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FTIR spectroscopy and technological characterization of heat treated *Fraxinus excelsior* wood

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TECHNOLOGY OF FOREST PRODUCTS

ABSTRACT

Background: The wood heat treatment results in the partial degradation of its chemical constituents, mainly cellulose and hemicellulose, reducing the hygroscopicity of the material. This process improves the dimensional stability and resistance to biodeterioration and worsens the mechanical resistance. This work aimed to evaluate the effect of heat treatment on the physical, anatomical, chemical, and mechanical properties of *Fraxinus excelsior* wood. In untreated and heat-treated wood, the pH, buffering capacity, basic density, equilibrium moisture content, shrinkage, wood anatomy, thermogravimetric behavior, and chemistry by conventional and FTIR methods were determined.

Results: Heat treated wood had lower pH (5.50), equilibrium moisture content (6.26%), shrinkage (7,29%), holocellulose contents (55,96%) and higher buffering capacity (0,479 mmol/L), extractives (8,25%), and lignin contents (35,78%). Heat treatment reduced the pH and increased the buffering capacity of the wood, reduced the holocellulose content, and increased the lignin content, leaving the wood less hygroscopic and reducing its volumetric and linear variation. The process did not change the basic density and fiber length, but it reduced their width, lumen diameter, and wall thickness. The FTIR analysis confirmed the degradation of holocellulose and division of aliphatic side chains in lignin. The maximum dredging range of untreated and heat-treated wood occurred at 350 °C, and the heat-treated wood had a higher residual mass when subjected to 500 °C.

Conclusion: Heat-treated wood can be indicated for products used in external environments, such as floors, fences, coatings, door and window structures.

Keywords: Wood properties; thermogravimetric analysis, wood contraction.

HIGHLIGHTS

Heat treated wood (HTw) can be indicated for products for external environments. HTw had lower pH, equilibrium moisture content, shrinkage, and holocellulose contents. HTw was less hygroscopic and its volumetric and linear variation was lower. HTw and untreated wood maximum degradation temperature occurred at approximately 350 °C.

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INTRODUCTION

The world is looking for alternatives to reduce the use of raw materials from non-renewable sources, such as plastic and metals. Wood emerges as a viable alternative, as it has a high ratio between strength and specific mass, thermal and acoustic insulation capacity, aesthetic value, low energy expenditure in processing, and ease of handling (Balasbaneh; Sher, 2021). However, this material presents limitations for its use, such as high dimensional instability, hygroscopicity (Hou et al., 2022), and vulnerability against xylophagous agents (Paes et al., 2021; Madeiros Neto et al., 2022).

Heat treatment is a viable option to mitigate the undesirable wood characteristics, allowing its access to different markets (Rajković; Miklečić, 2019). This technique consists of heating the wood between 160 and 260°C, combined with variables such as time (Paula et al., 2023), atmosphere (Bal, 2018; Sivrikaya et al., 2020), and pressure (Chung et al., 2017). The heat treatment consists of the partial degradation of its chemical constituents, mainly the hemicelluloses, reducing the hydrophilic sites and the water adsorption capacity (Senneca et al., 2020; Kubovský et al., 2020). The increase in dimensional stability and resistance to biodeterioration are the main benefits of heat treatment (Candelier et al., 2016; Brito et al., 2019; Zanuncio et al., 2022).

Heat-treated wood is mainly used in outdoor applications, such as garden furniture, fences, floors, cladding, door and window frames, and structural elements in the construction industry. *Fraxinus excelsior* wood is widely used in the United States and Europe, which are large consumers of wood for construction and furniture. This wood has high density (0.65 – 0.69 g/cm³), easy to work with, straight grain, and little differentiation between heartwood and sapwood, good dimensional stability, and desirable characteristics of elasticity, hardness, and shock resistance, high mechanical strength (1289 MPa) and durability (Beck et al., 2016; Moliński et al., 2016; Vastern Timber, 2018; Roszyk et al., 2020; Aytin et al., 2022).

Changes in wood due to heat treatment are known. However, the intensity of these changes varies according to the treatment and quality of the wood, making specific studies necessary for each species and treatment. This work aimed to analyze changes in the *Fraxinus excelsior* wood properties by heat treatment and evaluate the effect of thermal modification on the thermal degradation of *Fraxinus excelsior* wood, considering the increasing use of heat-treated wood.

MATERIAL AND METHODS

Biological material

This study used commercial batches of *Fraxinus* excelsior wood, untreated and heat-treated at 215°C, for 35 hours, harvested in France. The material was prepared for physical, chemical, and anatomical characterization, and analyzes of thermal degradation and chemical groups through FTIR spectroscopy. The physical analysis of the wood used 2x2x5 samples (radial, tangential and longitudinal),

totaling 25 samples taken from different radial positions along the sample. The samples for anatomical analysis (2 x 2 x 2 cm) were taken on the border between heartwood and sapwood. Samples for chemical analysis were taken from different radial positions to be subsequently crushed.

Wood characterization

PH and buffering capacity of wood

The pH of the wood was determined according to TAPPI 252 om-02 (2002) standard. The Fraxinus excelsior wood samples, untreated and heat treated, were ground in a Wiley-type knife-mill (Fortinox, STAR FT-50) to obtain sawdust, the fraction retained between the 40/60 mesh sieves was used in the tests. The analyzes were carried out in triplicate, 2 g of absolutely dry sawdust were weighed for each repetition, which was transferred to a beaker, and then 100 mL of distilled water at a temperature of \pm 99 °C was added. The material was boiled in a water bath (QUIMIS, Q334M-28) for 1 hour, and then filtered to obtain the extracts. After cooling to room temperature, pH measurements were made with a pH meter (Digimed, DM-22) calibrated for 4 and 7 using standardized buffer solutions. To determine the basic buffering capacity in mmol/L, 50 mL of the extracts were titrated with a 0.025N H₂SO₄ solution to pH 3, using methyl orange as an indicator.

Physical, anatomical, and chemical characterization of wood

Basic density was determined by the ratio between the dry mass and saturated volume of the wood, as described in the ABNT NBR 11941 (2003) standard, with six replicates per treatment. Equilibrium moisture content (EMC), tangential, radial, axial, and volumetric shrinkage were determined according to ABNT NBR 7190 (1997). Six specimens per treatment were stored in a climatic chamber at 20 °C temperature and 65% relative humidity, weighed after reaching equilibrium with the environment, and subsequently dried in an air circulation oven (FANEM, 320-SE) at 103 \pm 2°C to determine the equilibrium moisture content. For shrinkage determination, the linear dimensions of six specimens were measured after saturation in water and after drying in the oven (103 \pm 2 °C).

For anatomical characterization, the tangential diameter (μ m) and frequency (mm⁻²) of vessels; length (μ m), width (μ m), lumen diameter (μ m), and fiber wall thickness (μ m) were measured according to the criteria established by the Pan-American Commission of Technical Standards (COPANT, 1974). Histological sections with nominal thickness ranging from 18 to 20 μ m of the transverse surface were obtained using a sliding microtome (LEICA, SM 2000R), and subsequently mounted on semi-permanent slides for later visualization and measurement of vessels under an optical microscope (IAWA, 1989; Pereira et al., 2016; Costa et al., 2017).

The preparation of the fiber macerate for dissociation of the anatomical elements and their respective measurements was performed according to the method described by

Ramalho (1987). Thirty vessels and fibers were measured for each treatment using an optical microscope (Zeiss, Axiostar plus) with an image capture system (Pixelink, PL-A662) with the help of Axio-Vision software.

For chemical characterization, the samples were transformed into sticks and subsequently ground into sawdust to obtain the fraction of sawdust classified in the 40/60 mesh sieves, according to TAPPI T 257 om-92 (1992) standard. Chemical analyses were carried out on the sawdust fraction using two replicates per treatment. The material was stored in glass jars and conditioned in climate-controlled chamber at 50 \pm 2% relative humidity and 23 \pm 1 °C temperature.

The total extractive contents (TAPPI T 204 cm-97, 1997) and the insoluble lignin contents were determined by the Klason method modified according to the procedure proposed by Gomide; Demuner (1986). The soluble lignin was determined by spectrometry according to Goldschimid (1971), from the dilution of the filtrate from the procedure to obtain insoluble lignin. The total lignin content was obtained by adding the values of soluble and insoluble lignin. The holecellulose content was calculated by subtracting the total lignin and extractives content from 100.

Infrared Spectroscopy of Wood

In the analysis of wood by infrared spectroscopy, ground wood, classified in the 40/60 mesh sieves, was directly placed on the crystal (Diamond/ZnSe) of the infrared spectrometer (Varian, Cary 5000), in the range of 175 to 3300 nm in units of absorbance, reflectance, and/or transmittance, for spectrum acquisition. The contact between the crystal and the sample was ensured by applying a force (150 N) using a screwing device that presses the sample under the crystal. For each spectrum, 16 scans were performed with a resolution of 2 cm⁻¹ in the range of 4000 to 600 cm⁻¹. Origin Pro 8 software was used for data analysis.

Thermogravimetric analysis

For the wood thermogravimetric analysis, the DTG-60H Shimadzu apparatus was used. The analyses were performed under a nitrogen atmosphere with a constant flow rate of 50 ml.min⁻¹, using approximately 2 mg of ground wood in the sawdust fraction classified in the 40/60 mesh sieves. The thermogravimetric curves were obtained from 30 °C up to a maximum temperature of 500 °C, with a heating rate of 10 °C.min^{-1.} The thermogravimetric (TG) curve was used to evaluate the mass loss as a function of temperature. and the first derivative of the mass loss (DTG) curve was also obtained. From the TG curves, the mass loss was calculated in the following temperature intervals: 100-150 °C, 150-200 °C, 200-250 °C, 250-300 °C, 300-350 °C, 350-400 °C, and 400-450 °C. The residual mass at 450°C was also calculated, considering the wet mass of the sample at room temperature and the absolutely dry mass at 100 °C. The thermogravimetric (TG) curves represent the percentage mass loss as a function of temperature, while the DTG curves correspond to the first derivative of the TG curves and show the variation of mass as a function of temperature.

Experimental design

The experiment was set up according to a completely randomized design (CRD) with 2 treatments (raw wood and heat-treated wood). The data were subjected to Lilliefors for normality and Cochran for homogeneity of variances. To evaluate the effect of the heat treatment on the wood properties, the t-Student test was applied with a confidence level of 95%. Statistical analyses were conducted using STATISTICA 8.0 software (STATSOFT, 2007).

RESULTS

Physical and chemical characterization of the material

The heattreatment changed the wood characteristics, except for basic density and axial contraction. The main modifications observed in the wood characteristics were the decrease in pH, equilibrium moisture content, holocellulose contents, and shrinkage. Furthermore, it was observed higher buffering capacity, lignin content and extractives content. (Table 1).

Wood Anatomical characterization

The structure of *Fraxinus excelsior* wood was slightly altered by heat treatment, with small deformations and an increase in vessel diameter observed in the transverse plane (Figure 1). The growth rings of *Fraxinus excelsior* wood are distinct and stand out due to ring porosity, where there is a higher concentration of larger diameter vessels at the beginning of the growing season. The vessels are predominantly solitary with rare occurrence of paired vessels, unobstructed and with circular to oval shapes. The fibers are libriform, non-septate, with simple pits. The predominant axial parenchyma is of the scanty paratracheal type. The rays are biseriate with rare occurrence of uniseriate and multiseriate rays (Figure 1).

The length of the fibers was not influenced by the heat treatment, but there was a significant reduction in their width, lumen diameter, and wall thickness (Table 2).

FTIR spectroscopy of wood

The FTIR spectroscopy was effective in detecting wood chemical alterations due to heat treatment (Figure 2). The interpretation of these modifications is complex because several reactions occur simultaneously (Esteves et al., 2013). The changes in the absorption bands are related to the functional groups and the aromatic system of lignin.

Wood thermogravimetric analysis of wood

Untreated and heat-treated *Fraxinus excelsior* wood exhibited similar behavior, with small differences in the temperatures corresponding to the maximum peaks of degradation related to hemicelluloses and cellulose (Figure 3).

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Treatment	рН	Buffer capacit (mmol/L)	y Basic Dens (g.cm³)	ity Equilibrium moistur content (%)	e Volumetric contraction (%)	
Untreated	6.31* ^{0.1}	0.292* 0.1	0.54 ^{ns 0.03}	12.41* ^{0.1}	14.46*2.1	
Heat treated	5.50 ^{0.1}	0.479 0.2	0.53 0.01	6.26 0,2	7.29 0.9	
Treatment	Radial contractior	n (%)	Tangencial contraction (%)	Axial contraction (%)	Anisotropy coefficient	
Untreated	5.91*0.2	1	7.83*2.0	0.22 ^{ns 0.1}	1.32* 0.1	
Heat treated	2.64 0.5		4.32 ^{0.4}	0.19 0.1	1.63*0.1	
Treatment	Total extratives (%)	Holocelulose (%	%) Insoluble Lignin (%	e Soluble b) Lignin (%)	Total Lignin (%)	
Untreated	6.59 ^{* 0,1}	67.20* 0.4	24.74* 0.39	9 1.47* 0.07	26.21* 0.3	
Heat treated	8.25 ^{0,1}	55.96 ^{1.2}	35.23 ^{1.51}	0.55 0.01	35.78 0.1	

Table 1: Physical and chemical characterization of untreated and heat-treated wood of Fraxinus excelsior.

*: significant (t-test t, α = 5%). The values in superscript correspond to the standard deviation.



Figure 1: Photomicrographs of cross-sectional (A), tangential (B), and radial (C) sections of untreated wood, and crosssectional (D), tangential (E), and radial (F) sections of heat-treated *Fraxinus excelsior* wood.

The mass loss values (%) during the thermogravimetric analysis were different according to the temperature range (Table 3).

DISCUSSION

Physical and chemical characterization of the material

The heat treatment reduced the holocellulose content, which is formed by the sum of cellulose and hemicellulose, with the latter being less resistant when subjected to the temperatures used in this study (Carvalho et al., 2020; Wang et al., 2020), resulting in a decrease from 67.2 to 55.96%. Heat treatment volatilizes some classes of

compounds, mainly phenolics, but the depolymerization of hemicelluloses generates compounds that remain connected to the fibers through weak bonds. These compounds can be removed with solvents used to quantify extractives (Zanuncio et al., 2015; Mecca et al., 2019; Esteves et al., 2022), resulting in an increase in extractives content from 6.59% to 8.25%. Finally, lignins have a high carbon content and strong bonds between their monomers, which makes them highly resistant to thermal degradation (Zanuncio et al., 2018; Börcsök; Pásztory, 2021). Thus, heat treatment increased the total lignin content from 26.21 to 35.78%. Carvalho et al. (2020) reported values of 1.36%, 25.7%, 72.96%, and 2,86%, 26,9% e 70,28% for extractive content, lignin, and holocellulose in untreated and heat treated *Mimosa scabrella* wood at 220 °C.

Treatment	Vessel diameter (µm)	Vessel frequencies (mm ²)	Fiber length (µm)
In natura	103.32* (24.0)	10.8* (1.6)	1336.26 ^{ns} (225.7)
Heat treatment	164.37 (62.7)	9.5 (1.3)	1417.16 (182.5)
Treatment	fiber width (µm)	fiber diameter (µm)	fiber thickness (µm)
In natura	25.41* (4.0)	14.53* (3.8)	5.44* (0.7)
Heat treatment	21.81 (2.7)	11.98 (2.9)	4.86 (0.5)

Table 2: Anatomical characterization of <i>Fraxinus excelsior</i> wood, untreated and neat	t treateo
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Values in parentheses represent the standard deviation.



Figure 2: FTIR spectrum of *Fraxinus excelsior* wood, untreated and heat treated. Wavenumber (cm⁻¹) with their respective assignments: 3340 - O-H stretching of hydroxyl groups; 2894 - C-H stretching of CH2-CH3 groups; 1734 - C = O in xylans (hemicelluloses); 1600 - Aromatic skeleton (lignin); 1510 - Aromatic skeleton (lignin); 1315 - C-O (syringyl); 1245 - C-O (hemicelluloses); 1105 - Aromatic skeleton (lignin); 1024 - C-O-C; 897 - C1, carbon in hemicelluloses and cellulose (pyranoid ring).





Treatments -	Temperature range (°C)						Residual	
	100 - 150	150 - 200	200 - 250	250 - 300	300 - 350	350 - 400	400 - 450	Mass (%)
Untreated	10.6	0.2	1.4	7.9	21.7	31.4	9.0	17.8
Heat treated	6.9	0.3	1.1	4.1	17.3	34.7	8.5	27.1

Table 3: Mass loss (%) based on dry mass of untreated and heat-treated wood according to temperature ranges.

Heat treatment reduces the pH of the wood, as the increased temperature and consequent degradation of hemicelluloses release organic acids that remain in the wood (Gurleyen et al., 2019). Changes in the pH values of wood can affect adhesion, as the acidic or alkaline nature of the wood surface can interfere with the curing process of the adhesive. The reduction of pH in heat-treated wood makes the use of alkaline adhesives, such as resorcinolphenol-formaldehyde, unfeasible. On the other hand, low pH on the wood surface can accelerate acid-catalyzed chemical reactions of adhesives, such as urea-formaldehyde and melamine-formaldehyde.

Buffer capacity represents the ability of wood to resist pH variations in the environment. There was a 64% increase in its value in heat-treated wood. This means that extracts from heat-treated wood may be less available, less soluble in water, and/or degraded, and therefore less reactive (Pereira, 2013). Thus, wood becomes more resistant to pH variations in the environment, requiring a more acidic titrant solution to lower the extract's pH to 3. The heat treatment reduced the pH and increased de buffer capacity of pine and eucalyptus woods treated at 220°C (Souza et al., 2017).

The chemical changes in wood have influenced its hygroscopicity and, consequently, its dimensional and volumetric variation. The reduction in holocellulose content and degradation of the amorphous regions of cellulose reduces the number of hydrophilic sites present in wood, resulting in a lower equilibrium moisture content. The reduction in the wood's adsorption capacity reduces its volumetric, radial, and tangential shrinkage. Radial and tangential shrinkage occur in the same proportion, and therefore, the coefficient of anisotropy was not affected by heat treatment. The lower variation in wood dimensions due to heat treatment enhances its use in environments with high moisture variation. The radial and tangential shrinkage of untreated Fraxinus excelsior wood was 6.96% and 9.00%, respectively, in contrast, heat-treated wood (200 °C for 48 hours) exhibited lower shrinkage values, with radial and tangential shrinkage of 3.45% and 2.15%, respectively (Sinković et al. 2012).

Wood Anatomical characterization

The significant reduction in the fibers width, lumen diameter, and wall thickness is related to the degradation of the chemical components of the cell wall, mainly holocellulose. Cellulose is the primary component of wood and serves a structural function; its degradation resulted in fiber contraction and reduced its dimensions. The changes in wood anatomy by thermal modification were similar to those found for the carbonization of *Eucalyptus urophylla* and *Corymbia citriodora* wood, with an increase in vessel diameter (Abreu Neto et al., 2021).

FTIR spectroscopy of wood

In heat-treated wood, there is a reduction in the most significant absorption peak of the carbonyl group (C = O) at 1734 cm⁻¹ and (C-O) at 1245 cm⁻¹. These changes are associated with the breakage and alteration of carboxylic groups that are linked to hemicelluloses, mainly the acetate groups in hardwoods. The reduction of these bands confirms the deacetylation of hemicelluloses and their partial degradation due to the heat treatment. The same behavior was observed for heat-treated *Fagus silvatica* wood, which was subjected to heat treatment at 185 °C, resulting in the complete disappearance of the band related to acetate groups (Tjeerdsma and Militz, 2005).

The degradation of polysaccharides during heat treatment was also observed by the decrease in absorption at 895 cm⁻¹, which corresponds to the opening of the pyranoside rings of cellulose and hemicelluloses (González-Peña et al., 2009; Hoseinzadeh et al., 2019). Piernik et al (2022) reported decrease in the strength of the band at 3550 cm⁻¹ for heat treatment of pine wood, this band associated with hydroxyl groups when compared to untreated wood, highlighting the degradation of holocellulose.

The absorption band of lignin is stronger in heattreated wood due to the increase in its proportion with the loss of some hemicelluloses. In the spectrum, lignin is represented by the bands at 1600, 1510, and 1105 cm⁻¹, which correspond to vibrations in the aromatic ring of lignin. The greater intensity of these vibrations in thermally modified wood can be seen as a consequence of the splitting of aliphatic side chains in lignin and/or condensation reactions (Hader et al., 2019; Li et al., 2020).

Wood thermogravimetric analysis of wood

The TG/DTG curves exhibit three thermal degradation ranges (Figure 3). The first range is attributed to wood drying, which involves moisture loss and occurs at temperatures below 110 °C, with the maximum mass loss occurring at approximately 50 °C for both treatments. The other two ranges correspond to the thermal degradation of the main chemical components of wood. It is worth noting that each component degradation occurs over a wide temperature range, and its final degradation temperature is higher than that of holocellulose (Yang et al., 2007; Grycova et al., 2021). The second temperature range, which corresponds to the thermal degradation mainly of hemicelluloses and cellulose and smaller proportions of lignin, began at 183 and 170 °C for untreated and thermally modified wood, respectively. In this range, it was observed that for untreated wood, a peak was formed at a temperature of approximately 285 °C, which is associated with more intense degradation of hemicelluloses (Diez et al., 2020). Thus, in thermally modified wood, this peak does not appear since it has already undergone partial degradation of this constituent during the thermal treatment. This second temperature range ends at 352 and 350 °C for untreated and thermally modified wood, respectively, with a peak formation at this point, which corresponds to maximum mass loss, and which was shorter for heat-treated wood.

The third stage of thermal degradation began immediately after and extended up to 400°C for untreated and heat-treated wood. This temperature range corresponds mainly to the degradation of cellulose. Grześkowiak; Bartkowiak (2015) evaluated *Fraxinus excelsior* wood and found higher levels of thermal degradation in the range of 195 to 372°C, with a mass loss of 64.8% in this range and a temperature of maximum degradation at 343°C. In the same study, for heat-treated wood thermally at 205°C for 3 hours, similar results were obtained, with higher levels of degradation occurring between 191 to 375°C (mass loss of 60.6%) and a temperature of maximum degradation at 340°C.

The mass loss at temperatures up to 150 °C represents the drying phase and was 8.36% and 5.99% for raw and heattreated wood, respectively. This means that the raw wood had a higher equilibrium moisture content (EMC) and experienced greater mass loss in this temperature range. Mass loss up to 150 °C was similar for *Eucalyptus* sp. clones, ranging from 6.47% to 7.25% (Santos et al., 2012; Pereira et al., 2013).

The smallest mass losses occurred between 150 and 200°C, indicating the stability of the wood's chemical components at these temperatures. In this range, the mass loss is caused by drying and the volatilization of polar extractives. In the temperature range of 200 to 250°C, it corresponds mainly to the beginning of hemicellulose degradation, which intensifies in the temperature range of 250 to 300°C, with mass losses of 7.9% and 4.1% for natural and thermally treated wood, respectively. Higher mass losses were reported for Eucalyptus sp. wood in the same temperature range of 250 to 300°C, ranging between 17.0 and 19.73% (Santos et al., 2012; Pereira et al., 2013). The highest mass losses were observed in the temperature ranges of 300-350°C and 350-400°C, mainly corresponding to the degradation of cellulose, which occurs completely at temperatures between 300 and 500°C, but intensifies at temperatures between 325 and 375°C (Santos et al., 2012).

The heat-treated wood presented a higher mass loss only between 350 and 400 °c compared to untreated wood, with a difference of 3.3%. This result is due to the higher crystalline fraction of cellulose in heat-treated wood, which is the fraction most resistant to heat and therefore its degradation occurred more intensely in the higher temperature range (between 350 and 400 °c), while in untreated wood, the greater degradation occurred between 300-350°C. The untreated wood showed lower residual mass because a large part of the wood constituents in the heat-treated wood were degraded during the production process, resulting in less mass loss during thermogravimetric analysis and, consequently, higher residual masses. Based on the results, future research should test other heatsetting temperatures and how other process variables, such as residence time, temperature, atmosphere and pressure, can affect the quality of heat-set wood.

CONCLUSIONS

The heat-treated *Fraxinus excelsior* wood showed lower pH, higher buffering capacity, higher lignin and extractives content, and lower holocellulose content. The equilibrium moisture content and shrinkage of the wood were reduced by the heat treatment. The basic density was not altered. The heat treatment increased the vessel diameter and reduced the width, lumen diameter, and fiber wall thickness. The fiber length was not altered. The maximum degradation temperature of the wood's chemical constituents occurred at approximately 350°C, both for untreated and heat-treated wood.

AUTHORSHIP CONTRIBUTION

Project Idea: ACOC, TPF, VRC, Funding: ACOC, TPF, Database: ACOC, TPF, IFD, Processing: ACOC, TPF, Analysis: ACOC, TPF, SOA, Writing: ACOC, TPF, AJVZ Review: ACOC, AMMLC, TPF, ALC, DPSG, SOA, AJVZ

REFERENCES

ABREU NETO, R.; LIMA, J. T.; TAKARADA, L. M.; TRUGILHO, P. F. Effect of thermal treatment on fiber morphology in wood pyrolysis. Wood Science and Technology, v. 55, n. 1, p. 95-108, 2021.

ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS - ABNT. NBR 11941: madeira - determinação da densidade básica. Rio de Janeiro, 2003. 6p.

ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS - ABNT. NBR 7190: Projeto de estruturas de madeira. Rio de Janeiro, 1997. 107p.

AYTIN, A.; ÇAKICIER, N.; BIRTÜRK, T. Chemical, Hygroscopic, and Mechanical Properties of Various Wood Species Heat Treated via the ThermoWood® Method. BioResources, v. 17, n. 1, p. 785-801, 2022.

BAL, B. C. A comparative study of some of the mechanical properties of pine wood heat treated in vacuum, nitrogen, and air atmospheres. BioResources, v. 13, n.3, p. 5504-5511, 2018.

BALASBANEH, A. T.; SHER, W. Comparative sustainability evaluation of two engineered wood-based construction materials: Life cycle analysis of CLT versus GLT. Building and Environment, v. 204, p. 108-112, 2021.

BECK, P.; CAUDULLO, G.; TINNER, W.; DE RIGO, D. *Fraxinus excelsior* in Europe: distribution, habitat, usage and threats. In: SAN-MIGUEL-AYANZ, J.; DE RIGO, D.; CAUDULLO, G.; HOUSTON DURRANT, T.; MAURI, A. (Eds.), European Atlas of Forest Tree Species. Publ. Off. EU, Luxembourg, 2016.

BÖRCSÖK, Z.; PÁSZTORY, Z. The role of lignin in wood working processes using elevated temperatures: an abbreviated literature survey. European Journal of Wood and Wood Products, v. 79, p. 511-526, 2021.

BRITO, J. O.; DIAS JÚNIOR, A. F.; LANA, A. Q.; ANDRADE, C. R.; BERNARDES, F. F. Biological resistance of heat-treated wood of *Pinus caribaea* and *Eucalyptus saligna*. Maderas. Ciencia y tecnología, v. 21, n. 2, p. 223-230, 2019.

CANDELIER, K.; THEVENON, M.F.; PETRISSANS, A.; DUMARCAY, S.; GERDARDIN, P.; PETRISSANS, M. Control of wood thermal treatment and its effects on decay resistance: a review. Annals of Forest Science, v. 73, p. 571-583, 2016.

CARVALHO, A. G.; ANDRADE, B. G.; DONATO, D. B.; et al. Bonding performance of structural adhesives on heat-treated mimosa scabrella and pinus oocarpa wood. Cellulose Chemistry and Technology, v. 54, n. 7-8, p. 663-668, 2020.

COMMISSION PANAMERICANA DE NORMAS TÉCNICAS - COPANT. Descripcion de caracteristicas generales, macroscopicas de las maderas angiospermas dicotiledoneas. COPANT, v.30, p. 1-19, 1974.

CHUNG, H.; PARK, Y.; YANG, S.Y; KIM, H.; HAN, Y.; CHANG, Y.S.; YEO, H. Effect of heat treatment temperature and time on sound absorption coefficient of Larix kaempferi wood. Journal of Wood Science, v. 63, p. 575-579, 2017.

COSTA, A. C. S.; LEAL, C. S.; SANTOS, L. C.; CARVALHO, A. M. M. L.; OLIVEIRA, A. C.; PEREIRA, B. L. C. Propriedades da madeira de cerne e alburno de *Eucalyptus camaldulensis*. Brazilian Journal of Wood Science, v. 8, n. 1, p. 10-20, 2017.

DÍEZ, D.; URUEÑA, A.; PIÑERO, R.; BARRIO, A.; TAMMINEN, T. Determination of hemicellulose, cellulose, and lignin content in different types of biomasses by thermogravimetric analysis and pseudocomponent kinetic model (TGA-PKM method). Processes, v. 8, n. 9, p. 1048, 2020.

ESTEVES, B.; AYATA, U.; CRUZ-LOPES, L.; BRÁS, I.; FERREIRA, J.; DOMINGOS, I. Changes in the content and composition of the extractives in thermally modified tropical hardwoods. Maderas. Ciencia y tecnología, v. 24, 2022.

ESTEVES B.; VELEZ MARQUES A.; DOMINGOS I.; PEREIRA H. Chemical changes of heat-treated pine and eucalypt Wood monitored by FTIR. Maderas Ciencia y tecnología. v. 15, n. 2, p. 245-258, 2013.

GOLDSCHIMID, O. Ultraviolet spectra. In: SARKANEN, K. V.; LUDWING, C. H. Lignins. New York: Wiley Interscience, 1971, p. 241-266.

GOMIDE, J. L.; DEMUNER, B. J. Determinação do teor de lignina em material lenhoso: método Klason modificado. O papel, v. 47, n. 8, p. 36-38, 1986.

GONZÁLEZ-PEÑA, M. M.; CURLING, S. F.; HALE, M. D. C. On the effect of heat on the chemical composition and dimensions of thermally-modified wood. Polymer Degradation and Stability, v. 94, n. 12, p. 2184-2193, 2009.

GRYCOVA, B.; PRYSZCZ, A.; KRZACK, S.; KLINGER, M.; LETINSKY, P. Torrefaction of biomass pellets using the thermogravimetric analyser. Biomass Conversion and Biorefinery, v. 11, p. 2837-2842, 2021.

GRZEŚKOWIAK, W. Ł.; BARTKOWIAK M. Thermogravimetric analysis of commercial thermally modified wood. Drewno, v. 58, n. 194, p. 23-36, 2015.

GURLEYEN, L.; AYATA, U.; ESTEVES, B.; GURLEYEN, T.; CAKICIER, N. Effects of thermal modification of oak wood upon selected properties of coating systems. BioResources, v. 14, n. 1, p. 1838-1849, 2019.

HOSEINZADEH, F.; ZABIHZADEH, S. M.; DASTOORIAN, F. Creep behavior of heat-treated beech wood and the relation to its chemical structure. Construction and Building Materials, v. 226, p. 220-226, 2019.

HOU, S.; WANG, J.; YIN, F.; QI, C.; MU, J. Moisture sorption isotherms and hysteresis of cellulose, hemicelluloses and lignin isolated from birch wood and their efects on wood hygroscopicity. Wood Science and Technology, v.56, p. 1087-1102, 2022.

IAWA COMMITTE E. IAWA list of microscopic features for hardwood identification. IAWA Bulletin, Leiden, v.10, n.3, p.221-332, 1989.

KUBOVSKÝ, I.; KAČÍKOVÁ, D.; KAČÍK, F. Structural changes of oak wood main components caused by thermal modification. Polymers, v. 12, n. 2, p. 485, 2020.

LI, X.; LI, T.; LI, G.; LI, M.; LU, Q.; QIN, S.; LI, J. Effects of UV light irradiation on color changes in thermally modified rubber wood based on FTIR. BioResources, v. n. 15, p. 5179-5197, 2020.

MECCA, M.; D'AURIA, M.; TODARO, L. Effect of heat treatment on wood chemical composition, extraction yield and quality of the extractives of some wood species by the use of molybdenum catalysts. Wood Science and Technology, v. 53, p. 119-133, 2019.

MEDEIROS NETO, P. N.; PAES, J. B.; GONÇALVES, F. G.; LÓPEZ, Y. N.; BARAÚNA, E. E. P.; RIBEIRO, L. S. Relation of physicochemical characteristics on biological resistance of eucalypts woods to xylophagous termites. Journal of Building Engineering, v. 52, p. 104462, 2022.

MOLIŃSKI, W.; ROSZYK, E.; JABŁOŃSKI, A.; PUSZYŃSKI, J.; CEGIEŁA, J. Mechanical parameters of thermally modified ash wood determined by compression in radial direction. Maderas, Ciencia y tecnologia, v. 18, n. 4, p. 577-586, 2016.

PAULA, M. H.; GONÇALEZ, J. C.; ANANÍAS, R. A.; JANIN, G. Effect of heat treatment on physical, mechanical and chemical properties of angelim wood. Maderas. Ciencia y tecnologia, v.25, p. 1-12, 2023.

PAES, J. B.; BROCCO, V. F.; LOIOLA, P. L.; SEGUNDINHO, P. G. A.; SILVA, M. R.; JUIZO, C.G.F. Effect of thermal modification on decay resistance of *Corymbia citriodora* and *Pinus taeda* wood. Journal of Tropical Forest Science, v. 33, n. 2, p. 185-190, 2021.

PEREIRA, B. L. C.; CARVALHO, A. M. M. L.; OLIVEIRA, A. C.; SANTOS, L. C.; CARNEIRO, A. de C. O.; MAGALHÃES, M. A. Efeito da carbonização da madeira na estrutura anatômica e densidade do carvão vegetal de *Eucalyptus*. Ciência Florestal, v. 26, n. 2, p. 545-557, abr. 2016.

PEREIRA, B. L. C.; CARNEIRO, A. C. O.; CARVALHO, A. M. M. L.; COLODETTE, J. L.; OLIVEIRA, A. C.; FONTES, M. P. F. Influence of Chemical composition of eucalyptus wood on gravimetric yield and charcoal properties. BioResources, v. 8, n. 3, p. 4574-4592, 2013.

PEREIRA, F. A. Propriedades de painés OSB, fabricados com flocos de Eucalyptus sp. tratados termicamente. 2013. 82p. Tese (Doutorado em Ciência Florestal) – Universidade Ferderal de Viçosa, Viçosa.

PIERNIK, M.; WOZNIAK, M.; PINKOWSKI, G.; SZENTNER, K.; RATAJCZAK, I.; KRAUSS, A. Impact of the heat treatment duration on color and selected mechanical and chemical properties of scots pine wood. Materials, v. 15, n. 15, p. 5425, 2022.

RAJKOVIĆ, V. J.; MIKLEČIĆ, J. Heat-treated wood as a substrate for coatings, weathering of heat-treated wood, and coating performance on heat-treated wood. Advances in Materials Science and Engineering, v. 2019, p. 1-9, 2019.

RAMALHO, R. S. O uso de macerado no estudo anatômico de madeiras. Viçosa: UFV, 1987. 4p.

ROSZYL, E.; STACHOWSKA, E.; MAJKA, J.; MANIA, P.; BRODA, M. Moisturedependent strength properties of thermally-modified *Fraxinus excelsior* wood in compression. Materials, v. 13, n. 7, p. 1647, 2020.

SANTOS, R. C.; CARNEIRO A. C. O.; TRUGILHO P. F.; MENDES L. M.; CARVALHO A. M. M. L. Análise termogravimétrica em clones de eucalipto como subsídiopara a produção de carvão vegetal. Cerne, v. 18, n. 1, p. 143-151, 2012.

SENNECA, O.; CERCIELLO, F.; RUSSO, C.; WÜTSCHER, A.; MUHLER, M.; APICELLA, B. Thermal treatment of lignin, cellulose and hemicellulose in nitrogen and carbon dioxide. Fuel, v. 271, p. 117656, 2020.

SINKOVIĆ, T.; GOVORČIN, S.; SEDLAR, T. Comparison of physical properties of heat treated and untreated hornbeam wood, beech wood, ash wood and oak wood. In: CONFERENCE ON HARDWOOD RESEARCH AND UTILISATION IN EUROPE, 5, 2012, Sopron. Anais ... Sopron: University of West Hungary Press, 2012, p. 63-70.

SIVRIKAYA, H.; HOSSEINPOURPIA, R.; AHMED, S. A.; ADAMOPOULOS, S. Vacuum-heat treatment of Scots pine (*Pinus sylvestris* L.) wood pretreated with propanetriol. Wood Material Science & Engineering, v. 17, n. 5, p. 328-336, 2022.

SOUZA, E. R. N.; ESCOBAR, C. G.; NUNES, L. C.; NOVAES, D. S.; KREFTA, S. C.; DUARTE, P. G. S.; PEREIRA F. Influência do tratamento térmico no pH e capacidade tampão das madeiras de Eucalyptus spp. e Pinus spp. In: CONGRESSO BRASILEIRO DE CIENCIA E TECNOLOGIA DA MADEIRA, 3, 2017, Florianópolis. Anais eletrônicos... Florianópolis: SBCTEM, 2017. Disponível em: https://proceedings.science/cbctem/papers. Acesso em: 03 mai. 2023.

TECHNICAL ASSOCIATION OF THE PULP AND PAPER INDUSTRY – TAPPI. Sampling and preparing wood for analysis: T 257 om-92. Atlanta, v. 1, 1992.

TECHNICAL ASSOCIATION OF THE PULP AND PAPER INDUSTRY – TAPPI. Solvent extractives of wood and pulp: 204 cm-97. Atlanta, 1997, p. 4-10.

TJEERDSMA, B. F.; MILITZ, H. Chemical changes in hydrothermal treated wood: FTIR analysis of combined hydrothermal and dry heat-treated wood. Holzforschung, v. 63, p. 102-111, 2005.

VASTERN TIMBER. Brimstone Ash. 2018. Disponível em: <https://www.vastern. co.uk/decking/brimstone-ash/>, Acesso em: 16 de novembro de 2018.

WANG, J.; MINAMI, E.; KAWAMOTO, H. Thermal reactivity of hemicellulose and cellulose in cedar and beech wood cell walls. Journal of Wood Science, v. 66, n. 1, p. 1-10, 2020.

YANG, H. et al. Characteristics of hemicellulos, cellulose and lignin pyrolysis. Fuel, v. 86, n. 12-13, p. 1781-1788, 2007.

ZANUNCIO, A. J. V.; COSTA, E. A.; CARVALHO, A. G.; CASTRO, V. R.; CARNEIRO, A. C. O.; ARAÚJO, S. O. Artificial intelligence and colorimetry as a combined non-destructive method to predict properties of heat-treated wood. Cellulose Chem. Technol., v. 56, p. 941-948, 2022.

ZANUNCIO, A. J. V. CARVALHO, A. G.; SOUZA, M. T.; JARDIM, C. M.; CARNEIRO, A. C. O.; COLODETTE, J. L. Effect of extractives on wood color of heat-treated *Pinus radiata* and *Eucalyptus pellita*. Maderas. Ciencia y tecnología, v. 17, n. 4, p. 857-864, 2015.

ZANUNCIO, A. J. V.; HEIN, P. G. R.; CARVALHO, A. G.; ROCHA, M. F. V.; CARNEIRO, A. C. O. Determination of heat-treated eucalyptus and pinus wood properties using NIR spectroscopy. Journal of Tropical Forest Science, v. 30, n. 1, p. 117-125, 2018.