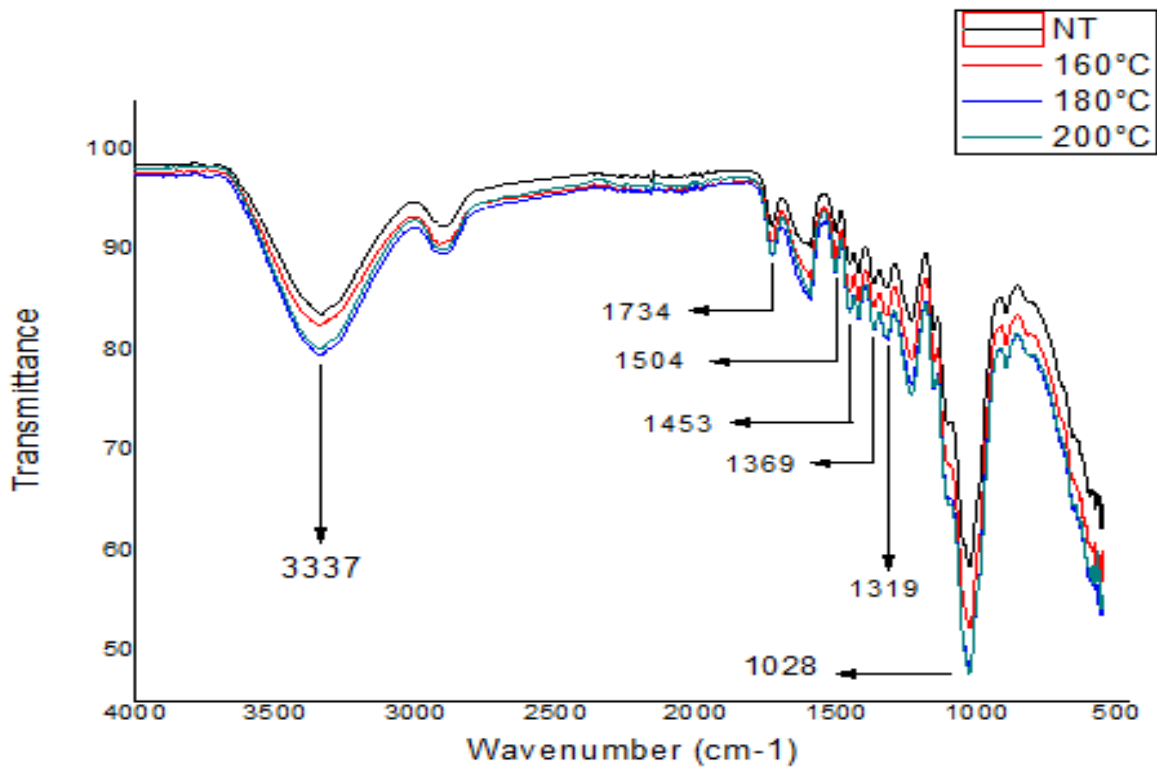
In the infrared spectra of both studied species (Figures 1 and 2), a band at $\sim 3337 \text{ cm}^{-1}$ can be observed, indicating the stretching of hydroxy groups (OH) in aliphatic and phenolic structures (Boeriu *et al.*, 2004). The band at $\sim 1734 \text{ cm}^{-1}$ refers to the vibration of carboxylic groups (C = O) of esters, aldehydes, or hemicellulose ketones (Herrera *et al.*, 2014). The band at $\sim 1504 \text{ cm}^{-1}$ indicates the vibration (C = C) of aromatic rings (Sills & Gosset, 2012). Band at $\sim 1369 \text{ cm}^{-1}$ is attributed to C-H deformation of cellulose and hemicelluloses (Popescu *et al.*, 2007; Müller *et al.*, 2009); at $\sim 1455 \text{ cm}^{-1}$ refers to the lignins' and hemicellulose's in plane asymmetric C-H deformation; O-H in plane deformation for cellulose, hemicellulose and lignin (Müller *et al.*, 2009; Chen *et al.*, 2010; Herrera *et al.*, 2014). The band at $\sim 1027 \text{ cm}^{-1}$ is attributed to the C-O deformation of cellulose; the C-H (aromatic) deformation present in lignins; and the asymmetric C-O-C stretching of dialkyl ethers (Hakkou *et al.*, 2005; Popescu *et al.*, 2007; Özgenç *et al.*, 2017). For *Pinus caribaea* var. *caribaea*, the infrared spectrum indicated a band at $\sim 1265 \text{ cm}^{-1}$, attributed to C-O bonds of aromatic methoxy groups of guaiacyl (G) lignin (Popescu *et al.*, 2007; Müller *et al.*, 2009). For *Khaya ivorensis*, the band at $\sim 1320 \text{ cm}^{-1}$ was related to syringolic ring (S) phenolic group (Kubo & Kadla, 2005).

Figure 1. (a) Spectra of *Pinus caribaea* var. *caribaea*, treated at 160° C, 180° C and 200° C and untreated; (b) Spectra of *Khaya ivorensis* wood, treated similarly.

(a)



(b)



4 DISCUSSION

The infrared spectrum for both species exhibited characteristic bands of structural elements (cellulose, hemicellulose, and lignin) in samples with and without heat treatment (Timar *et al.*, 2016; Fahey *et al.*, 2017). The *Pinus caribaea* var. *caribaea* showed a high proportion of guaiacyl units, characterizing type G lignin, commonly found in conifers (Wagner *et al.*, 2015). In the spectra of *Khaya ivorensis*, a high proportion of syringolic units was noted, characterizing type S lignin, usually found in hardwoods (Kawamoto, 2017).

Pinus caribaea var. *caribaea* spectra showed that, with the increase of the thermal treatment temperatures, there were alterations mainly related to increased intensity of structural elements bands. It might indicate that these elements on the cell wall were undergoing modifications. For the species of *Khaya ivorensis*, it was observed that, with the increase in the treatment temperature, there were also changes in the cell wall, however the treatments of 180 and 200°C resulted in similar behavior.

In both samples, the bands at $\sim 1027\text{cm}^{-1}$ (CO, C = C, CCO) and at $\sim 3337\text{cm}^{-1}$ (OH) which indicate the presence of the structural elements (Hakkou *et al.*, 2005; Popescu *et al.*, 2007; Özgenç *et al.*, 2017) were more intense with the increase of heat treatment temperature. This might suggest that these elements were progressively degraded with the treatment temperature rise (Yeo *et al.* 2017). It means that a macromolecule was broken into smaller molecules that may be able to present more freedom of movement (vibrational modes).

Yeo *et al.* (2017) attributed to hemicelluloses the beginning of wood degradation. They are the first wood carbohydrates to degrade with heat treatment due to their heterogeneous structure. The non-crystalline nature of their structure and their low molecular weight in compared to other wooden polymers. Cellulose has a progressive degradation that includes depolymerization and dehydration. Lignin is thermally more resistant than other wood's carbohydrates.

5 CONCLUSIONS

The results obtained demonstrate that the Fourier transform technique by Infrared Spectroscopy is an important source of information for a qualitative characterization of changes on the structural elements (cellulose, hemicelluloses, and lignin). The temperature changes the structure of the studied elements of the wood, being hemicelluloses the most affected.

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