UNIVERSIDAD DE LA REPÚBLICA

FACULTAD DE INGENIERÍA

Tesis para optar al título de
Magíster en Ingeniería Química

MODIFICACIÓN TÉRMICA DE MADERA DE *Eucalyptus grandis* Y *Pinus taeda*

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Montevideo, Uruguay

2020

UNIVERSIDAD
DE LA REPÚBLICA
URUGUAY

FACULTAD DE INGENIERIA

UNIVERSIDAD DE LA REPÚBLICA

FACULTY OF ENGINEERING

Thesis submitted in partial fulfillment of the requirements for the Degree of Master of Chemical Engineering

THERMAL MODIFICATION OF *Eucalyptus grandis* AND *Pinus taeda WOOD*

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Montevideo, Uruguay

2020

ISSN 1688-2806

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Tesis de Maestría en Ingeniería Química

Facultad de Ingeniería

Universidad de la República

Montevideo, Uruguay, 2020.

“Apply them constantly, to everything that happens: Physics. Ethics. Logic.”

Marcus Aurelius

RESUMEN

La industria de la modificación de madera se encuentra actualmente bajo un proceso de grandes cambios, motivados principalmente por el riesgo para la salud y las implicancias ambientales de los métodos tradicionales. En las últimas décadas, nuevas tecnologías de modificación de madera han comenzado a comercializarse, como es el caso de la modificación térmica de madera, que logra mejorar las propiedades de la madera sin el agregado de agentes químicos.

El presente trabajo se centra en el estudio de los cambios en las propiedades de la madera de *Eucalyptus grandis* Hill ex Maiden y *Pinus taeda L.* sometida a modificación térmica a temperaturas de entre 160 °C y 220 °C en vacío, aire y nitrógeno.

Se estudió la pérdida de masa y la reducción de volumen producto de la modificación térmica, así como la degradación de la pared celular, medida a través del contenido de lignina y de los azúcares glucosa, xilosa, galactosa y manosa. También se analizaron los cambios en la higroscopicidad, tanto como en las propiedades mecánicas, que fueron medidas a través del módulo de elasticidad y la resistencia a la flexión. Finalmente, se estudió la reversibilidad de los cambios en la higroscopicidad y la estabilidad dimensional de la madera de *Eucalyptus grandis* modificada a 200 °C.

Se constató pérdida de masa y reducción de volumen en ambas especies y en todas las condiciones ensayadas. Se evidenció degradación de la pared celular, principalmente debido a la reducción del contenido de xilosa, galactosa y manosa de la madera sometida a modificación térmica. El contenido de humedad en equilibrio con el ambiente se vio reducido y la resistencia a la flexión se vio afectada por la modificación térmica, mientras que el módulo de elasticidad mostró comportamientos distintos en ambas especies, viéndose disminuido en la especie *P. taeda*. Por último, se comprobó que existe reversibilidad en la reducción de la higroscopicidad y la mejora en la estabilidad dimensional de madera de *E. grandis* modificada térmicamente.

A partir de este trabajo se proporciona un profundo estudio de las variaciones en las propiedades de dos especies maderables uruguayas sometidas a modificación mediante la utilización de una tecnología con potencial para colaborar con el desarrollo de la industria forestal local.

ABSTRACT

The wood modification industry is currently undergoing major changes, mainly motivated by the environmental and health implications of traditional methods. In the last decades, new technologies for wood modification have reached the market, such is the case of thermal modification, which improves the properties of wood without the addition of chemicals.

This work studies the changes in the properties of *Eucalyptus grandis* Hill ex Maiden and *Pinus taeda* L. wood subjected to thermal modification at temperatures between 160°C and 220°C in vacuum, air and nitrogen.

Mass loss and volume reduction due to thermal modification were studied, as well as cell wall degradation, measured through lignin content and sugars, namely glucose, xylose, galactose and mannose. The changes in hygroscopicity were also analyzed, in addition to the mechanical properties, measured through the modulus of elasticity and bending strength. Finally, the reversibility of changes in hygroscopicity and dimensional stability of *Eucalyptus grandis* modified at 200°C was studied.

All tested conditions in both species presented mass loss and volume reduction. Degradation of the cell wall constituents was exhibited, mainly due to the reduction of the xylose, galactose and mannose content of thermally modified wood. Equilibrium moisture content was reduced and

bending strength was negatively affected by the thermal modification, while the modulus of elasticity presented different behaviors in the two species, showing a decreasing trend in *P. taeda* wood. Lastly, a certain degree of reversibility in the reduction of hygroscopicity and the improvement in the dimensional stability of thermally modified *E. grandis* wood was observed.

This work provides a comprehensive study of the variations in the properties of two Uruguayan timber species modified with a technology that has the potential to help with the development of the local forestry industry.

PREFACE

This work was conducted by Leandro Cantera and supervised by Dr. Andrés Dieste, who helped with the experimental design, interpretation of the results and drafting of the manuscript.

Most of the work was carried out in the Forest Process Engineering group, in the Chemical Engineering Institute at the Faculty of Engineering, Universidad de la República, Uruguay. The mechanical tests were performed in the Uruguayan Technological Laboratory (LATU). The studies on the reversibility of wood properties were done in the Department of Wood Biology and Wood Products at the Georg-August Universität Göttingen, Germany.

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LIST OF ABBREVIATIONS

CV	Coefficient of variation
DMDHEU	1,3-dimethylol-4,5-dihydroxyethyleneurea
DTA	Differential thermal analysis
DV	Density variation
E	Modulus of elasticity
EMC	Equilibrium moisture content
f	Bending strength
FSP	Fiber saturation point
G	Guaiacyl
H	p-hydroxyphenyl
HMF	5-Hydroxymethylfurfural
HPLC	High-Performance Liquid Chromatography
MC	Moisture content
$\mathbf{M_d}$	Equilibrium moisture content associated to the dissolved water
$\mathbf{M_h}$	Equilibrium moisture content associated to the wood-water hydrate
ML	Mass loss

$\mathbf{M_{meas}}$	Equilibrium moisture content measured
$\mathbf{M_{model}}$	Equilibrium moisture content calculated by Hailwood-Horrobin model
n	ideal sample size for 15% precision and 90% confidence
nd	Not detected
NREL	National Renewable Energy Laboratory
OH	Hydroxyl
PL	Proportional limit
RH	Relative humidity
S	Syringyl
$\mathbf{S_{max}}$	Maximum volumetric swelling
VR	Volume reduction
XGM	Xylose, galactose and mannose

1 INTRODUCTION

The concept of sustainable development was described by the United Nations in 1987 as a development that "*meets the needs of the present without compromising the ability of future generations to meet their own needs*"[1]. In order to embrace the paradigm of sustainable development it is imperative to adopt new technologies, enabling the usage of renewable materials that do not compromise the environment.

The long history of sawmill industry provides excellent examples of a renewable material being processed, utilized and finally disposed with minimal environmental impact (Hill, 2006). However, just like any other resource, it is paramount to focus on renewability and minimize negative impact throughout the whole productive chain, from forest management until final disposal. If said renewability and minimal impact are achieved, it is then possible to talk about a product that can be used indefinitely.

To achieve this, two main aspects must be considered. On the one hand, the production of sustainably sourced wood should be increased, both by allocating more land for sustainable managed production and by increasing its productivity. On the other hand, service life of timber-based products should be improved.

[1] (United Nations World Commission on Environment and Development, 1987)

The efforts allocated towards the improvement of total plantation yields has led to an increase in the production of fast-growing species, namely *Pinus spp*. and *Eucalyptus spp*., encouraging growth through fertilization and thinning regimens that lead to timber with high proportion of juvenile wood, poorly developed heartwood and wide growth rings. This derives in low density timber with diminished durability and mechanical properties, which demands for some way to upgrade it (Hill, 2006).

In Uruguay, since the approval of the Forestry Law in 1987, there has been a sustained increase in the amount of forested area, reaching one million hectares of affected area by 2013 (Uruguay XXI, 2016), mainly of *Eucalyptus grandis* Hill ex Maiden and *Pinus taeda* L.

The need to improve wood's properties led to the development of the wood modification industry, which has traditionally relied on a few first-generation preservatives like Creosote, Chromated Copper Arsenate (CCA), Oilborne Pentachlorophenol and ammonium based organic biocides (Freeman, et al., 2005). However, increasing awareness in the consumers regarding the harmful effects that these preservatives have on human and animal health, as well as the environmental issues associated with the leaching of toxic chemicals into the environment (Peek, 2004; Helsen & Van den Bulck, 2004; Sotome & Muniz, 2004) are shifting the focus of the wood preservation industry towards more environmentally friendly methods for increasing the properties of timber.

Thermal modification of wood has historically been known for its capability to improve wood's dimensional stability and decay resistance. The main attribute of thermal modification is the absence of chemical reagents in the process, only energy is needed to elevate the temperature of wood and generate the desired changes in its chemical structure (Hill, 2006).

In the case of Uruguay, thermally modified wood has been identified as a product with great potential to add value to both pine and eucalypt wood, being the second product with most added value per unit (only below Cross Laminated Timber) and the one with most added value per unit of biomass (Dirección de Planificación, 2019; Dieste, et al., 2019).

Nowadays, thermal modification methods typically heat wood up to a temperature between 160°C and 240°C, and vast differences are found among the varying processes being used, not only in terms of temperature, but also in several other aspects, like total duration of the process, initial moisture content (MC) of the wood, MC during treatment, treatment pressure and treatment environment (heat transferring medium) (Militz & Altgen, 2014). Also, the wood specie being subjected to thermal modification is of great relevance for the determination of treatment conditions, thus a fundamental understanding of the effect of thermal modification on the desired species is needed. Therefore, the study of the chemical, physical and mechanical characteristics of modified wood is of great importance in order to properly understand this technology.

From a chemical standpoint, the composition of wood is changed at a cellular level, leading to physical and mechanical changes, the more aesthetically being color, where thermally modified wood acquires shades of brown darker than untreated wood. But changes also include loss of mass, reduction of volume, reduction of the equilibrium moisture content (EMC), increased dimensional stability and decreased strength.

Considering the relevance and variation of the changes that take place in wood due to thermal modification, the lack of knowledge regarding the effects that this technology has on Uruguayan timber species represent a barrier for its adoption, and for said barrier to be lowered, the following questions need to be addressed:

- What changes occur in the chemical composition of Uruguayan timber species when subjected to different thermal modification conditions?
- What is the relevance of the difference in the anatomy and composition between *E. grandis* and *P. taeda* in the chemical, physical and mechanical changes that take place due to thermal modification?
- Is it possible to find relationships between the changes in the different properties measured?
- Is it technically feasible to produce thermally modified wood from Uruguayan *E. grandis* and *P. taeda*?

The purpose of this work was to quantify the changes in chemical, physical and mechanical properties that occur in *Eucalyptus grandis* and *Pinus taeda* wood when subjected to thermal modification processes with varying conditions of temperature and heating environment, with the aim to gain knowledge that will start to lower the barrier for the adoption of this technology in Uruguay.

This work is linked to the activities that were previously carried out in the Chemical Engineering Institute of the Faculty of Engineering (Amilivia, et al., 2017), where *E. grandis* wood was modified with the same equipment that was used in the present work, at temperatures between 160°C and 200°C for 1, 2 and 3 hours in a vacuum environment, finding that the treatment temperature was a relevant parameter both in the loss of mass and in the reduction of the hygroscopicity of the wood, and that the time of treatment did not represent a variable of relevance for these two parameters. These results provided a favorable background for the selection of the working conditions that were used in this work.

1.1 OBJECTIVES

The product obtained from thermal modification is highly dependent on process variables, which directly influence the intensity and general characteristics of the chemical changes that wood undergoes, as well as changes on physical and mechanical properties of the modified material. Having said that, a comprehensive analysis of the technology and the

product must consider different process variables and the relation they have with wood chemical, physical and mechanical changes.

It is therefore imperative to devote efforts to understand the changes that occur in the chemical composition of Uruguayan timber species when thermally modified in different conditions, as well as the relevance of the composition and amount of hemicelluloses of *E. grandis* and *P. taeda* in the changes that occur during treatment. Moreover, it is relevant to comprehend the relationships between the chemical, physical and mechanical changes. Finally, the overall feasibility of the application of this technology to Uruguayan species must be assessed.

Within the framework of the national interest in the development of the forestry industry, the main objectives of this work were to foster the knowledge regarding thermal modification technology in Uruguay through the evaluation of the changes that take place on *E. grandis* and *P. taeda* wood after being subjected to thermal modification.

With that in mind, the following specific objectives were set:

1. Successfully thermally modify *E. grandis* and *P. taeda* boards while recording the loss in dry mass and the variations in dimensions due to the process.
2. Analyze the changes in wood's chemical composition.
3. Study the changes in valuable properties from a technological standpoint.

4. Asses the degree of reversibility that the hygroscopicity changes due to thermal modification can have during service life of the material.
5. Evaluate the prediction capability that the changes in the properties measured in objectives 1 and 2 can have over the technological properties measured in objective 3.

2 LITERATURE REVIEW

2.1 INTRODUCTION

This chapter aims to present the state of the art regarding thermal modification of wood as a technology that improves the properties of wood. Before addressing wood modification in general and particularly thermal modification, a description of wood anatomy and wood technology is provided.

The objectives, need and challenges associated with wood modification are discussed, as well as the main methods currently used, and how thermal modification of wood presents itself as an alternative of growing interest. Then, attention is given to the effects of thermal modification on the physical, chemical and mechanical properties of wood. Finally, durability and other properties affected as a result of the process are discussed, as well as current applications of thermally modified wood.

2.2 WOOD STRUCTURE AND COMPOSITON

Wood is regarded as a biological structure of vast complexity. It is a composite of many cell types working together to meet the needs of a living plant. To understand this material from a wood technology viewpoint, it is often overlooked that wood evolved to serve three main functions:

Conduction of water from the roots to the leaves, mechanical support of the plant body and storage of biochemicals. All properties of wood (physical, mechanical, chemical, biological or technological) are rooted in one or more of those three functions (Wiedenhoeft, 2010).

2.2.1 ANATOMIC DESCRIPTION

Any tree has two domains, the shoot and the roots. While roots are the underground structure responsible for the uptake of water and mineral nutrients, mechanical anchoring and storage of biochemicals, the shoot is composed by the trunk, branches and leaves (Raven, et al., 1999). The description in this chapter will focus solely on the trunk.

Figure 2.1 shows how the trunk is composed of different materials which form concentric bands. From the outside to the center are the outer bark, inner bark or phloem, vascular cambium, sapwood, heartwood and the pith.

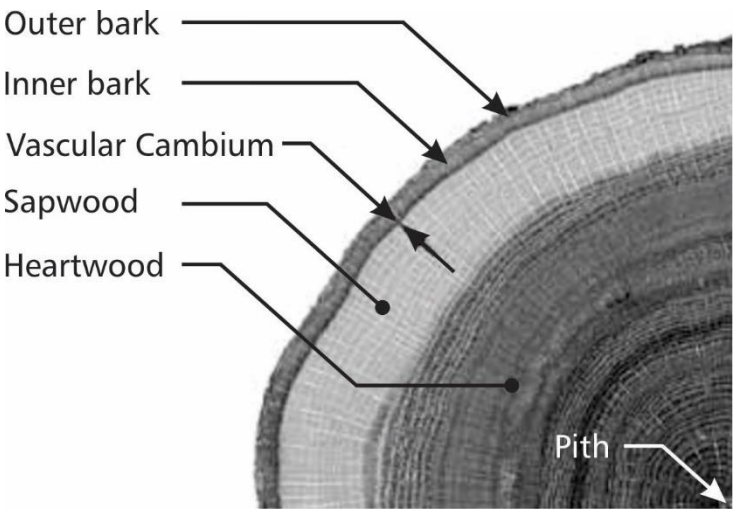

Figure 2.1. Transverse section of a tree trunk. Adapted from Wiedenhoeft (2010).

Outer bark provides mechanical protection to the inner bark and helps limit the evaporative water loss. Inner bark, or phloem, acts as a conduit for the translocation of photosynthates (manufactured foodstuffs) from the leaves to the roots. The vascular cambium layer, located between the bark and the wood, is responsible for the production of these two tissues, phloem outward and xylem inwards. The sapwood, or xylem, is the part of the tree responsible for the transportation of water and nutrients from the roots to the leaves. It is often referred as *living* wood in contrast to the darker and non-conductive heartwood, which does not transport water and has the purpose of mechanically supporting the tree. The pith at the center of the trunk is the remnant of the early growth of the tree (Wiedenhoeft, 2010).

2.2.1.1 SOFTWOODS AND HARDWOODS

Wood is mainly obtained from two broad categories know as *softwood* and *hardwood*. However, these general names cannot be used only referring to the actual physical hardness or density of wood. Some softwoods are quite hard while some hardwoods are relatively soft. Still, these names and their reference to softness or hardness do accurately apply to many woods within these categories and are practical designation of commercial timber (Parham & Gray, 1984).

Softwoods, or more scientifically precise, *gymnosperms*, have a simpler basic structure when compared against hardwoods, or *angiosperms*. Softwoods have two cell types and little variation in structure within them. On the other hand, hardwoods have both more cell types and

grater variation within them. Nonetheless, a relevant similarity between both groups is that most of the cells are dead at maturity, even in sapwood. Living cells are called parenchyma and can be found in both softwoods and hardwoods (Wiedenhoeft, 2010).

2.2.1.2 WOOD CELL

Any living plant cell is composed of a protoplast, which consists in the living contents inside the cell membrane, and a non-living cell wall, a protective and supportive matrix that surrounds the protoplast, mainly made of carbohydrates (Esau, 1977; Raven, et al., 1999).

In many cases, for transportation and mechanical support purposes, only the cell wall of a wood cell is useful, meaning that the protoplast must be removed for them to be functionally mature. The portion left unoccupied by the protoplast is called *lumen*, an unoccupied void space in the interior of the cell (Wiedenhoeft, 2010). Hence, from the point of view of the technological use of wood as a load-caring material, the cell wall is of greatest interest.

2.2.1.3 CELL WALL

The structure of cell walls is highly regular from one cell type to another, and even between softwoods and hardwoods. It consists of three main regions: the middle lamella, the primary wall and the secondary wall (Figure 2.2). All three regions have the same three major components:

cellulose microfibrils, hemicelluloses and a matrix of encrusting material, typically pectin in primary walls and lignin in secondary walls.

The middle lamella is the layer of cell wall material between two cells, in wood it is predominantly made of lignin. The next layer is the primary wall, generally thin and indistinguishable from the middle lamella. It is characterized by the random orientation of cellulose microfibrils, which contrast with the heavily organized microfibril pattern in the secondary wall (Wiedenhoeft, 2010; Shmulsky & Jones, 2011).

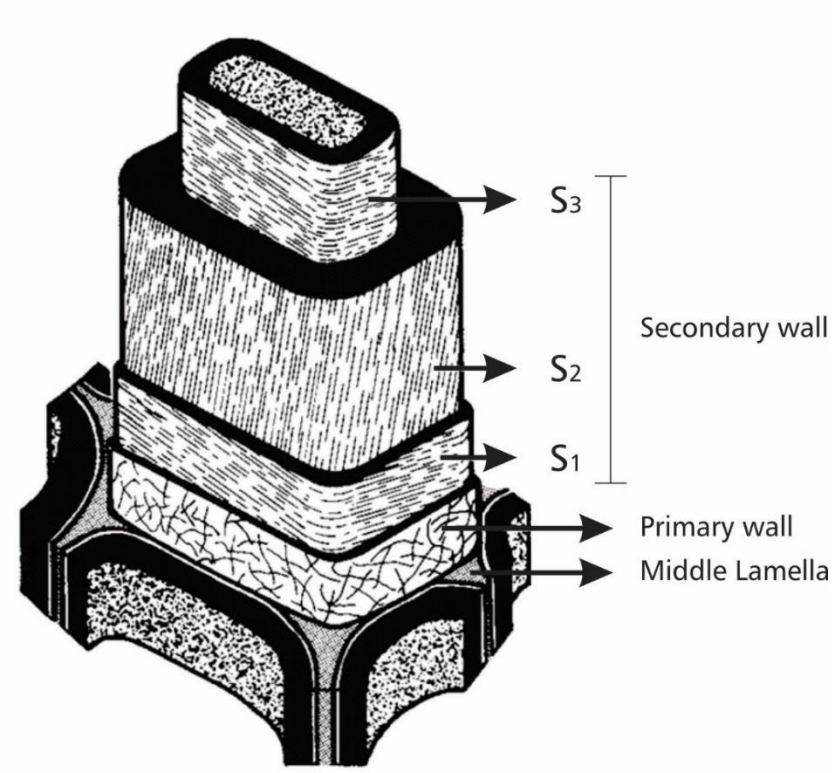

Figure 2.2. Layering of a mature cell wall. Adapted from Shmulsky and Jones (2011).

The secondary cell wall is composed of three layers. The first formed secondary cell wall layer (S_1) is characterized by the spiraled way in which cellulose microfibrils are distributed, with the long axis of the microfibrils almost perpendicular to the long axis of the cell. The second layer (S_2) of the secondary cell wall is regarded to be the most relevant one because of its importance in the determination of the properties of the cell, and as a consequence, the macroscopic properties of wood (Panshin & DeZeeuw, 1980). It is the thickest layer and is characterized by a lower lignin percentage than the S_1, as well as a microfibril distribution that is in alignment with the long axis of the cell. Finally, the third layer (S_3) of the secondary cell wall is the one in direct contact with the lumen, and consequently, with the fluid being transported inside it. Its microfibril arrangement is similar to the one of S_1 and is the least lignified layer (Wiedenhoeft, 2010; Shmulsky & Jones, 2011).

2.2.2 CHEMICAL COMPOSITION

There are three major chemical components of wood, cellulose, hemicelluloses and lignin. Also, minor amounts of extractives and inorganic minerals (ash) are present. Table 2.1 presents the approximate percentage of dry weight of each macro-component in hardwood and softwoods.

Table 2.1. Approximate composition of wood, expressed as percentage of dry weight (Shmulsky & Jones, 2011).

Type	Cellulose	Hemicelluloses	Lignin
Hardwood	40 – 44	15 – 35	18 – 25
Softwood	40 – 44	20 – 32	25 – 35

It must be emphasized that wood is not a homogenous material, thus its composition is not constant throughout the tree. Variations are found within a single tree from the center of the stem to the bark, or from the stump to the crown (Kollmann & Côté, 1968).

2.2.2.1 CELLULOSE

Cellulose is a glucan polymer formed by 1,4-β-bonded anhydroglucose units (Figure 2.3). The number of sugar units in one chain is referred as degree of polymerization (DP) and the length of a glucan chain can be as large as 10,000 or 15,000 monomers (Pettersen, 1984; Shmulsky & Jones, 2011). Oligomers of cellulose with a DP of 7-8 are still partially soluble in water. However, chains with a DP of 30 already present a polymer like behavior (Sixta, 2006).

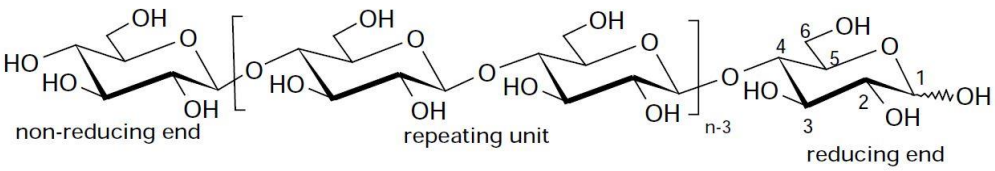

Figure 2.3. Molecular structure of cellulose in the 1,4-β-D-glucopyranose form (Sixta, 2006).

Despite its apparently simple molecular structure, the supramolecular organization of cellulose makes it an incredibly complex material, with the ability to form different types of hydrogen bonds within the same cellulose chain (intramolecular) or between different chains (intermolecular). Intramolecular hydrogen bonds are of importance for the stiffness and conformation of cellulose, while intermolecular bonds are necessary for the formation of crystallin structures and fibrils (Sixta 2006).

Both intra- and intermolecular hydrogen bonds are responsible for keeping the chain straight and stacked. These straight chains aggregate in a layered compact structure and weak van der Waals forces are thought to be responsible holding the layers together (Pettersen, 1984; Saxena & Brown, 2005). These highly ordered structures are referred to as *crystalline* cellulose, because they exhibit a distinct X-ray pattern. Less ordered regions are called *amorphous* cellulose, although not as ordered as crystallin cellulose, this domain has a certain degree of order in their glucan chains (Sixta, 2006).

2.2.2.2 HEMICELLULOSES

Hemicelluloses are a branched heteropolymer formed of a mixture of polysaccharides that are synthesized in wood almost entirely from glucose, mannose, galactose, xylose, arabinose, 4-O-methylglucuronic acid and galacturonic acid residues (Figure 2.4). In general, hemicelluloses are of much lower molecular weight than cellulose, with a DP in the range of 50-200. Because of these characteristics (heterogenic, branched, low DP) they tend to exhibit an amorphous form rather than the crystallinity of cellulose. They are intimately linked to cellulose fibers and cross-linked with lignin, this creates a network of bonds that provide structural strength to the wood (Pettersen, 1984; Sixta, 2006).

The main chain of hemicelluloses, called *backbone*, can consist of only one unit (e.g. xylans), or of two or more units (e.g. glucomannans). Significant differences can be found between softwoods and hardwoods in

relation to the type and content of hemicelluloses in the cell wall. While softwood have a high proportion of mannose units and more galactose units, hardwoods have a high proportion of xylose units and more acetyl groups than softwoods (Sixta, 2006).

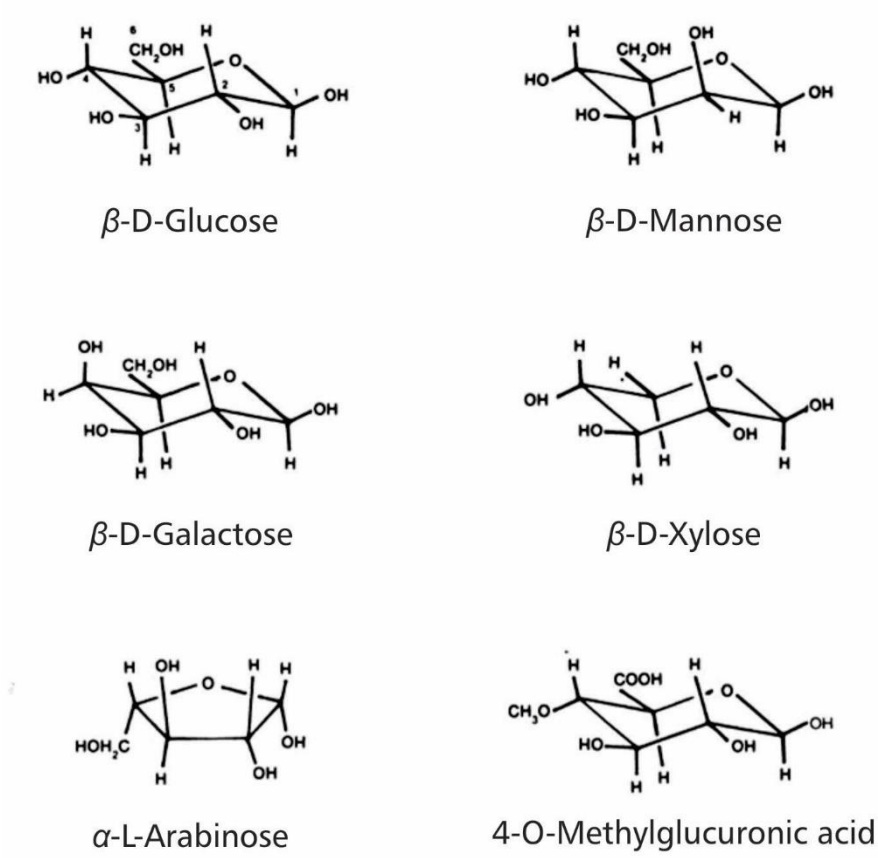

Figure 2.4. Monomer components of wood hemicelluloses (Pettersen, 1984).

Figure 2.5 shows hemicelluloses chains of hardwoods and softwoods. In hardwoods, the xylan chains are laced at irregular intervals with groups of 4-O-methylglucuronic acid linked to the xylose backbone. Also, many of the hydroxyl (OH) groups at C_2 and C_3 of the xylose units are substituted by O-acetyl groups, producing O-acetyl-4-O-methylglucuronoxylan, which is the main component of hemicelluloses in

hardwoods. Softwood and hardwood xylans differ by the lack of acetyl groups and the presence of arabinose units in the former. The simplest structure of glucomannans is shown in hardwood glucomannan and consists of units of glucose and mannose linked by β-(1,4) glucosidic bonds forming slightly branched chains. Softwood glucomannan consists of a glucomannan backbone with acetyl groups and galactose residues attached to it (Sixta, 2006).

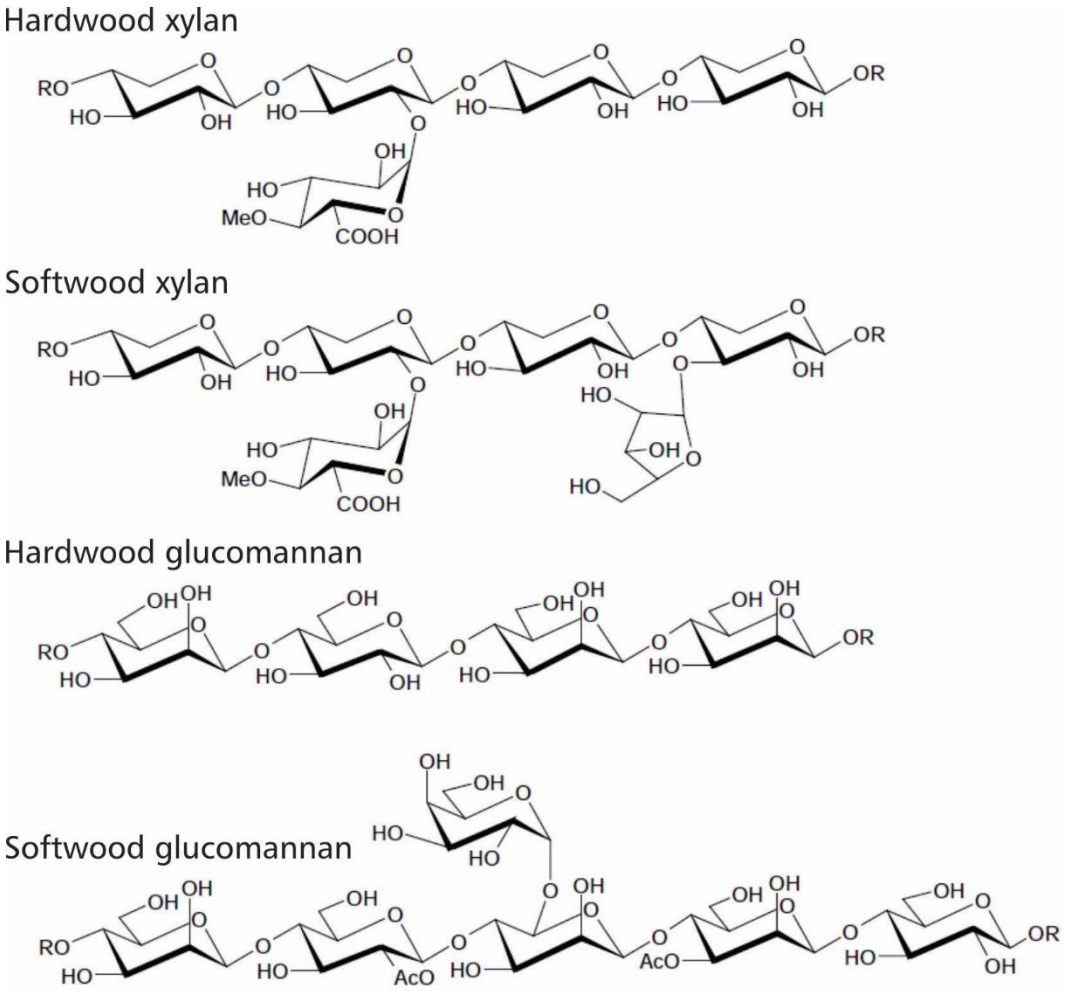

Figure 2.5. Molecular structure of xylans and glucomannans (Sixta, 2006).

2.2.2.3 LIGNIN

Lignin is a phenolic substance consisting of an irregular arrangement of variously bonded hydroxy- and methoxy-substituted phenylpropane units, namely p-hydroxyphenyl (H) derived from p-coumaryl alcohol, guaiacyl (G) derived from coniferyl alcohol and syringyl (S) derived from sinapyl alcohol (Figure 2.6). P-hydroxyphenyl units are minor precursors of softwood and hardwood lignin, guaiacyl is the predominant precursor of softwood lignin and both guaiacyl and syringyl are precursors of hardwood lignin (Alder, 1977).

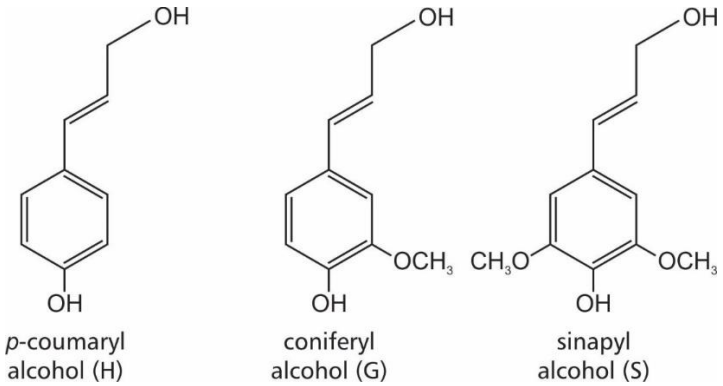

Figure 2.6. Lignin precursors.

Lignin is found between cells and within them. Between cells, it serves the purpose of binding them together. Within the cell wall, it is very intimately associated with both cellulose and hemicelluloses, providing rigidity to the cell. Said rigidity is also responsible for reducing the dimensional changes that take place in wood with moisture content (MC) variation. Moreover, it enhances wood's decay resistance against insects and fungi attack (Shmulsky & Jones, 2011).

2.2.2.4 EXTRACTIVES

Extractives are defined as non-structural, organic or inorganic, hydrophilic or lipophilic substances that can be extracted from wood with natural solvents. They are a variety of fats, waxes, alkaloids, proteins, simple and complex phenolics, simple sugars, pectins, mucilages, gums, resins, terpenes, starches, glycosides, saponins and essential oils. They play relevant roles in the metabolism of trees, as energy reserves, or as part of the defense mechanism of the tree against microbiological damage and provide wood with color, odor, and decay resistance (Pettersen, 1984).

2.2.2.5 CARBOHYDRATES AND LIGNIN DISTRIBUTION

As shown in Figure 2.7, all three structural components of wood, cellulose, hemicelluloses and lignin, are present in all layers of the cell wall.

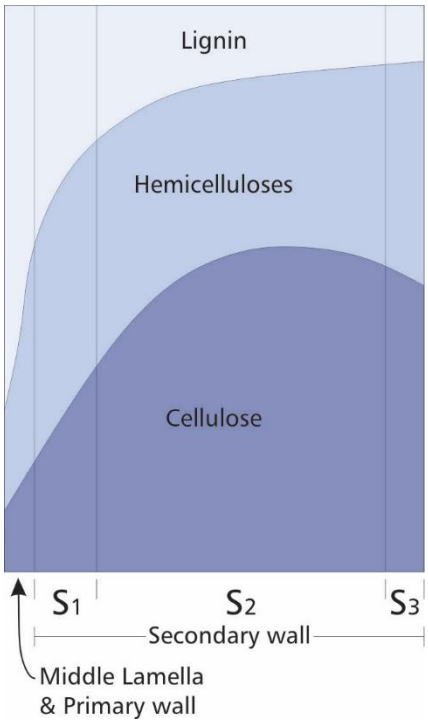

Figure 2.7. Distribution of macro-components in cell wall layers. Adapted from Shmulsky and Jones (2011).

Cellulose is present only in small amounts in the middle lamella, and it increases until the middle of the S_2 layer of the secondary wall, slightly declining in concentration across the end of the S_2 and the S_3 towards the lumen. Lignin is the predominant component in between cells, and consistently decreases in concentration towards the center on the cell, being the minoritarian component in the S_3. Finally, hemicelluloses consistently increase in concentration toward the lumen.

2.2.3 WOOD TECHNOLOGY

Macroscopic properties, like wood-water relationship, dimensional stability, mechanical resistance or density are derived from the chemical composition and anatomy of wood structure (Panshin & DeZeeuw, 1980).

2.2.3.1 WOOD-WATER RELATIONSHIP

As it was previously mentioned, the cell wall is largely made of cellulose and hemicellulose, whose OH groups make the cell wall hygroscopic. Lignin, on the contrary, has a comparatively hydrophobic nature (Glass & Zelinka, 2010). The capability of cell walls to take up water is then dependent on the amount of water-accessible OH groups of the carbohydrates that constitute cellulose and hemicelluloses.

Moisture can be present in wood as free water, liquid water or water vapor in cell lumen and cavities; or as bound water, which is held by intermolecular bonds between water and cell wall. The moisture content at which both the lumen and the cell wall are totally saturated with water

represents the maximum possible MC. On the other hand, the fiber saturation point (FSP) is that in which cell walls are completely saturated, but no water exists in cell lumina. It is generally accepted that FSP averages around 30% MC. However, different species as well as particular conditions may greatly affect this value. Although the FSP is a distinctive point which separates two ways in which wood takes up water, reality indicates that the transition is rather gradual. When wood is being dried, the cell wall can start to reduce its MC while the lumen is still partially filled with water (Glass & Zelinka, 2010).

The hygroscopic OH groups of cell wall polymers will make wood absorb water when located in an environment with moisture and release it when the environment is dry. This absorption and desorption of water changes wood volume, swelling or shrinking depending on the humidity of the environment (Hill, 2006). When green wood is exposed to atmospheric conditions, it reduces its moisture to a sufficiently low MC that is at equilibrium with the environment. Said MC is called equilibrium moisture content (EMC) and depends on the atmospheric conditions such as humidity and temperature, but it also depends on the species, extractive content, mechanical stress and exposure history (Skaar, 1988).

The main factor affecting EMC of wood is the relative humidity (RH) of the environment to which wood is exposed. Therefore, sorption and desorption of water is usually studied by the relationship between EMC and RH at a set temperature (Skaar, 1988; Hill, 2006). Figure 2.8 shows an

example of a typical sorption and desorption isotherm curve with hysteresis, that is the difference in EMC at any RH content depending on the history of the wood sample, presenting a higher EMC when wood had to loose water to achieve equilibrium and a lower one when it had to take up water.

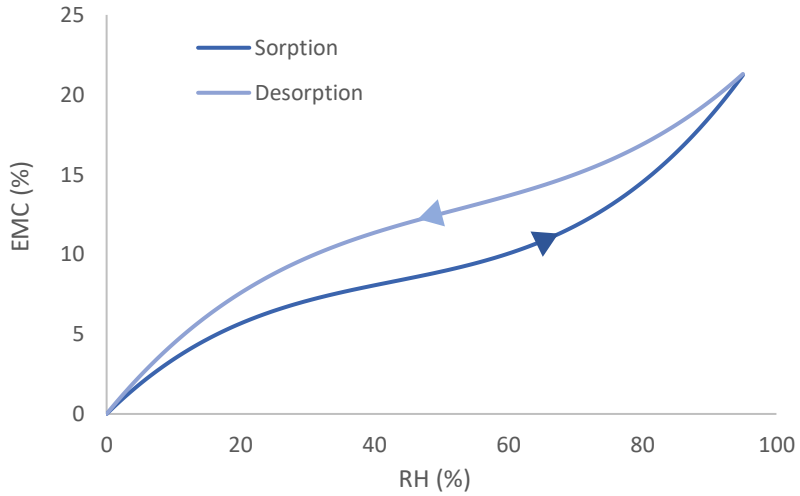

Figure 2.8. Typical sorption and desorption isotherm.

In wood-water systems, mainly 3 types of sorption isotherms are present (Figure 2.9). Type 1 can be regarded as the sorption of vapor on a substrate in which only a single layer of the sorbent (vapor) is found on the sorbate (wood), it can even be said that the vapor molecule forms a hydrate with the cell wall constituents (OH groups). In either case, there is greater attraction between wood and water than among water molecules. Type 3 is obtained when several layers of sorbent are formed in the substrate. In this case, the attraction of the water molecules to the wood is considered to be much lower than that of the type 1. Finally, type 2, which is the typical sigmoid sorption isotherm of wood appears to be a composite of types 1 and 3 (Skaar, 1988).

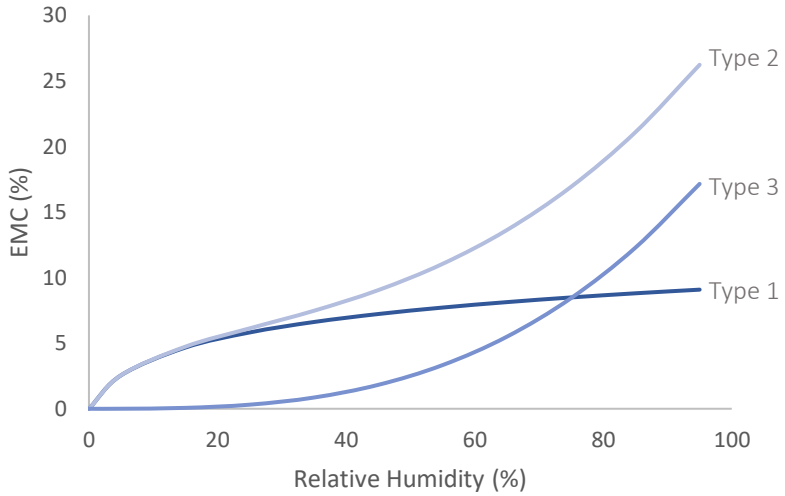

Figure 2.9. Typical shapes of the types 1, 2 and 3 isotherms. Adapted from Skaar (1988).

2.2.3.2 DIMENSIONAL STABILITY

The cell walls of a living tree are always in a fully swollen condition with no room for shrinkage or swelling except for that derived from hydrostatic tension of the water present in the lumen or temperature induced changes. However, when dried, hygroscopic shrinkage takes place. The amount of moisture loss, structural directions of shrinkage (radial, tangential, and longitudinal), the species and the drying conditions (e.g. moisture gradients) are all aspects that affect the drying process and final moisture content. Although wood is usually dried to approximately the EMC it will have during its use, environmental conditions are rarely constant, leading to recurring swelling and shrinkage throughout its service life (Skaar, 1988).

Regular changes in wood dimensions can lead to decreased utility and performance problems of wood products. It is therefore important to

carefully consider dimensional stability when wood products are designed to be exposed to large and sustained changes in relative humidity (Glass & Zelinka, 2010).

2.2.3.3 MODULUS OF ELASTICITY AND BENDING STREGTH

Elasticity implies a temporal deformation of a material when stress is applied. Higher loads derive in plastic deformation or even failure of the material. Modulus of elasticity (*E*) is a measurement of rigidity, the stiffer the material, the higher the value of *E* (Askeland, et al., 2010).

Although three moduli of elasticity can be measured in wood (along the longitudinal, radial and tangential axes), the most commonly used one is measured across the longitudinal axis through a bending test. Values may vary both between and within species, depending mainly on moisture content and density (Kretschmann, 2010).

The modulus of rupture, or bending strength (*f*), is a widely accepted criterion for wood strength, it indicates the maximum load that a material can withstand in a bending test. However, natural characteristics of trees, such as density, moisture content, knots must be taken into consideration when assessing the actual properties and estimating the performance of wood products (Kretschmann, 2010).

Figure 2.10 shows the relationship between stress (or load) and deformation (or strain). Before stress reaches the point called *proportional limit* (PL), the linear relationship between stress and deformation is used for

the determination of the modulus of elasticity. Plastic deformation takes place after the PL, and at some point, the piece of wood will break, the stress at failure is used to calculate the bending strength.

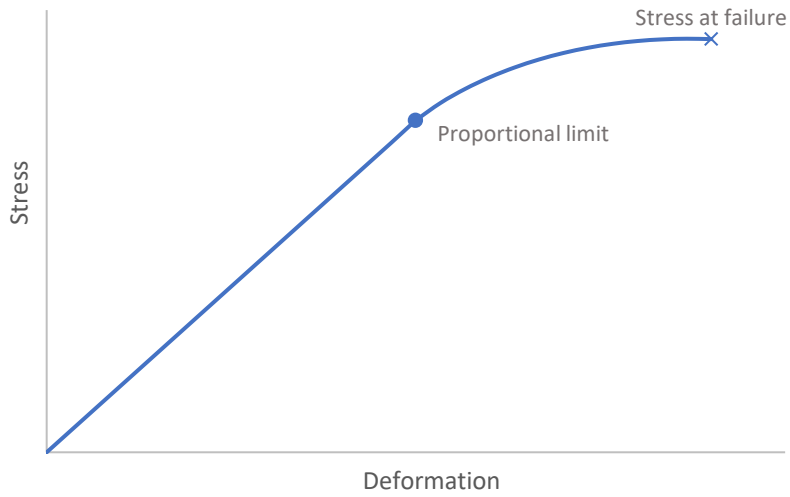

Figure 2.10. Relation between stress and deformation in a typical static bending test. Adapted from Shmulsky and Jones (2011).

The combination of components that constitutes wood has a density of around 1500 kg/m^3, regardless of wood species. However, wood cell cavities and pores account for a large portion of wood volume. Therefore, density is directly affected by the variations in the size of lumina and pores, as well as the thickness of the cell walls. Density is a good index of mechanical properties, if wood is clear, straight grained and free from defects (Kretschmann, 2010). Moreover, strength increases as wood dries below the FSP, generally peaking between 4% and 7% MC, so a reduction in MC below the usual 12% can benefit its bending strength, but overdrying might have detrimental effects on strength (Shmulsky & Jones, 2011).

2.3 WOOD MODIFICATION

As it was already mentioned, wood properties heavily depend on its chemical composition, so it is expected that changes at this very level occur when wood is modified with the aim of enhancing its properties. Nevertheless, enhancement of the material can be achieved without changes in a molecular level, thus some modifications do not necessary involve alteration of chemical composition (Hill, 2006).

The aim of wood modification is to enable the material to overcome, or at least reduce, one or more of its disadvantages. It can be to improve decay resistance or dimensional stability, reduce water uptake and so on. Therefore, the term *wood modification* can be regarded as the process in which properties of wood are altered in a way that allows the material to be fully operational during its lifetime, with no decrease in its performance (Hill, 2006).

Norimoto and Gril (1993) made a classification of the different ways in which wood can be modified (Figure 2.11). On a first level, the agent can work on the cell wall or on the lumen. On a second level, there is a distinction in the hydroxyl groups involved in the modification. Either none OH groups are chemically involved in the modification process (usually referred as impregnation) or OH groups are actively involved with the reagent (usually regarded as chemical modifications), which can be bonded to one OH group of the cell wall or cross-linked to two or more OH groups.

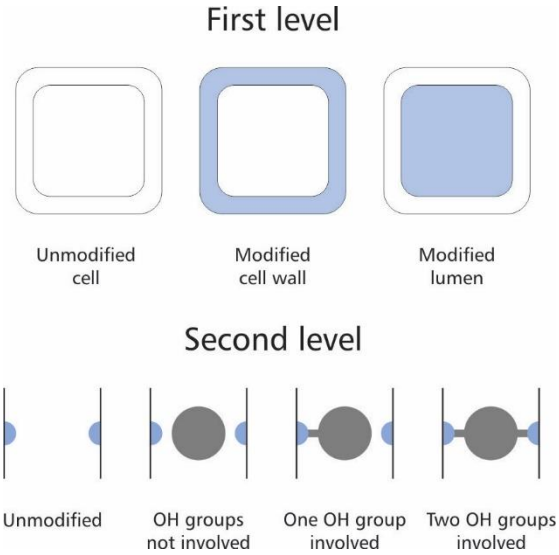

Figure 2.11. Classification of different types of wood modification at the cellular level according to Norimoto and Gril (1993). Figure adapted from Hill (2006).

2.3.1 NEED

The growing demand in the consumption of timber urges the development for new technologies to ensure the more efficient use of this resource. In this scenario, two main issues must be addressed. First, service life of timber-based products must be increased, in order to reduce the resources needed for its replacement. Second, sustainably managed plantations should increase their production (Hill, 2006).

Increasing amounts of timber are being produced with fast growing species, such as *Pinus spp*. or *Eucalyputs spp.*, where the total yield is the primary consideration for the species selection and the management methods used. The thinning regimens combined with fertilization of the soil encourages growth. However, this fast-grown wood generally presents a high proportion of juvenile wood and poorly developed heartwood, with wide growth rings that derives in a low-density timber (Hill, 2006). The usage of

this timber will need artificial protection in order to increase its potential uses (Dieste, 2014).

2.3.2 CHALLENGES

The industry of wood protection has traditionally relied on a few first-generation preservatives, which have some characteristics in common: they have a broad range of activity, low cost and long-term efficacy. Some examples are Creosote, Chromated Copper Arsenate (CCA), Oilborne Pentachlorophenol and ammonium based organic biocides (Freeman, et al., 2005).

In recent years, the wood preservation industry has been undergoing major developments. The harmful effects on human and animal health, combined with the environmental issues brought by the leaching of toxic chemicals into the environment (during its service life, but mainly after its disposal) are some of the issues that lead to the restriction or even prohibition of the usage of traditional chemicals in several countries (Peek, 2004; Helsen & Van den Bulck, 2004; Sotome & Muniz, 2004). Moreover, the market is willing to transition to more sustainable products, both by avoiding wood species that are typically sourced in a non-sustainable way and by choosing preservation methods which are more environmentally friendly during its service life and after disposal (Townsend, et al., 2005; Sandberg, 2017).

Different technologies, such as acetylation, furfulylation and thermal modification are already commercially available (Hill, 2011) and have been helping the market start its transition away from traditional preservatives.

As of 2012, the European and North American market of thermally modified wood accounted for about 415,000 m^3 (FAO, 2013), while the amount produced using the ThermoWood process accounted for around 120,000 m^3 in the same year, and has grown at an average of 10% per year to reach 209,000 m^3 in 2018 (International ThermoWood Association, 2019). Considering said growth rate, it can be estimated that the European and North American production in 2018 exceeded the 700,000 m^3. In relation to acetylated wood, Accoya, which is the main manufacturer, had a planned production of 60,000 m^3 for the year 2018. Kebony, the main manufacturer of furfurylated wood, reached a production of 22,000 m^3 in 2016 (Sandberg, 2017).

2.3.3 CHEMICAL MODIFICATION

Chemical modification of wood is the process by which a chemical reaction of a reagent occurs with the polymeric constituents of wood, resulting in a stable bond between the reagent and the cell wall polymers. In general, it can be regarded as an active modification due to the distinct changes in the cell wall molecules (Rowell, et al., 1994; Hill, 2006). As it was previously mentioned, OH groups are of great relevance when it comes to chemical modification, as they are chemically bonded to the reagent. As a result, the nature of the cell wall polymer is changed.

Currently, the aim is in using non-biocidal chemicals to modify the nature of wood. Examples of these technologies are the aforementioned acetylation of wood, where acetic anhydride is used to reduce hygroscopicity by formation of ester bonds with the OH groups of the cell wall (Rowell, 2014); or the use of 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU), which penetrates the cell wall and also reacts with OH groups (Krause, et al., 2008; Xie, et al., 2014; Emmerich, et al., 2019).

For chemical modification to take place, it is first necessary that the reagent permeates into the cell wall. However, when typical impregnation conditions are used (12 bar of maximum pressure), some species (including *Eucalyputs spp.*) present low permeability to chemicals, rendering them poorly suitable for impregnation treatments (Walker, 2006) that either derive in a chemical modification of the cell wall or not.

2.3.4 THERMAL MODIFICATION

As it was stated by Hill (2006), "*the thermal modification of wood is defined as the application of heat to wood in order to bring about a desired improvement in the performance of the material*". Based on this definition, only an increase in temperature –no chemical needed to react with the cell wall– is needed for performance enhancement, making it really appealing from a perspective of sustainability and reduction of chemical consumption.

The usage of temperature with the main objective of modifying wood properties is not new. Tiemann (1915) showed that high temperature

drying lowered EMC and consequently increased dimensional stability. Stamm and Hansen (1937) reported that hygroscopicity was reduced when wood was exposed to heat in various gases.

All current modification methods have in common a treatment temperature between 160°C and 240°C, which is greater than that of drying (80-120°C). However, they differ greatly within this range of temperatures, as well as in several other aspects, including duration of the process, initial MC of the wood, MC during treatment, treatment pressure and treatment environment (heat transferring media) (Militz & Altgen, 2014).

Both treatment temperature and time are directly related to its severity. Besides, the environment in which the process takes place can go from steam (to displace air and avoid oxidation reactions) to immersion of timber in hot oil, but the treatment can also be performed simply in air (Hill, 2006; Militz & Altgen, 2014; Syrjänen & Kangas, 2000).

2.4 THERMAL MODIFICATION TREATMENTS

Several different commercial treatments are readily available, mostly in Europe. Table 2.2 shows some of the most relevant thermal modification methods that have been developed and are currently commercially available.

Table 2.2. Thermal modification processes commercially available.

Name	Maximum temp. (°C)	Pressure	Environment
ThermoWood	185 – 230	Atmospheric	Steam
PLATO	170 – 190	High pressure	Steam and air
OHT	180 – 220	Atmospheric	Linseed oil
Retification	200 – 240	Atmospheric	Nitrogen
WTT (2.0)	160 – 210	7 – 10 bar	Steam
FirmoLin	150 – 180	4.5 – 8 bar	Steam
VACU^3	170 – 230	0.15 bar abs.	Vacuum

ThermoWood

The process called ThermoWood, patented by Viitaniemi et al. (1995) is arguably the most successful thermal modification method used to this day. It consists in a high temperature treatment in overheated steam at atmospheric pressure with less than 3% to 5% of oxygen (Syrjänen & Kangas, 2000). The process starts with a rapid increase in temperature up to 100°C, followed by a gradual increase to 130°C in order to reduce the moisture content of wood to almost zero. Afterwards, a maximum of 185°C to 230°C is reached during 2 to 3 hours, depending on the species and the desired application of the product. In the last phase, temperature is reduced in a controlled way and a moisture content of 5% to 7% is reached (Finnish ThermoWood Asociation, 2003).

PLATO

This process, developed in the Netherlands, combines an hydrothermolysis step with a dry curing step. In the first step, a temperature of 170°C to 190°C is reached in a saturated steam environment with above atmospheric pressure (Boonstra, et al., 1998). In an intermediate step, wood is dried to 10% MC with conventional procedures for 3 to 5 days. The curing consists in a second heating step in dry conditions where temperatures of 170°C to 190°C are reached for 14 to 16 hours (Militz & Altgen, 2014).

OHT – Oil Heat Treatment

This process was developed in Germany and uses linseed oil as a heating medium, which both improves heat flow into timber and displaces oxygen. Fresh or pre-dried timber can be used. Temperature is held for 2 to 4 hours in the range of 180°C to 220°C, depending on species, timber dimensions and product desired (Rapp & Sailer, 2000).

Retification

In France, several companies produce thermally modified wood with the Retifiaction-process. It is a one step process in which pre dried wood (12% MC) is heated to 200-240°C in nitrogen with less than 2% of oxygen content. The total duration ranges from 9 to 12 hours. A similar process called Balz Holz was developed in Switzerland (Militz & Altgen, 2014).

WTT – ThermoTreat 2.0

In Denmark, the company Wood Treatment Technology has developed a process in which wood is heated to 160-210°C in a pressurized autoclave with no oxygen and with little addition of steam. Pressure can reach 7 to 10 bar. High pressure treatment can shorten the treatment time and reduce the maximum temperature needed (Dagbro, et al., 2010).

FirmoLin

This process appears to be an improvement to the ThermoTreat 2.0. It uses a pressurized reactor, benefiting from the same reduction in treatment temperature and time. Peak temperature ranges from 150°C to 180°C (Willems, 2008).

VACU^3 – Vacuum Press Dewatering Method

This process, developed in Germany, uses vacuum (0.15 bar abs.), which decreases the boiling point of water, thus accelerating the drying process. Heat is transferred form heating plates just below the wood pieces (170-230°C) while pressure is being applied from the top to avoid deformation. By-products of wood degradation are removed from the system (Wetzig, et al., 2012; Hofmann, et al., 2013; Militz & Altgen, 2014). A similar process, called SmartHeat was developed in the Netherlands (Michon, 2010).

2.5 EFFECTS OF THERMAL MODIFICATION IN WOOD

As it was shown by the wide variety of modification processes mentioned, it is evident that many alternatives are available for the enhancement of wood properties. The exact method used can have significant effects upon the properties of the final product. Variables such as time, temperature and treatment atmosphere are regarded to be the most relevant ones. However, other characteristics of the system can produce very different outcomes, some examples are closed or open, wet or dry, dimensions of the timber and specie being treated, or even the usage of catalysts (Hill, 2006).

This section will describe the changes observed in chemical, physical, mechanical and other properties due to thermal modification.

2.5.1 CHEMICAL PROPERTIES

Chemical composition of wood starts to be affected at temperatures of 120°C (Kollmann, et al., 1969). There are several reactions that take place simultaneously and affect the different components of wood. The chemical changes that thermal modification induces on each of the cell wall constituents are discussed in this section and summarized in Table 2.3.

Table 2.3. Chemical changes on the different constituents of Wood.

Constituent	Effect of thermal modification
Hemicelluloses	Cleavage of acetyl groups Depolymerization Dehydration
Cellulose	Increase in crystallinity Reduction of DP
Lignin	Condensation and cross-linking reactions Structural changes
Extractives	Emission of volatile organic compounds (VOCs) Formation of new compounds

Chemical changes are strongly dependent on treatment temperature. At lower temperatures (120-150°C), wood dries by losing both its free and bound water, and mild degradation starts to occur. When heated to 180-250°C, most of the desired chemical changes take place, among some undesired ones. When heated above 250°C, important degradation occurs, with heavy carbonization and CO_2 formation, as well as other pyrolysis products (Esteves & Pereira, 2009).

2.5.1.1 HEMICELLULOSES

Hemicelluloses are the first macro-component to be affected by thermal treatment, changes can be observed even at relatively low temperatures and degradation increases with temperature and time of heating exposure (Hill, 2006). There is good stability when heated up to 100°C for 48 hours (Fengel & Wegener, 1989). Between 100°C and 150°C, the holocellulose content (the sum of cellulose and hemicelluloses)

decreases while cellulose content remains unchanged (although changes in DP can be observed), thus hemicelluloses are the component being degraded (Fengel & Wegener, 1989; Hill, 2006).

Figure 2.12 shows a probable thermal degradation pathway for hemicelluloses. It starts with the cleavage of acetyl groups linked as an ester group to the hemicelluloses, which derives in the formation of acetic acid, which then catalyzes the further degradation of hemicellulose (Carrasco & Roy, 1992; Tjeerdsma, et al., 1998; Sivonen, et al., 2002; Nuopponen, et al., 2005). Besides acetic acid, formic acid and other organic acids are formed (Sundqvist, et al., 2006), as well as methanol. The polymer chain of hemicelluloses is hydrolyzed and monomers and oligomers are formed, which in turn degrade to produce furfural, 5-hydroxymethylfurfural (HMF), formaldehyde and other aldehydes (Tjeerdsma, et al., 1998; Garrote, et al., 1999). Furfural and HMF are products of the degradation of pentoses and hexoses, respectively (Nuopponen, et al., 2005; Peters, et al., 2009; Kotilainen, et al., 2000). In turn, both furans continue its degradation pathway, forming levunillic acid, pyromucic acid, γ-hydroxyvaleric acid, γ-valerolactone and furan, among several other degradation compounds (Fengel & Wegener, 1989). Sugars can degrade directly to organic acids without necessarily forming furfural or HMF first.

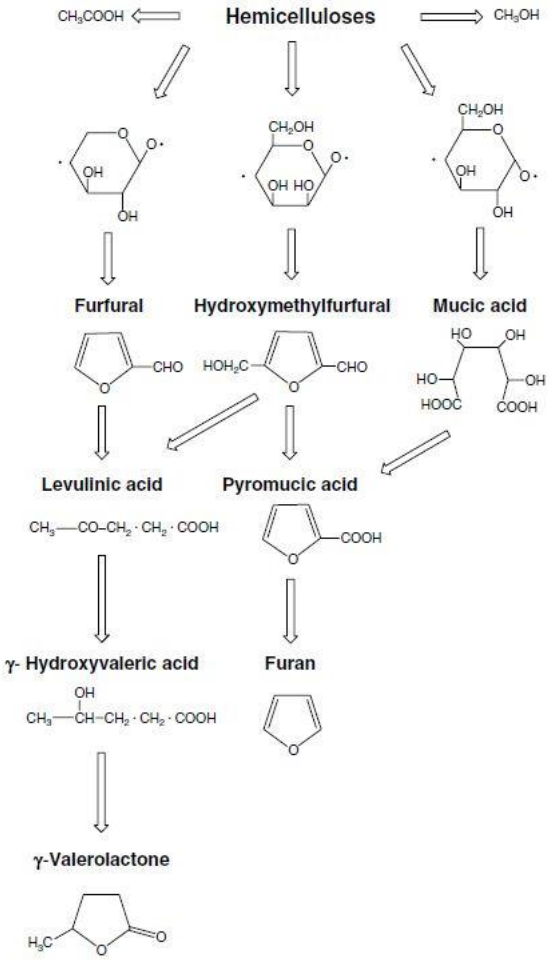

Figure 2.12. Probable pathway for thermal degradation of hemicelluloses proposed by Fengel and Wegener (1989). Figure adapted from Hill (2006).

As previously mentioned, acetyl content in hemicelluloses is dependent on wood species, and hardwoods tend to have more acetyl groups than softwoods (Sixta, 2006; Hill, 2006). Therefore, hemicelluloses degradation of the former is expected to be more catalyzed than the degradation of the latter.

Although it is accepted that hemicelluloses degrade at temperatures above 100°C, the exact temperature for the onset of said degradation is not well defined. Type of hemicelluloses seems to play a relevant role. The

lower thermal stability of hardwood versus softwood hemicelluloses has been well studied. Ramiah and Goring (1967) found that softwood hemicelluloses were more stable than hardwood xylan. Also, by Differential Thermal Analysis (DTA), xylan showed an endotherm onset at 180°C, while glucomannan presented it at a higher temperature (Beall, 1969). Moreover, recent studies with commercial hemicelluloses reported xylan to be thermally less stable than galactomannan or glucomannan (Werner, et al., 2014).

When taking into account the atmosphere in which hemicelluloses were tested, samples started to show degradation endotherms at lower temperatures and exposed higher degradation rates when heated in air, in comparison to samples tested in nitrogen (Beall, 1969).

As stated before, water-accessible OH groups from the polymeric cell wall are primarily found in hemicelluloses and are responsible for the take-up of moisture, leading to both dimensional instability and a more suitable environment for microbiological attack (Hill, 2006). During thermal modification, hemicelluloses suffer dehydration reactions due to loss of OH groups (Weiland & Guyonnet, 2003), which in turn derives in a reduction of EMC, leading to an increase in both dimensional stability and resistance against microbiological attack.

Because of the many thermal modification processes and the vast variety of species used for this purpose, as well as the focus on

technological properties rather than chemical composition of the final product, it is hard to come up with a general range to which hemicelluloses are degraded. Nonetheless, several studies have been performed, some including Eucalypt and Pine species. Table 2.4 shows the holocellulose content of different species of both Eucalypt and Pine that underwent thermal modification. In all cases, holocellulose content was reduced due to thermal modification, and in each study, an increase in temperature, while maintaining the other conditions unchanged, lead to a reduction in holocellulose content.

Table 2.4. Holocellulose content of Eucalypt and Pine species before and after thermal modification.

Species	**Temperature (°C)**	**Holocellulose content (%)**		**Reference**
		Before treatment	After treatment	
Eucalyptus nitens	180	75.7	67.3	(Wentzel, et al., 2019)
	200		62.9	
	220		62.0	
Eucalyptus grandis	160	69.4	53.4	(Batista, et al., 2016)
	180		52.8	
Eucalyptus saligna	160	67.9	64.68	(Brito, et al., 2008)
	180		62.17	
Pinus sylvestris	185	81.0	67.2	(Boonstra & Tjeerdsma, 2006)
Pinos caribaea	160	69.49	67.46	(Brito, et al., 2008)
	180		64.46	

In the case of *E. nitens,* the process was performed inside a treatment vessel where steam displaced air in an open system. In this study, the same species was modified in a closed system with high pressure and relative humidity of 30% and 100%, showing heavy hemicelluloses

degradation (76% of hemicelluloses degradation at 160°C and 100% RH) than in the open system (Wentzel, et al., 2019). Batista et al. (2016) performed the modification in an 8-hour staged process at atmospheric pressure, where steam was also used as the masking gas. Brito et al. (2008) modified both species in the presence of air in a 9-hour process where peak temperature was held for 1 hour. Finally, Boonstra and Tjeerdsma (2006) used a high-pressure process, which might explain the higher degradation of holocellulose.

2.5.1.2 CELLULOSE

It is widely accepted that the degradation of cellulose occurs at higher temperatures than that of hemicelluloses (Fengel, 1966; 1967; Tjeerdsma, et al., 1998; Tjeerdsma & Militz, 2005), though some minor changes are expected to take place at low temperatures, mainly to the amorphous regions, as these are expected to have a similar behavior as that of the chains of hexoses in hemicelluloses. This selective cleavage of amorphous cellulose increases its crystallinity, which further contributes to the reduction of water-accessible OH groups and a consequent reduction in EMC (Bhuiyan & Hirai, 2000; Bhuiyan, et al., 2001; Sivonen, et al., 2002; Wikberg & Maunu, 2004; Bhuiyan & Hirai, 2005; Boonstra & Tjeerdsma, 2006; Hill, 2006). Also, a reduction of the DP has been reported to take place at temperatures as low as 120°C (Fengel & Wegener, 1989) or 150°C (Shafizadeh, 1984). Crystalline cellulose, on the other hand, starts its degradation at temperatures between 300°C and 340°C (Kim, et al., 2001).

The presence of water protects cellulose from degrading, probably due to the capability of the amorphous cellulose to adopt more thermally stable structures that allows it to withstand higher temperatures (Fengel & Wegener, 1989).

Thermal modification in presence of air results in oxidation of the OH groups, producing carboxylic and carbonyl groups. To a minor extent, the heating of wood in nitrogen derives in the formation of carbonyl groups. Those groups are associated with a yellowing of the material. Also, CO and CO_2 are formed at temperatures above 170°C, not only when heating is carried out in air, but also in nitrogen, though yields are higher when oxygen is present (Shafizadeh, 1984).

2.5.1.3 LIGNIN

Lignin is generally regarded as the most thermally stable macro-component of wood (Hill, 2006), leading to an increase in its relative content in thermally modified wood (Kollmann & Fengel, 1965; Tjeerdsma & Militz, 2005; Esteves & Pereira, 2009). However, chemical changes are expected to occur even at relatively low temperatures (Sandermann & Augustin, 1964; Windeisen, et al., 2007). The study of isolated lignin by DTA in helium showed endotherm reactions extending from 50°C to 200°C. It was proposed that endotherms were a result of molecular rearrangement rather than loss of moisture. The main exotherms appeared only above 220°C and heavy decomposition did not start until temperatures of 280°C were reached (Nassar & MacKay, 1984).

Lignin from thermally treated beech at 230°C showed both de-polymerization and re-condensation reactions. Said condensation reactions affecting mainly guaiacyl (G) units rather than syringyl (S), with both furfural and HMF effectively acting as crosslinkers between two aromatic rings (Brosse, et al., 2010). The higher proportion of G units involved in these reactions suggests that the guaiacyl-rich softwood lignin is more prone to crosslinking reactions than hardwood lignin.

2.5.1.4 EXTRACTIVES

It is expected for the extractives of wood to either volatilize or be degraded when it is thermally modified, and degradation products to diffuse out of the wood during treatment (Esteves, et al., 2008; Poncsák, et al., 2006).

The emissions of volatile organic compounds (VOCs) of thermally modified Scots pine at 230°C for 24 hours in steam showed that, while emissions of terpenoids, a common wood extractive, were significantly reduced (from more than 70% to less than 10%), acetic acid and some furans (mainly furfural), which are products of cell wall breakdown and were absent in air-dried wood, were present in relatively high quantities (more than 20% each) (Manninen, et al., 2002).

Esteves (2008) showed that, even though some of the common extractives almost disappeared from Eucalypt wood when heated at 190°C and 200°C in steam and air (e.g. Glycerol, Palmitic acid), extractive content

increased due to thermal modification, in some cases even doubling that of the unmodified reference. This effect was due to the increase of water and ethanol extractives resulting from polysaccharide degradation.

2.5.2 PHYSICAL PROPERTIES

Thermal modification directly affects the mass, volume and density of wood, as well as its microstructure and hygroscopicity. This section discusses the changes in physical properties that wood undergoes due to thermal modification and their relationship with the changes taking place at a cellular level, both physical and chemical.

2.5.2.1 CHANGES IN MASS AND VOLUME

When wood is heated, its weight decreases, first, due to loss of moisture content and volatile extractives. Then, as temperature increases, the macromolecular components start to suffer chemical changes, depolymerization of cell wall constituents takes place, leading to the formation of organic acids and furans, which contribute to further degradation and reduction of weight (Fengel, 1966; Alén, et al., 2002).

Mass loss is arguably the most comprehensive parameter for the severity of the thermal modification process, as it strongly correlates with changes in several of the properties of wood after treatment (Metsä-Kortelainen, et al., 2006; Brischke, et al., 2007; Welzbacher, et al., 2007; Seborg, et al., 1953). Table 2.5 shows the effect that different parameters have on mass loss. Presence of oxygen, closed systems and wet conditions

are associated with higher mass loss (Hill, 2006; Chaouch, et al., 2013; Altgen & Militz, 2016; Bal, 2018; Wentzel, et al., 2019).

Also, differences have been found between species, but mostly between softwoods and hardwoods, as hardwoods species tend to present higher weight losses than softwood species when subjected to the same process (MacLean, 1954; Zaman, et al., 2000; Militz, 2002).

Table 2.5. Variables affecting weight loss (Hill, 2006).

Lower rate of mass loss	Higher rate of mass loss
Inert atmosphere (no oxygen)	Presence of oxygen
Open system	Closed system
Dry conditions	Wet conditions
Softwoods	Hardwoods

Esteves et al. (2008) studied the mass loss of Brazilian *Pinus pinaster* modified in air at 170°C to 200°C for times ranging from 2 hours to 24 hours, finding that mass loss increases both with treatment temperature and time (Figure 2.13). Temperature appears to be a more influencing parameter than treatment time. Similar results were obtained as early as 1972 (Millet & Gerhards), although lower temperatures were tested and time of exposure elapsed up to more than 200 days.

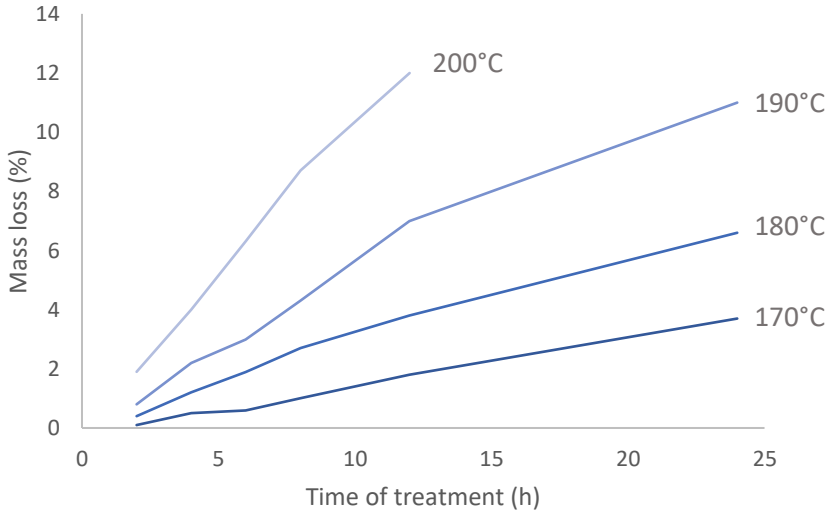

Figure 2.13. Relationship between mass loss and treatment time of thermally modified Pinus pinaster*. Adapted from Esteves et al. (2008).*

Apart from the loss of mass that was just described, a reduction in volume occurs with the modification. Some studies on *Eucalyptus grandis* suggest that the reduction in mass and volume are approximately of the same magnitude, which means that density will stay relatively unchanged after treatment (Batista, et al., 2011; Calonego, et al., 2012). In the case of Pine, although different species and different conditions show varying results, the general tendency is to see a slight decrease in density (Bal, 2018; Korkut & Hiziroglu, 2014; Rautkari, et al., 2014), meaning that, when thermally modified, volume is less affected than weight.

2.5.2.2 POROSITY

Due to the high temperatures that take place during thermal modification, the anatomy of the cell wall and the lumen are affected, which has a direct effect on the porosity and the pore size distribution of thermally modified wood. Zauer et al. (2014) studied the porosity and the pore size

distribution of Norway spruce, Sycamore maple and European ash treated at 200°C for 4 hours in nitrogen, finding a reduction in the total pore volume due to thermal modification in all species. Apart from the shrinkage of the cell wall, the flowing of lignin in the cell wall pores is thought to be one of the reasons for the reduction in total pore volume, as lignin softens when heated and then becomes rigid again when temperature decreases.

2.5.2.3 HYGROSCOPICITY

The decrease of the EMC is one of the most relevant consequences of the thermal modification of wood. As it has been said before, Tiemann (1915) already showed that the drying of timber at high temperatures reduces its absorption of water, and because of the relevance that the wood-water relationship has in properties like dimensional stability and decay resistance, it has been vastly studied (Seborg, et al., 1953; Tjeerdsma, et al., 1998; Kamdem, et al., 2002; Jalaludin, et al., 2010).

One of the reasons for the lower hygroscopicity of thermally modified wood is the reduction of the OH groups due to degradation of hemicelluloses. Also, the increase in crystallinity of cellulose further contributes to the reduction of water-accessible OH groups, as those hydroxyl groups located in the amorphous regions of cellulose are more accessible for water than those of the crystalline region. Nonetheless, it is insufficient to explain the reduction of hygroscopicity just by the changes in chemical composition, the reduction in the total pore volume explained

above, further contributes to the reduction of wood's capability to take up water (Zauer, et al., 2014).

Recently, several studies have started to show evidence of reversibility in wood's reduction of hygroscopicity due to thermal modification (Hill, et al., 2012; Altgen & Militz, 2016; Wentzel, et al., 2018). This fact should not be overlooked, as it might lead to underestimation of water uptake of the product during service. It has been proposed that the drying of wood at temperatures beyond the softening point of the amorphous matrix polymers results in residual stresses in the cell wall after it is cooled to room temperature, which can be reversed by the exposure of thermally modified wood to high moisture environments, or soaked in water (Altgen & Militz, 2016; Endo, et al., 2016; Wentzel, et al., 2018).

Besides the reversible effects due to high temperature drying, the presence of degradation products in thermally modified wood after the process may also be responsible for further reversibility of hygroscopicity reduction. As it has been explained before, thermally modified wood usually presents more extractive content than that of unmodified wood, and this is explained by the degradation products, mainly carboxylic acids and furans, that stay in the wood after the process is finished. When hygroscopicity of unextracted thermally modified wood is tested, those remaining compounds may occupy the different pores in wood, having a similar effect to that of the bulking of chemical modification or impregnation agents (Rowell & Ellis, 1978; Hill & Jones, 1996).

Wentzel (2018) has demonstrated that EMC of Chilean *Eucalyputs nitens* at 20°C and 65% RH increases after 4 cycles of soaking wood in water for two weeks, while its dry weight decreases, presumably due to extractives leaching out. Figure 2.14 illustrates the effect of said water soaking cycles.

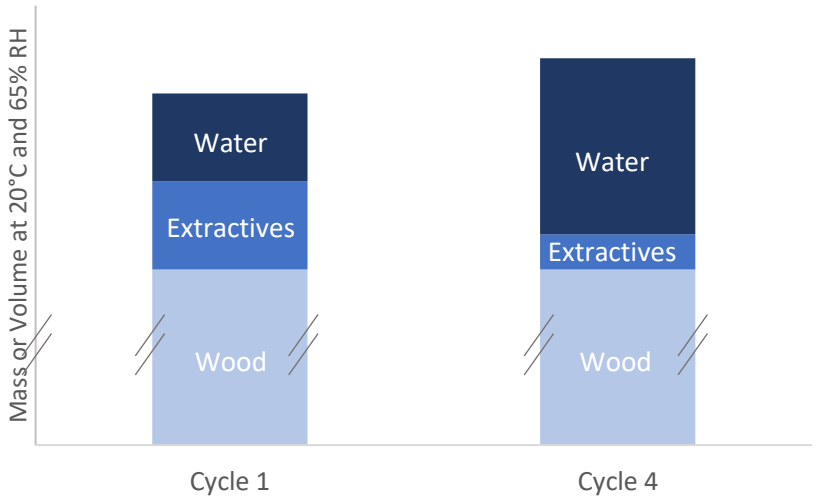

Figure 2.14. Water and extractive content of wood at 20°C and 65% RH before the first and after the fourth water soaking cycle. Adapted from Wentzel et al. (2018).

In that study, Wentzel showed that modification in open systems (atmospheric pressure) where air is displaced with steam, dry mass reached a reduction of around 4% in samples modified at 180°C, while in those modified at 230°C said reduction accounted for around 1%. Interestingly, EMC at 20°C and 65% RH showed an opposite behavior, it increased up to 4% in samples modified at 230°C and less than 2% in those modified at 180°C, indicating more reversibility in samples modified at higher temperatures. Probably, effects due to high temperature drying are greater in said samples. This can be backed up by the fact that, in the same study,

samples modified in a closed system at 100% RH, thus never being under the effects of high temperature drying, did not present any increase in its EMC after the water soaking cycles.

2.5.2.4 MOISTURE SOPRTION AND DESORPTION

Reduction in EMC at different RH contents in the environment lead to a change in the sorption and desorption curves. The effect that thermal modification has on EMC has been studied for different species. Samples of Poplar and European beech modified at 220°C in steam showed a reduction in EMC at 20°C and 95% RH from around 28% to less than 15% (Olek, et al., 2013). At the same moisture and temperature conditions, Scots pine heated to 200°C presented an EMC of 17% and 15% for non-densified and previously densified samples, respectively, while the unmodified reference presented an EMC of 25% (Hill, et al., 2012). Finally, Wentzel et al. (2018) found that the EMC of *Eucalyptus nitens* samples that underwent thermal modification at 210°C in an open system filled with steam decreased from around 23% to less than 10% at 20°C and 95% RH. However, said low value was not due to permanent changes, as after four water-soaking cycles it increased back to around 15%.

2.5.2.5 DIMENSIONAL STABILITY

Early on, Seborg et al. (1953) studied the enhancement in dimensional stability of *Pinus ponderosa* heated to 300°C for up to 4 hours in different conditions, finding a maximum at a mass loss of around 20% (treatment of around 30 minutes). Treatment conditions were relevant, as

samples heated in air presented a reduction in their dimensional stability when mass loss increased over 20%, while samples heated in nitrogen did not. Nonetheless, the temperature in this study was higher than that currently used for thermal modification.

Esteves et al. (2007) studied the dimensional stability of *Pinus pinaster* and *Eucalyptus globulus* thermally modified at temperatures from 190°C to 210°C for 2 to 12 hours. In all cases, thermally modified samples presented better dimensional stability than that of the untreated references, with better results found in Eucalypt than in Pine. For instance, when comparing the increase in dimensions of oven dry samples and samples that reached EMC at 35% RH, the increase was 3.4% and 2.4% for untreated *E. globulus* and *P. pinaster*, respectively. After thermal modification at 210°C for 12 hours, swelling was reduced to 0.8% for *E. globulus* and 1.1% in the case of *P. pinaster*. Also, a strong correlation was found between mass loss and the increase in dimensional stability in both species.

Besides reduction in water-accessible OH groups that lower the EMC, another probable reason for dimensional stability enhancement is the previously discussed condensation of lignin due to cross-linking reactions, with the subsequent increased rigidity.

2.5.3 MECHANICAL PROPERTIES

It has been known for several years that the heating of wood at high temperatures derives in a reduction of mechanical properties, mainly strength (MacLean, 1954). Similarly to the behavior regarding mass loss (Table 2.5), loss of strength is greater in closed systems as well as in the presence of oxygen (MacLean, 1954; Stamm, 1956), and hardwoods exhibit higher strength losses than softwoods when modified under the same conditions. The fact that the same parameters responsible for higher rates of mass loss are responsible for higher strength loss indicates the correlation between these two properties.

It is possible to study the changes of mechanical properties of wood by measuring various properties. Yet, this work will focus on the study of the modulus of elasticity (*E*) and the bending strength (*f*).

Figure 2.15 shows the effect on the modulus of elasticity and bending strength of different thermal modification processes performed on Eucalypt wood. The study of the mechanical properties of thermally modified Chilean *Eucalyptus nitens* in an open system where steam displaced air inside the reactor showed an increase in the modulus of elasticity from the lower temperature (160°C) until 200°C, always presenting a higher *E* from that of the reference, followed by a decrease starting at 210°C and reaching the lowest *E* at 230°C. Nevertheless, no statistical analysis was performed, thus it is not possible to know if these variations are statistically significant. Bending strength presented similar results, an

increase at lower temperatures (160°C and 180°C), followed by a decrease, also starting at 210°C and reaching a reduction of 26% at 230°C (Wentzel, et al., 2019). Calonego et al. (2012) chose a non-inert environment for the thermal treatment of Brazilian *Eucalyptus grandis* at temperatures from 140°C to 220°C for 2.5 hours. In the case of the bending strength, it was reduced 24% and 52.3% when comparing untreated wood against samples modified at 180°C and 220°C, respectively. However, modulus of elasticity did not present significant changes, being reduced only 8.4% when modified at 220°C. Similar results were obtained by De Cademartori et al. (2015) with Brazilian *Eucalyptus grandis* modified in similar conditions (4 hours in air), with non-statistically significant differences in modulus of elasticity and a reduction in bending strength of 39% and 49% when comparing the unmodified sample with the ones subjected to temperatures of 220°C and 240°C, respectively.

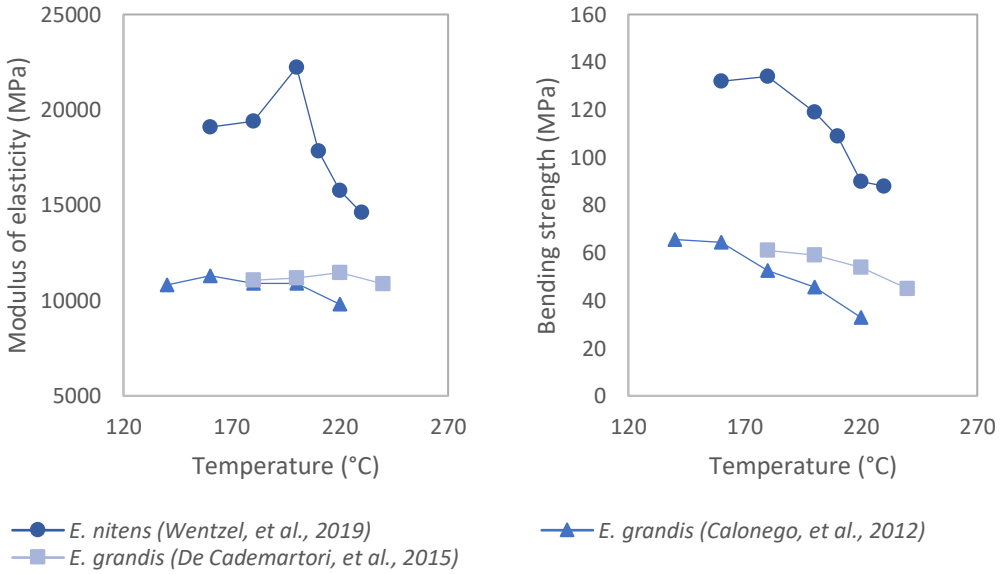

Figure 2.15. Effect on modulus of elasticity and bending strength of different thermal modification processes on Eucalypt wood.

When it comes to Pine, results appear to be similar to those of *Eucalyptus* just discussed. Already in 1987, a study of the mechanical properties of thermally modified North American *Pinus taeda* was carried out (Mitchell). Although it was performed in a closed system with high pressure and treatment temperature was relatively low (150°C), the reduction in bending strength was similar in the three heating environments (oxygen, nitrogen and air) for samples treated with an initial moisture content of around 12%, meaning that, at least in said conditions, presence of oxygen (even an atmosphere filled with oxygen) did not lead to a lower *f*. However, oven-dry samples showed a much higher decrease on its bending strength (maximum decrease of 19%) than samples treated in nitrogen and air, which did not present a big difference from each other, nor with the reference.

Figure 2.16 shows the results of a comprehensive study done on Turkish *Pinus nigra* modified in air, vacuum and nitrogen for 2.5 hours, in which modulus of elasticity only presented statistically significant differences at modification temperatures of 220°C, and those processes performed in inert atmosphere (vacuum and nitrogen) were similar to each other, and different to those of the unmodified reference and the one heated in the presence of oxygen. On the other hand, bending strength was clearly reduced at temperatures of 200°C and 220°C when compared against the reference, regardless of the heating medium (Bal, 2018).

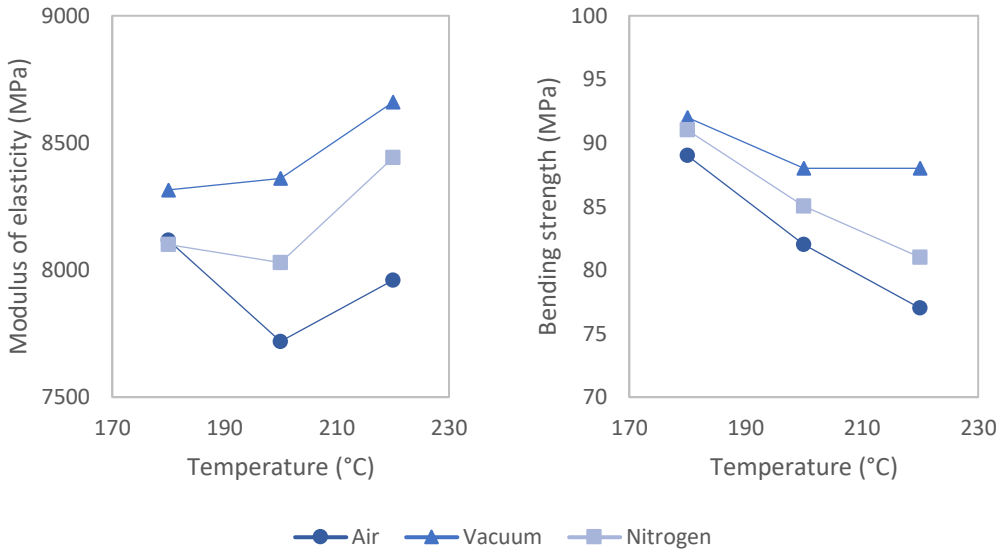

Figure 2.16. Effect on modulus of elasticity and bending strength of different thermal modification processes on Pinus nigra *wood. Adapted from Bal et al (2018).*

2.5.4 DURABILITY

The increase in the resistance of thermally modified wood against decay has been widely studied (Boonstra, et al., 2007; Hakkou, et al., 2006; Kamdem, et al., 2002). However, the actual result is heavily dependent on the species, the type of fungus (or insect) and the process conditions (Militz & Altgen, 2014). The mechanism behind decay resistance improvement has not been well stablished yet, but it is undoubtedly linked to the polysaccharide degradation, as well as the reduction in the MC of the cell wall. The reduction of OH groups may also affect the proper functioning of enzymes in the metabolization of the substrate. Also, the biocidal products formed and retain in wood due to degradation should be considered (Hill, 2006).

A comprehensive study subjected wood modified with four industrial thermal modification process (including the previously explained PLATO and OHT) to laboratory test and field test both above ground and in soil contact, reporting that all thermally modified materials showed a significant improvement in its natural durability in lab and above ground field tests. However, thermally modified samples in contact with the ground where regarded as not durable or slightly durable (Welzbacher, et al., 2007). Similar results have been obtained for *Eucalyptus grandis* in lab tests, where heat treatment at 220°C in air lead to a decrease in mass loss due to fungal attack by *Pycnoporus sanguineus* of 82% (Calonego, et al., 2010). Also, above ground field tests of Scots pine (*Pinus sylvestris*) and Norway spruce (*Picea abies*) modified by the ThermoWood Process proved that, while both white- and brown-rot fungi heavily attacked untreated boards after 9 years of exposure, thermal modification improved substantially the fungal durability of both wood species (Metsä-Kortelainen, et al., 2011).

Because of the strong correlation that treatment temperature has both with durability and chemical degradation of the cell wall polymers, it has been proposed that chemical changes of wood are the most plausible hypothesis to explain the improvement in decay resistance. Apart from the heavy degradation of hemicelluloses, which are regarded as an important nutritive source for wood rotting fungi, modification of the lignin network should be considered influential as well, due to the increase in resistance against white rot fungi (Hakkou, et al., 2006).

In relation to termite attack, a non-choice feeding test showed that modified wood of *Pinus pinaster* was highly degraded (Surini, et al., 2012). It has been reported that thermal modification can make wood less durable against termites, supposedly due to removal of some termite inhibiting compounds (Shi, et al., 2007).

2.5.5 OTHER PROPERTIES

2.5.5.1 COLOR

A noticeable darkening of the wood occurs due to thermal modification, with changes in color being related to the treatment intensity, becoming darker with the increase of temperature and duration of the process (Militz & Altgen, 2014). Darkening has even been proposed as a possible parameter to measure treatment intensity and predict mass loss due to thermal modification (Brischke, et al., 2007). With time, wood color becomes gray, either after natural or artificial weathering, as the surface is not stable against UV light (Jämsä, et al., 2000; Huang, et al., 2012).

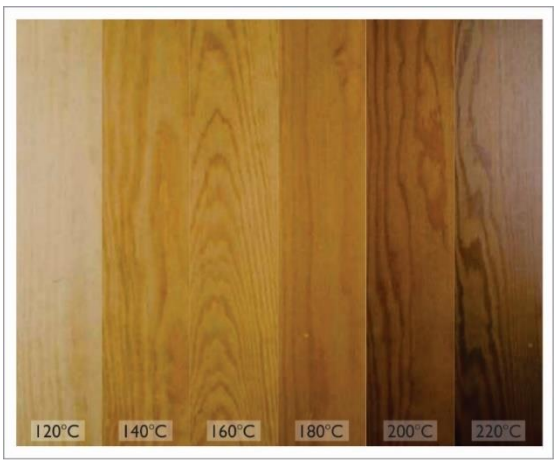

Figure 2.17. Color of thermally modified Pine from 120°C to 220°C (Finnish ThermoWood Asociation, 2003).

2.5.5.2 THERMAL CONDUCTIVITY

Lower thermal conductivity of heat-treated wood when compared against an unmodified reference was reported, generally decreasing with the increase of treatment temperature or time (Finnish ThermoWood Asociation, 2003; Pásztory, et al., 2017). This can represent an advantage in applications where modified wood is located between an interior and an exterior environment, such as doors, windows or even facade cladding.

2.5.5.3 BEHAVIOR WITH ADHESIVES

Thermally modified wood can be glued with many industrial adhesives (e.g. Polyvinyl alcohol, polyurethane, isocyanate and resorcinol-phenolic glues). However, lower shear strength and tension strength perpendicular to grain lead to higher wood failure. Moreover, the more hydrophobic surface of thermally modified wood causes lower penetration of the solvent into the wood (Militz & Altgen, 2014). Therefore, gluing products might need some adjustment to adapt to the different properties of thermally modified wood.

2.6 USES AND APPLICATIONS

The main applications of thermally modified wood take advantage of its improved durability and dimensional stability. There is potential for both indoor and outdoor applications including uses like cladding, windows, doors, garden products, flooring and specialty products (sauna, bathrooms, etc.) (Militz, 2002; Finnish ThermoWood Asociation, 2003). A survey of the

North American market showed that thermally modified wood was used mainly in decking, siding and indoor flooring, but it also extended to components for musical instruments, moldings, doors, gunstock, fences and docks (Espinoza, et al., 2015).

3 MATERIALS AND METHODS

3.1 EXPERIMENTAL DESIGN

The experimental design is presented in Table 3.1. First, wood from *E. grandis* and *P. taeda* was subjected to thermal modification at four different temperatures that ranged from 160°C to 220°C in a controlled environment of vacuum, air or nitrogen (N_2). Mass and volume of all samples were determined before and after treatment. The temperature range and the three environments were selected taking into account the literature presented in Chapter 2 and the technology available for this work.

On a second stage, chemical composition of unmodified and thermally modified wood was assessed. Extractive content of the modified wood pieces was determined by Soxhlet extraction (Sluiter, et al., 2008) and the extractive-free wood was used to measure structural carbohydrates, and lignin by acid hydrolysis (Sluiter, et al., 2012). These experiments were carried out by the candidate at the Chemical Engineering Institute, in the Faculty of Engineering, Universidad de la República, Montevideo, Uruguay.

On a third stage, EMC and mechanical properties were measured. A three-point bending test was performed to measure modulus of elasticity and bending strength (ASTM International, 2000). These tests were

conducted in the Technological Laboratory of Uruguay (LATU), Montevideo, Uruguay.

Finally, the reversibility of changes in EMC and dimensional stability was assessed to samples of *E. grandis* modified at 200°C. This condition was selected after evaluating the changes in chemical composition presented in section 4.3. In this case, the difference in the sorption isotherms of modified samples with and without extraction of the degradation products was measured, followed by a modeling of said sorption isotherms (Hailwood & Horrobin, 1946; Skaar, 1988). Moreover, the variations in EMC at 20°C and 65% relative humidity (RH) and maximum volumetric swelling (S_{max}) were measured during successive water-soaking cycles. These tests were carried out at the Department of Wood Biology and Wood Products, in the Faculty of Forest Sciences and Forest Ecology, Georg-August Universität, Göttingen, Germany.

Table 3.1. Stages of the experimental design for the project.

Stage	Activity	Measurements
0	Acquisition of wood	Basic density
1	Thermal modification	Mass loss Volume reduction Density variation
2	Chemical composition	Extractives Lignin Structural Carbohydrates
3	EMC and Mechanical Properties	EMC Modulus of elasticity Bending strength
4	Reversibility of changes in EMC and dimensional stability	Sorption isotherm EMC and S_{max}

3.2 WOOD

Boards with a section of 25×100 mm^2 and a length of 450 mm were obtained from a local sawmill (Figure 3.1). *E. grandis* boards had an average basic density of (599 ± 48) kg/m^3. Average density of *P. taeda* boards was (447 ± 50) kg/m^3.

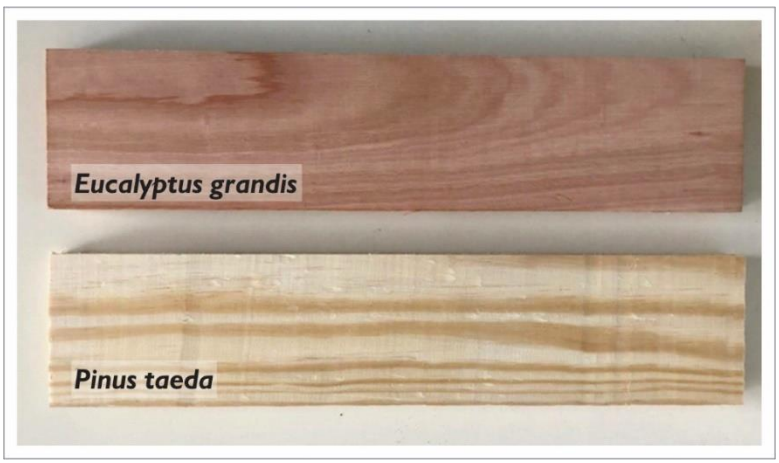

Figure 3.1. Unmodified boards of E. grandis *and* P. taeda.

3.3 MOISTURE CONTENT

Each of the boards of the dimensions mentioned above was crosscut 2 cm from its upper end immediately before registering its mass, this piece was used to determine the initial MC of each board. This was done immediately before thermal modification.

The same procedure was carried out for all boards after thermal modification. Immediately after registering the mass and the dimensions of the modified piece, a cross-section cut was made 2 cm from its upper end and that piece was used to determine MC.

The pieces of 2 cm of thickness (dimensions 20×25×100 mm^3) were weighed with an accuracy of 1 mg and placed at 105ºC until constant weight, the mass difference corresponded to the moisture content of each piece.

3.4 THERMAL MODIFICAITON

Thermal modification was carried out in a Cole Parmer vacuum oven, model G05053-22. Figure 3.2 shows a diagram of the modification system.

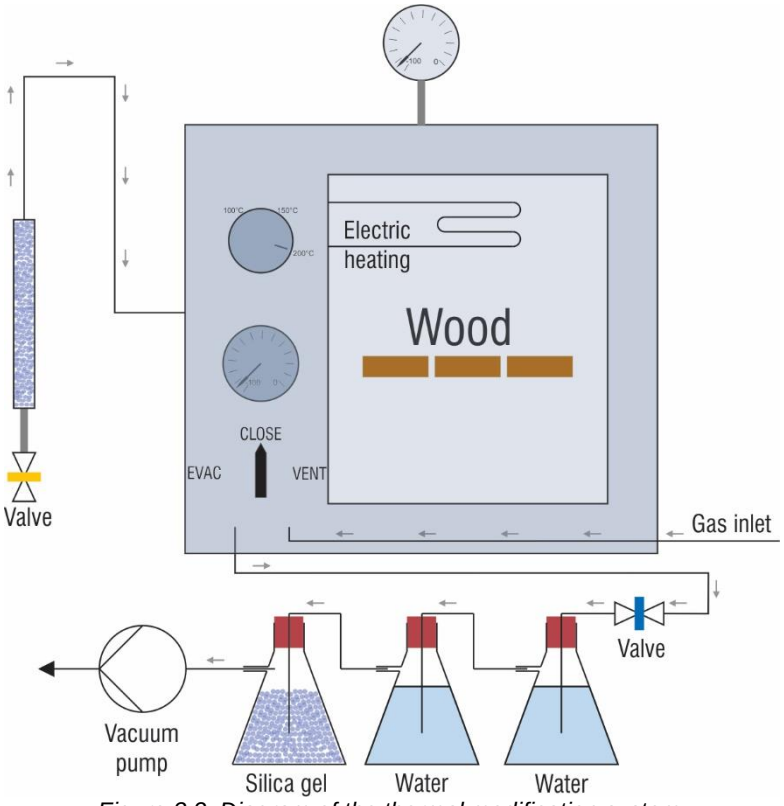

Figure 3.2. Diagram of the thermal modification system.

Table 3.2 shows the matrix of 12 different conditions tested for each specie. Four temperatures were tested, 160ºC, 180ºC, 200ºC and 220ºC, and treatment was carried out in three different environments: vacuum, air and nitrogen.

Table 3.2. Conditions for thermal modification.

Species	Environment	Temperature (ºC)
E. grandis	Vacuum	160, 180, 200, 220
	Air	160, 180, 200, 220
	Nitrogen	160, 180, 200, 220
P. taeda	Vacuum	160, 180, 200, 220
	Air	160, 180, 200, 220
	Nitrogen	160, 180, 200, 220

For each of the conditions tested, three boards of the dimensions specified in the preceding section were placed inside the treatment oven. Figure 3.3 illustrates the stages of the thermal modification process. Heating was carried out in air up to 100°C (stage I), from that temperature on, air inside the oven was replaced if the tested condition required it (vacuum or nitrogen). Vacuum treatment took place at (-85 ± 5) kPa manometric pressure and, as the equipment used was a vacuum oven, air and nitrogen treatments were performed at a manometric pressure of (-12.5 ± 2.5) kPa to guarantee optimal sealing. When the desired peak temperature was reached (end of stage II), it was kept constant for 3 hours (stage III). After the modification time had elapsed, samples were allowed to cool inside the oven without changing the treatment environment until room temperature was reached (stage IV).

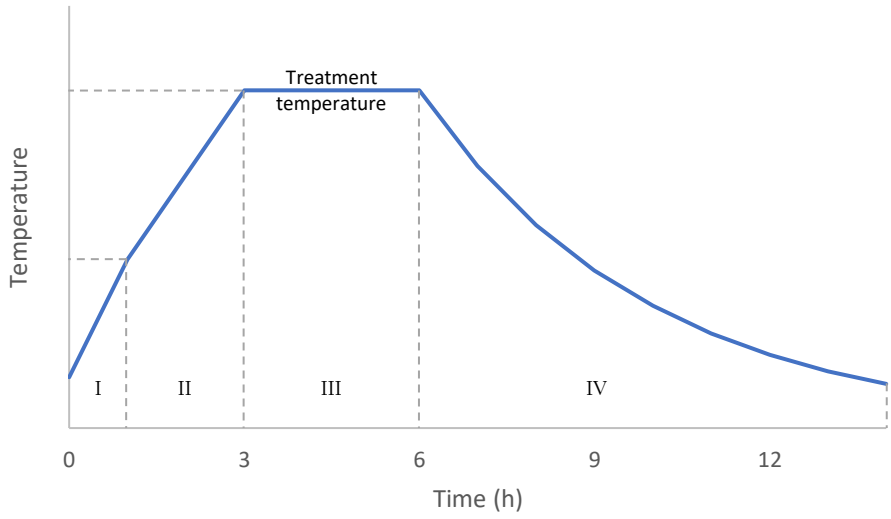

Figure 3.3. Diagram of the stages of the thermal modification process. I - First heating stage in air. II - Second heating stage in corresponding treatment environment. III - Stage at peak temperature. IV - Cooling stage.

3.5 MASS LOSS

Mass loss (ML, calculated as percentage) was calculated using the dry weight of each board before and after treatment. The calculation was made according to the following equation:

$$ML = \frac{(m_1 - m_2)}{m_1} \cdot 100 \qquad \textit{Eq. 3.1}$$

Where m_1 is the dry weight of the board before treatment and m_2 is the dry weight of the same board after treatment, both in grams.

3.6 VOLUME REDUCTION

Volume was measured to each board immediately before and immediately after thermal modification. Each of the dimensions (width, thickness and length) was recorded to the nearest 0.1 mm.

Volume reduction (VR) was calculated as the percentage difference of the board dimensions before and after modification, according to the following equation:

$$VR = \frac{(v_1 - v_2)}{v_1} \cdot 100 \qquad \textit{Eq. 3.2}$$

Where v_1 is the volume of the board before treatment and v_2 is the volume of the same board after treatment, both in mm^3.

3.7 DENSITY AND DENSITY VARIATION

Having recorded the mass and volume of each board before and after modification, it was possible to calculate the density of each board in both stages. Then, it was also possible to calculate the density variation (DV) as the percentage difference of the board density before and after modification, according to the following equation:

$$DV = \frac{(d_1 - d_2)}{d_1} \cdot 100 \qquad \textit{Eq. 3.3}$$

Where d_1 is the density of the board before treatment and d_2 is the density of the same board after treatment, both in kg/m^3. In all cases, density was calculated using the weight and dimensions of the boards in dry state.

3.8 EXTRACTIVE CONTENT

Extractives were determined by Soxhlet method, according to the technical report NREL/TP-510-42619 (Sluiter, et al., 2008). Samples of treated wood were milled to a particle size between 0.17 mm and 0.84 mm. Around 8 grams of milled sample (weight recorded to the nearest 0.1 mg) were inserted into a thimble, which was then put into a Soxhlet tube. Samples were extracted for 6 hours with distilled water, followed by 6 hours with Ethanol. Extractive content was then determined by the difference in dry weight of the boiling flask before extraction and after extraction (and evaporation of solvent). Water extractive content ($Extractives_{water}$), ethanol extractive content ($Extractives_{ethanol}$) and total extractives

($Total\ Extractives$) were calculated in grams per 100 grams of dry wood according to equations 3.4, 3.5 and 3.6, respectively.

$$Extractives_{water} = \frac{(W_{flask\ a.e.\ water} - W_{flask\ b.e.\ water})}{W_{wood}} \cdot 100 \qquad Eq.\ 3.4$$

Where $W_{flask\ b.e.\ water}$ is the dry weight of the boiling flask before extraction with water, $W_{flask\ a.e.\ water}$ is the dry weight of the boiling flask after extraction with water and W_{wood} is the dry weight of the wood used for extractive determination, all in grams.

$$Extractives_{ethanol} = \frac{(W_{flask\ a.e.\ ethanol} - W_{flask\ b.e.\ ethanol})}{W_{wood}} \cdot 100 \qquad Eq.\ 3.5$$

Where $W_{flask\ b.e.\ ethanol}$ is the dry weight of the boiling flask before extraction with ethanol, $W_{flask\ a.e.\ ethanol}$ is the dry weight of the boiling flask after extraction with ethanol and W_{wood} is the dry weight of the wood used for extractive determination, all in grams.

$$Total\ Extractives = Extractives_{water} + Extractives_{ethanol} \qquad Eq.\ 3.6$$

3.9 DETERMINATION OF STRUCTURAL CARBOHIDRATES AND LIGNIN

Structural carbohydrates and total lignin were determined to extractive-free samples of thermally modified wood according to the technical report NREL/TP-510-42618 (Sluiter, et al., 2012). Where carbohydrates and organic acids are separated form lignin through acid hydrolysis.

3.9.1 ACID HYDROLYSIS

0.3 g (recorded to the nearest 0.1 mg) of the extractive-free milled samples were weighted and placed into pressure tubes. Hydrolysis was done in two steps. First, 3 mL of 72% sulfuric acid were added to each pressure tube and they were placed in a water bath at 30ºC for one hour while regularly stirring with a glass rod. Then, 84 mL were added, and the tubes were put into an autoclave at 121ºC for one hour.

After the autoclave cycle was completed, samples were filtrated using glass filters. Each filter was dried at 105°C until constant weight, and its dry weight recorded to the nearest 0.1 mg before being used. After filtration, filters containing the insoluble fraction were dried at 105°C until constant weight, mass of solid fraction was calculated by subtracting the weight of the clean and dry filter to the weight of the dry filter containing the solid fraction.

The solid fraction represented the insoluble lignin and the liquid fraction was used to determine soluble lignin and structural carbohydrates. After filtration, the volume of the liquid fraction was made up to 0.1 L.

3.9.2 LIGNIN

The amount of insoluble lignin was calculated in grams per 100 grams of dry wood according to the following equation:

$$Insoluble\ Lignin = \frac{W_{solid\ fraction}}{m_{dry}} \cdot 100 \qquad \textit{Eq. 3.7}$$

Where $W_{solid\ fraction}$ is the dry weight of the solid fraction in grams and m_{dry} is the dry mass of the sample, also in grams.

Soluble lignin was measured to the liquid fraction by determination of its absorbance on a UV/VIS spectrophotometer (Shimadzu Corporation, Kyoto, Japan), at a wavelength of 205 nm and an absorptivity factor of 110 L/(g·cm) for *E. grandis* (Kaar & Brink, 1991) and 240 nm and absorptivity factor of 12 L/(g·cm) for *P. taeda* (Sluiter, et al., 2012). It was calculated in grams per 100 grams of dry wood as presented in the following equation:

$$Soluble\ Lignin = \frac{abs}{af} \cdot df \cdot V_{liquid\ fraction} \cdot 100 \qquad \textit{Eq. 3.8}$$

Where abs is the absorbance of the sample in AU (absorbance units), af is the absorptivity factor in L/(g·cm), df is the dilution factor used for measuring samples in the spectrophotometer, and $V_{liquid\ fraction}$ is the total volume of the liquid fraction.

3.9.3 STRUCTURAL CARBOHYDRATES

The determination of structural carbohydrates was made by High-Performance Liquid Chromatography (HPLC) separation (Shimadzu Corporation, Kyoto, Japan) equipped with a Refractive Index Detector (RID) (RID 10A, Shimadzu) and a Photodiode Array Detector (PDA) (SPD 20A, Shimadzu). The column used was a Bio-Rad Aminex HPX-87H (Bio-Rad Laboratories Inc., EEUU), temperature was set at 30°C and flow at

0.6 mL/min with H_2SO_4 0.005 M mobile phase. Results were presented in grams of sugar per 100 grams of dry wood.

3.10 EQUILIBRIUM MOISTURE CONTENT

Pieces of 20×20×50 mm^3 (tangential × radial × longitudinal) were conditioned at 20°C and 65% RH for three weeks. After that period, mass was recorded (to the nearest 1 mg) in two successive days to confirm constant weight. Afterwards, samples were oven dried at 105°C until constant weight and mass was recorded to the nearest 1 mg. EMC was calculated according to the following equation:

$$EMC = 100 \times \frac{(m_{20/65} - m_{dry})}{m_{dry}} \qquad \textit{Eq. 3.9}$$

Where $m_{20/65}$ is the weight after conditioning at 20°C and 65% RH and m_{dry} is the oven-dry weight.

3.11 MECHANICAL PROPERTIES

Modulus of Elasticity (*E*) and bending strength (*f*) were measured through a three-point bending test (Figure 3.4), using the NMB TG-50Kn press (Techno Graph, Japan) located in the Technological Laboratory of Uruguay (LATU), according to the ASTM D143-94 standard (ASTM International, 2000).

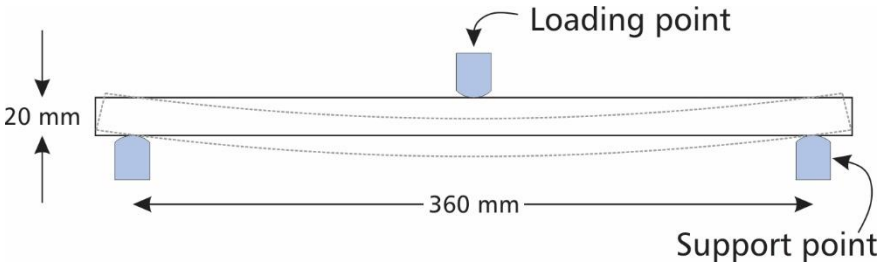

Figure 3.4. Diagram of bending test. The dotted grey line represents the strained sample after load was applied.

For this test, samples of section 20×20 mm^2 and length of at least 360 mm were used. A total of 9 samples per condition were tested. Before bending tests was performed, all samples were conditioned at 20°C and 65% RH.

For the bending test, the distance between the two support points was 360 mm and the load advanced at a constant speed of 3.5 mm/min. The press recorded the displacement of the load (in mm) and the stress (in Newtons) applied in order to maintain constant speed.

For the calculation of *E*, only the section of the graph (see Figure 2.10) that is between 10% and 40% of the maximum load that the sample was able to withstand was used. A section that provides a regression coefficient of at least 0.99 was used for this calculation, with the condition that said section includes the segment between 20% and 30% of maximum load. *E* (in MPa) is then calculated according to the following equation:

$$E = \frac{1}{4} \cdot \frac{\Delta P}{\Delta D} \cdot \frac{span^3}{width \cdot thickness^3} \qquad \textit{Eq. 3.10}$$

Where $\frac{\Delta P}{\Delta D}$ is the slope of the section of the graph used for the regression in Newton/mm, $span$ is the distance between the two support points in mm (in all cases it was 360 mm), $width$ and $thickness$ are the dimensions of the section of the sample in mm. Then, *f* (in MPa) is calculated based on the maximum load recorded, according to the following equation:

$$f = \frac{3}{2} \cdot Load_{max} \cdot \frac{span}{width \cdot thickness^2} \qquad Eq.\ 3.11$$

Where $Load_{max}$ is the maximum load supported by the sample before breaking (in Newton); $span$, $width$ and $thickness$ are the same as Eq. 3.10.

3.12 REVERSIBILITY OF CHANGES IN EMC AND DIMENSIONAL STABILITY

Samples of *E. grandis* modified at 200°C in the three different heating environments were selected for these tests, along with the unmodified reference.

3.12.1 SORPTION ISOTHERM

Sorption isotherms were measured to the previously mentioned samples in two different conditions:

- **Non-extracted samples**

  No further processing took place between thermal modification and hygroscopicity test.

- **Extracted samples**

  Samples were subjected to extraction between thermal modification and hygroscopicity tests.

In the case of the extracted samples, pieces of 20×20×10 mm^3 (tangential × radial × longitudinal) were subjected to extraction with water for 10 hours using a Soxhlet apparatus.

3.12.1.1 FIRST SORPTION ISOTHERM

The first adsorption isotherm was measured to the samples modified in the three environments. For each condition (both non-extracted and extracted), 4 pieces of 20×20×10 mm^3 (tangential × radial × longitudinal) were used. EMC was determined at 20°C and RH of 30%, 65%, 80% and 90%. Dry weight was determined by placing the samples in an oven at 103°C until constant weight.

The EMC ratio of the modified samples to the non-extracted reference was determined for each RH step according to the following equation:

$$EMC_{ratio,x\%} = \frac{EMC_{sample,x\%}}{EMC_{ref,x\%}} \qquad \textit{Eq. 3.12}$$

Where $EMC_{sample,x\%}$ is the EMC of the sample and $EMC_{ref,x\%}$ is the EMC of the non-extracted reference, both measured at an RH of $x\%$.

3.12.1.2 MODELING OF SORPTION ISOTHERMS

The experimental results from the first adsorption isotherm were modeled using the Hailwood-Horrobin equation (Hailwood & Horrobin, 1946):

$$\frac{H}{M_{meas}} = A + BH - CH^2 \qquad \textit{Eq. 3.13}$$

Where H is the relative humidity expressed as fraction, M_{meas} is the measured EMC of the wood, expressed as fraction; and A, B and C are empirical parameters (Skaar, 1988).

Likewise, equilibrium constants K_d, and K_h were calculated with equations 3.14 and 3.15. K_d being the equilibrium constant between the dissolved water and the vapor in the atmosphere, and K_h the ratio of the activity of the hydrate (wood-water) to the product of the activities of the two reactants: dissolved water and anhydrate wood. The apparent molecular weight of a wood molecule capable of absorbing a water molecule, W, was calculated with equation 3.16.

$$K_d = \frac{0.5\left(-B+\sqrt{B^2+4AC}\right)}{A} \qquad \textit{Eq. 3.14}$$

$$K_h = 1 + \frac{B^2+B\sqrt{B^2+4AC}}{2AC} \qquad \textit{Eq. 3.15}$$

$$W = 18\sqrt{B^2 + 4AC} \qquad \textit{Eq. 3.16}$$

The equilibrium moisture content of the wood (M_{model}) was then calculated using the two parameters obtained from equations 3.18 and 3.19:

one that quantifies the water that forms the first layer attached to the wood (M_h) and one that describes the water in the successive layers (M_d), all expressed as fraction.

$$M_{model} = M_h + M_d \qquad \textit{Eq. 3.17}$$

$$M_h = \frac{18}{W}\left(\frac{K_d K_h H}{1+K_d K_h H}\right) \qquad \textit{Eq. 3.18}$$

$$M_d = \frac{18}{W}\left(\frac{K_d H}{1-K_d H}\right) \qquad \textit{Eq. 3.19}$$

3.12.1.3 DYNAMIC VAPOR SORPTION

Non-extracted and extracted samples modified at 200°C in nitrogen were selected for the measurement of sorption isotherms in a Dynamic Vapor Sorption apparatus (DVS advantage, Surface Measurement Systems, London, United Kingdom).

Sorption isotherms were measured following a similar procedure to the one stated by Wentzel et al. (2018). For each measurement, thin sections of 40 µm with a mass of 20 mg were prepared on a sliding microtome. Temperature was kept at 20°C and RH content decreased to 0% to determine the initial dry weight of the specimen. Then, RH was increased to 5% and then to 95% in 10% steps, followed by a decrease to 0% in the reverse sequence. This sequence was repeated in a second sorption cycle. Each RH step remained constant until the weight change ($\partial m/\partial t$) was less than 0.002 $w\%/min$ over a 10-minute period. The final mass measured at each RH was used to calculate the EMC of each step.

3.12.2 WATER-SOAKING CYCLES

Samples modified in the three environments were studied in the water-soaking cycle test, along with the unmodified reference. 30 specimens per sample, with dimensions 10×10×10 mm^3 (tangential × radial × longitudinal) were used.

EMC and maximum volumetric swelling (S_{max}) were measured in each cycle. Mass and dimensions of each specimen were recorded after each of the following three steps:

- **Step A:** After conditioning at 20°C and 65% RH.
- **Step B:** After air drying at room conditions for 5 days followed by progressive drying in four 24-hour steps at 40°C, 60°C, 80°C and 103°C.
- **Step C:** After immersion in water for 10 days with daily water changes.

Upon competition of these three steps, specimens were air-dried for 5 days and the cycle repeated. EMC (as percentage, at 20°C and 65% RH) was determined for each sample and each water-soaking cycle using the following equation:

$$EMC = 100 \times \left[\frac{(m_{xA} - m_{xB})}{m_{1B}}\right] \qquad \textit{Eq. 3.20}$$

Where m_{xA} and m_{xB} are the mass at the end of step A and B of cycle x, respectively, and m_{1B} is the mass at the end of step B of cycle 1.

S_{max} (expressed in percentage) was measured based on the volume of the samples at the end of step B and C of each cycle, using the following equation:

$$S_{max} = 100 \times \left[\frac{(v_{xC} - v_{xB})}{v_{1B}}\right] \qquad \textit{Eq. 3.21}$$

Where v_{xB} and v_{xC} are the sample volumes at the end of step B and C of cycle x, respectively, and v_{1B} is the volume at the end of step B of the first cycle.

4 RESULTS AND DISCUSSION

4.1 INTRODUCTION

This chapter presents the results of the study on thermally modified Uruguayan *Eucalyptus grandis* and *Pinus taeda*, and the effects of this process in wood properties and composition. Figure 4.1 shows unmodified and thermally modified boards of both species.

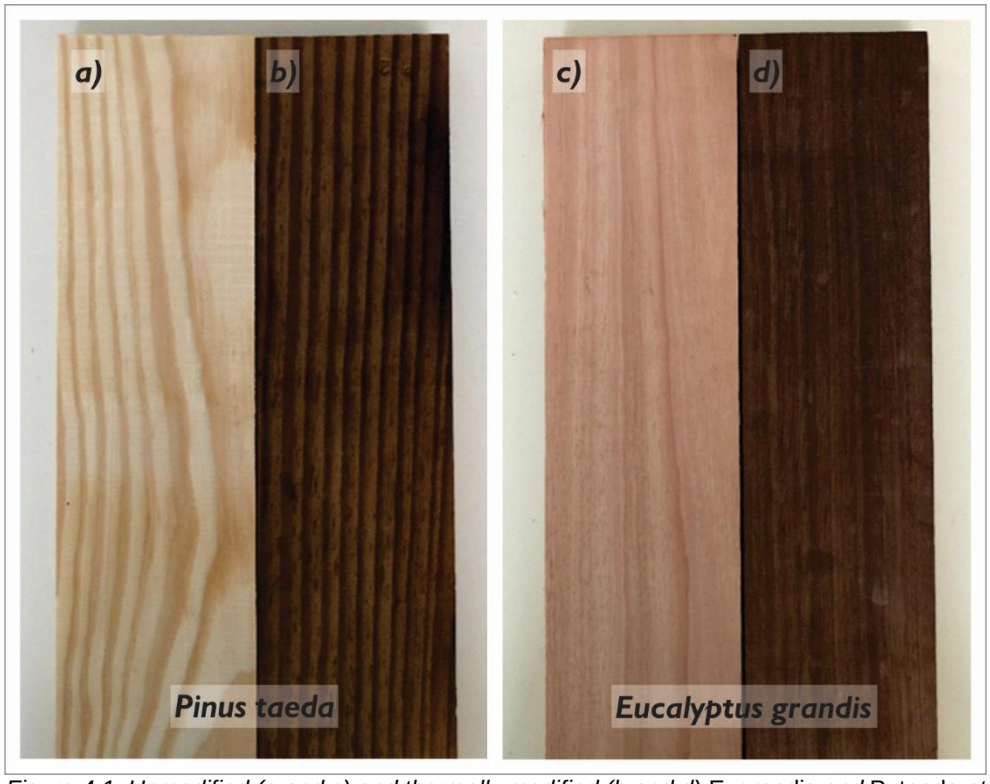

Figure 4.1. Unmodified (a and c) and thermally modified (b and d) E. grandis *and* P. taeda *at 200°C in Nitrogen.*

In this section, the results on the variations of mass and volume due to thermal treatment are presented, as well as the study on the relationship between these two variables.

The effect of the different treatment conditions on the changes in chemical composition are discussed. Also, focus was made on the relationship between mass loss and the degradation of the carbohydrates derived from hemicelluloses.

The reduction in equilibrium moisture content is presented, and the relationship that this parameter has with mass loss and hemicelluloses was studied.

The effects on mechanical properties are presented through the changes on bending strength and modulus of elasticity. Again, the link of these parameters with chemical and physical changes is discussed.

Finally, the reversibility of the changes in hygroscopicity and dimensional stability is presented through the discussion of the variations on the sorption isotherms of non-extracted and extracted samples of modified *E. grandis* and through the study of the changes in mass and dimensions of water-soaked *E. grandis*.

4.2 VARIATIONS IN MASS AND VOLUME

The results of mass loss and volume reduction of *E. grandis* and *P. taeda* are shown in Table 4.1 and Table 4.2, respectively. All boards lost

mass and showed a reduction in its dimensions due to thermal modification. As a rule, the higher the treatment temperature, the greater the values of mass loss and volume reduction.

Table 4.1. Mass loss, volume reduction and density variaton of E. grandis*. Results presented as mean ± standard deviation.*

Temperature	**Environment**	**Mass loss**	**Volume reduction**	**Density variation**
(°C)			**(%)**	
160	Vacuum	0.57 ± 0.37	4.6 ± 2.0	4.2 ± 1.8
	Air	2.32 ± 0.17	2.33 ± 0.58	0.01 ± 0.43
	Nitrogen	2.176 ± 0.062	1.74 ± 0.63	-0.44 ± 0.65
180	Vacuum	1.24 ± 0.33	7.33 ± 0.55	6.57 ± 0.75
	Air	3.4 ± 3.0	3.3 ± 3.0	0.0 ± 4.6
	Nitrogen	3.26 ± 0.63	5.97 ± 0.19	2.88 ± 0.84
200	Vacuum	6.3 ± 1.1	8.4 ± 3.4	2.4 ± 3.5
	Air	6.73 ± 0.65	6.25 ± 0.55	-0.51 ± 0.11
	Nitrogen	5.33 ± 0.43	8.1 ± 2.0	3.0 ± 2.0
220	Vacuum	12.3 ± 1.7	10.8 ± 1.0	-1.6 ± 2.4
	Air	10.1 ± 2.1	11.2 ± 2.7	1.2 ± 3.6
	Nitrogen	14.4 ± 4.9	10.5 ± 1.9	-4.2 ± 7.4

Table 4.2. Mass loss, volume reduction and density variation of P. taeda*. Results presented as mean ± standard deviation.*

Temperature (°C)	Environment	Mass loss	Volume reduction (%)	Density variation
160	Vacuum	3.25 ± 0.84	1.214 ± 0.010	-2.06 ± 0.85
	Air	1.29 ± 0.76	2.4 ± 3.2	1.3 ± 3.9
	Nitrogen	1.52 ± 0.30	1.44 ± 0.23	-0.08 ± 0.46
180	Vacuum	5.10 ± 0.19	1.97 ± 0.44	-3.18 ± 0.62
	Air	3.01 ± 0.48	3.6 ± 2.0	0.6 ± 2.3
	Nitrogen	3.6 ± 1.0	3.6 ± 1.8	0.0 ± 1.8
200	Vacuum	5.12 ± 0.22	8.3 ± 2.9	3.6 ± 3.5
	Air	5.5 ± 1.0	6.79 ± 0.86	1.40 ± 0.15
	Nitrogen	4.57 ± 0.59	5.5 ± 2.2	1.0 ± 2.4
220	Vacuum	9.2 ± 1.1	11.44 ± 0.29	2.48 ± 0.96
	Air	11.3 ± 1.9	12.8 ± 4.3	1.9 ± 6.3
	Nitrogen	8.9 ± 1.1	10.63 ± 0.39	2.0 ± 1.4

4.2.1 MASS LOSS

As it can be seen in Table 4.1 and in Figure 4.2, for *E. grandis*, in all cases (except for samples treated at 180°C in vacuum), an increase in temperature led to a higher mass loss, regardless of the modification environment. A maximum of 14.4% was reached when treated at 220°C in nitrogen.

Contrary to what could be predicted, samples of *E. grandis* treated at 220°C in air showed a lower rate of mass loss than the ones modified at the same temperature but without oxygen (10.1% in air compared to 12.3% in vacuum and 14.4% in nitrogen). A hypothesis can be postulated, which indicates that superficial changes (charring) due to combustion taking place in the boards derives in two main things: firstly, a lower thermal conductivity, which affects heat transportation into the inner parts of the boards;

secondly, a lower diffusion rate (Richardson, 2002), affecting the rate at which compounds derived from thermal degradation volatilize into the environment.

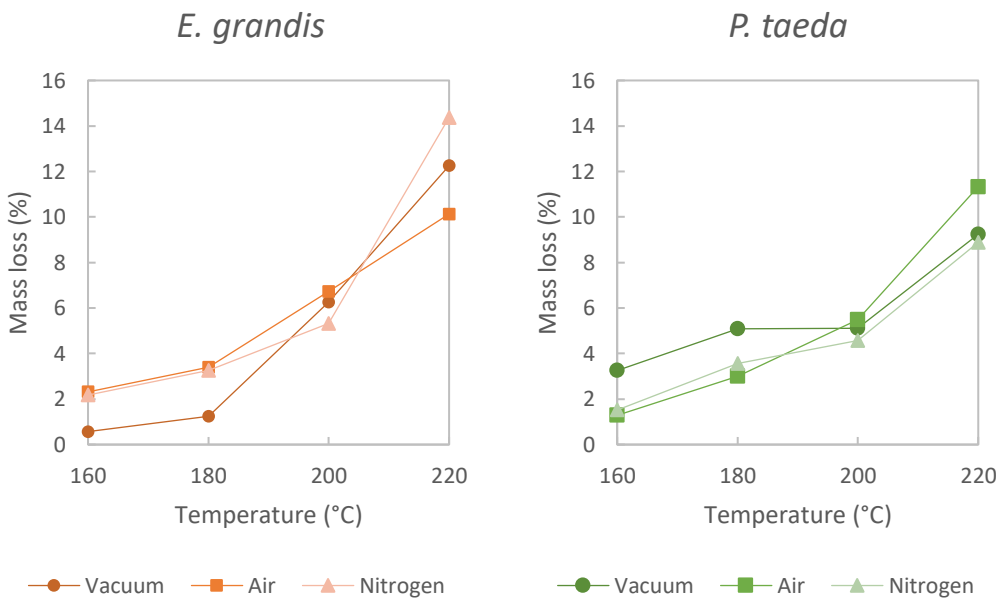

Figure 4.2. Mass loss of thermally modified E. grandis *and* P. taeda.

The behavior of *P. taeda* differs from that of *E. grandis*. In this case (Table 4.2 and Figure 4.2), mass loss was relatively low when samples were modified at temperatures of 200°C or lower (mass loss below 6%), possibly indicating more thermal stability than *E. grandis* at those temperatures. Only at 220°C a mass loss higher than 8% was achieved, reaching a maximum of 11.3% at 220°C in air.

In the case of *P. taeda*, the effect of the treatment environment at 220°C did not show the same behavior as *E. grandis*. Therefore, the same hypothesis cannot be proposed. Charring was not observed in the boards of *P. taeda* modified at 220°C in air.

As shown in Figure 4.3, the heating environment was not as determinant as treatment temperature when it comes to the effects on mass loss. In the case of *E. grandis*, samples modified at the same temperature did not show a statistically significant difference, except for the already discussed effect at the highest temperature (220°C). In the case of *P. taeda*, at lower temperatures (160°C and 180°C), samples heated in vacuum reached higher rates of mass loss, whereas at 200°C it even out, and at 220°C it was the sample modified in air that presented a statistically higher mass loss.

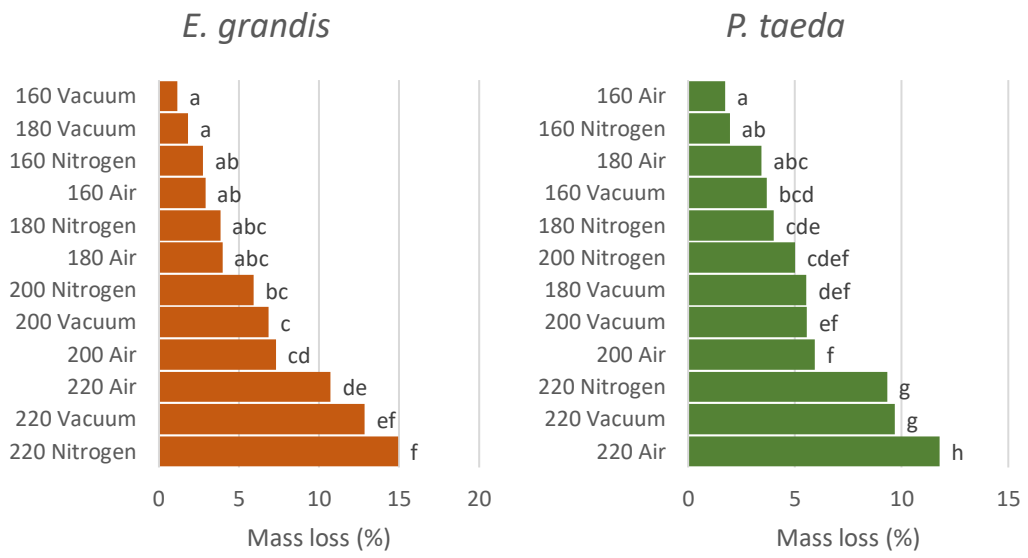

Figure 4.3. Analysis of variance and Tukey test for mass loss of E. grandis *and* P. taeda*. Each letter means a statistically different group.*

4.2.2 VOLUME REDUCTION

As it can be seen in Figure 4.4, volume reduction follows the same trend as mass loss, volume decreases as treatment temperature increases.

In both species, the maximum volume reduction was reached when samples were modified at 220°C in air (*E. grandis*: 11.2%, *P. taeda*: 12.8%).

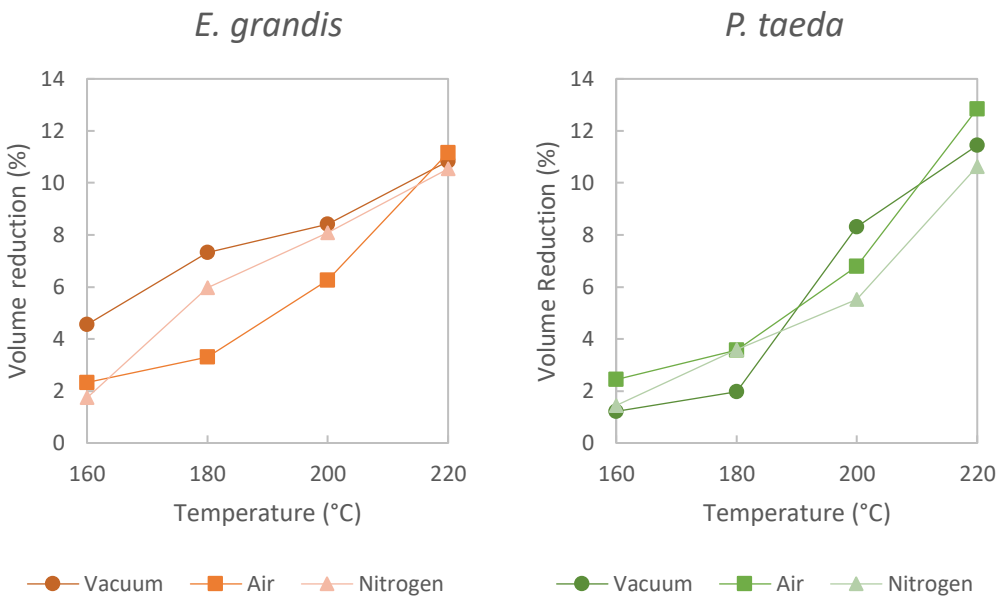

Figure 4.4. Volume reduction of thermally modified E. grandis *and* P. taeda.

Figure 4.5 shows the analysis of variance and Tukey test for the volume reduction of both species. In the case *E. grandis*, only samples modified at 180°C showed a statistically significant difference. However, treatment performed in vacuum presented higher rates of volume reduction at temperatures up to 200°C. *P. taeda* did not show a clear trend in terms of the effect of the heating medium, nor presented statistically significant differences between them at the same treatment temperature.

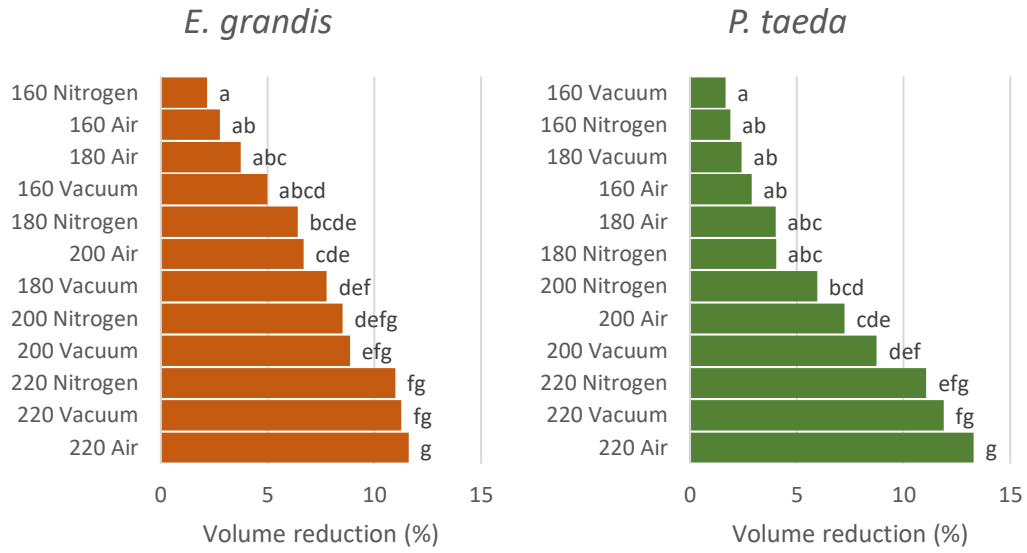

Figure 4.5. Analysis of variance and Tukey test for volume reduction of E. grandis *and* P. taeda*. Each letter means a statistically different group.*

As expected, the reduction in both mass and volume due to thermal modification derived in a relatively unchanged density (except for the samples of *E. grandis* modified in vacuum at 180°C, which presented an increase in density of 6.57% (Table 4.1), mainly due to a relatively low mass loss.

4.3 CHANGES IN CHEMICAL COMPOSITOIN

Table 4.3 and Table 4.4 present the chemical composition of unmodified and thermally modified *E. grandis* and *P. taeda*, respectively. The composition of the unmodified samples of both species is similar to what has been reported by Batista (2016) and Sannigrahi (2008).

Table 4.3. Chemical composition of unmodified and thermally modified E. grandis*. Results presented as mean ± standard deviation.* ***nd****: not detected*

Temperature	Environment	Extractives	Lignin	Glucose	Xylose
(°C)		(g/100g)			
-	-	3.93 ± 0.14	27.19 ± 0.18	49.30 ± 0.14	12.87 ± 0.20
160	Vacuum	3.42 ± 0.74	26.96 ± 0.45	44.53 ± 0.14	11.6 ± 1.2
	Air	3.70 ± 0.57	26.02 ± 0.99	42.0 ± 2.3	11.3 ± 1.0
	Nitrogen	5.14 ± 0.61	29.76 ± 0.86	43.1 ± 1.0	12.47 ± 0.43
180	Vacuum	3.69 ± 0.63	27.7 ± 1.8	48.8 ± 1.2	9.0 ± 1.1
	Air	7.10 ± 0.79	30.8 ± 1.0	46.10 ± 0.15	8.4 ± 1.9
	Nitrogen	4.57 ± 0.93	25.56 ± 0.27	46.92 ± 0.79	7.75 ± 0.79
200	Vacuum	7.88 ± 0.73	25.86 ± 0.54	46.0 ± 1.0	8.51 ± 0.74
	Air	8.64 ± 0.70	30.54 ± 0.22	43.6 ± 1.4	7.23 ± 0.64
	Nitrogen	8.41 ± 0.97	25.22 ± 0.46	45.31 ± 0.03	5.126 ± 0.068
220	Vacuum	5.85 ± 0.27	35.48 ± 0.16	57.02 ± 0.33	*nd*
	Air	7.77 ± 0.92	35.7 ± 3.9	47.0 ± 2.4	*nd*
	Nitrogen	8.859 ± 0.058	27.99 ± 0.47	46.6 ± 1.5	*nd*

Table 4.4. Chemical composition of unmodified and thermally modified P. taeda*. Results presented as mean ± standard deviation.*

Temperature	Environment	Extractives	Lignin	Glucose	Xylose + Galactose + Mannose
(°C)		(g/100g)			
-	-	4.47 ± 0.22	28.5 ± 1.7	41.91 ± 0.24	13.0 ± 2.1
160	Vacuum	5.37 ± 0.40	28.87 ± 0.26	43.1 ± 1.2	13.16 ± 0.35
	Air	4.89 ± 0.04	31.4 ± 1.5	42.74 ± 0.54	10.48 ± 0.39
	Nitrogen	4.50 ± 0.12	31.0 ± 1.2	39.9 ± 3.8	10.74 ± 0.16
180	Vacuum	4.38 ± 0.51	29.35 ± 0.66	44.3 ± 1.0	12.6 ± 1.7
	Air	5.31 ± 0.45	28.7 ± 1.9	42.11 ± 0.49	10.1 ± 1.3
	Nitrogen	3.91 ± 0.36	29.51 ± 0.91	42.3 ± 1.8	12.78 ± 0.91
200	Vacuum	4.37 ± 0.29	31.64 ± 0.42	44.32 ± 0.90	9.44 ± 0.72
	Air	5.52 ± 0.14	30.66 ± 0.42	45.40 ± 0.24	10.36 ± 0.86
	Nitrogen	4.34 ± 0.15	29.65 ± 0.40	46.04 ± 0.45	11.6 ± 1.1
220	Vacuum	5.72 ± 0.18	32.96 ± 0.76	46.87 ± 0.66	7.73 ± 0.61
	Air	5.60 ± 0.22	41.48 ± 0.82	44.80 ± 0.49	5.2 ± 1.8
	Nitrogen	5.15 ± 0.10	38.1 ± 6.5	47.2 ± 2.1	6.6 ± 2.8

4.3.1 EXTRACTIVES

On the one hand, the total extractive content of *E. grandis* increased with higher treatment temperature, reaching a maximum of 8.859 g/100g of dry wood at 220°C in nitrogen. This trend is similar to the one found by Wentzel (2019) for modified Chilean *Eucalyptus nitens*, Esteves (2008) for Portuguese *Eucalyptus globulus* and Batista (2016) for Brazilian *Eucalyptus grandis*, where all samples presented higher extractive content than the unmodified reference.

On the other hand, extractives of *P. taeda* samples did not show any significant trend. Although it is reported that extractives tend to increase with mass loss in different Pine species, only slight changes are seen when mass loss is not significant. Mohareb (2012) found an increase of only 0.4% in the extractive content for samples of Kenyan *Pinus patula* that showed a mass loss of 6.1% after being thermally treated at 240°C in nitrogen. Moreover, some Pine species present lower extractive content than that presented in this work. While Esteves (2011) found an increase in extractive content of thermally modified Portuguese *Pinus pinaster*, extractive content of unmodified samples accounted for 2.6%, increasing to 4.8% both at a mass loss of 0.4% and 7.7%.

As explained in section 2.5.1, the extractives of wood are expected to degrade when thermally modified, but new extractable material is generated, as degradation products are formed and retained in wood during the process. Due to the production of said new extractable compounds, it is

possible for the extractive content of thermally modified wood to be greater than that of unmodified wood. However, not all those degradation products are expected to stay inside wood, high temperature favors their diffusion and subsequent volatilization into the environment. Therefore, there is a compromise between the formation of degradation products as a result of the thermal modification and their volatilization towards the environment that affects the total extractive content.

4.3.2 XYLOSE, GALACTOSE AND MANOSE

Xylose content of thermally modified *E. grandis* denotes degradation of hemicelluloses. At temperatures of 220°C, xylose was not even detected (Table 4.3), indicating heavy degradation of this constituents of the cell wall.

Figure 4.6 shows the level of xylose remaining at every treatment condition, where 100% corresponds to the unmodified reference. Although at 160°C, a relatively mild condition, xylose content was reduced to 87% when exposed to air (mass loss of 2.32%), at 180°C the reduction of xylose content was significatively higher, between 30% (vacuum) and 40% (nitrogen).

For *P. taeda*, hemicelluloses suffered from degradation at 160°C, except for the samples modified in vacuum, which showed the same content of the sum of xylose, galactose and mannose (XGM) as the reference. However, changes in hemicelluloses sugars stayed relatively constant up to

the temperature of 200°C. Only at 220°C was the XGM content significantly reduced. For example, at 160°C, the maximum reduction in XGM content was 19% (to 81% of that of the reference - Figure 4.6). However, when temperature was increased to 180°C or 200°C, the results only slightly changed (78% and 73%, respectively). Only at 220°C was XGM content reduced to less than 40%.

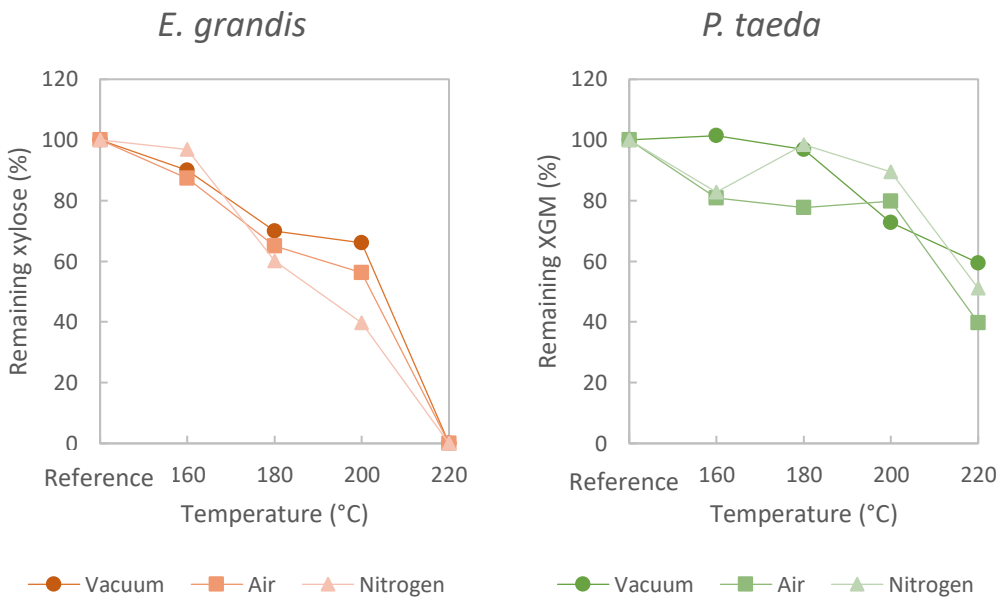

Figure 4.6. Hemicelluloses sugars remaining in each treatment condition, represented as percentage of remaining xylose for E. grandis*, and remaining XGM for* P. taeda*. In both cases, unmodified reference accounted for 100%.*

In comparison, samples of *E. grandis* suffered from more degradation than *P. taeda* when modified at temperatures of 180°C and higher. The lower thermal stability of hardwood xylan in comparison to softwood hemicelluloses explained in section 2.5.1 supports these results.

Similarly to mass loss and volume reduction, treatment temperature appears to be more relevant than heating environment when it comes to the

effects on hemicelluloses degradation. In most cases, samples modified at the same temperature did not present statistically significant differences (Figure 4.7).

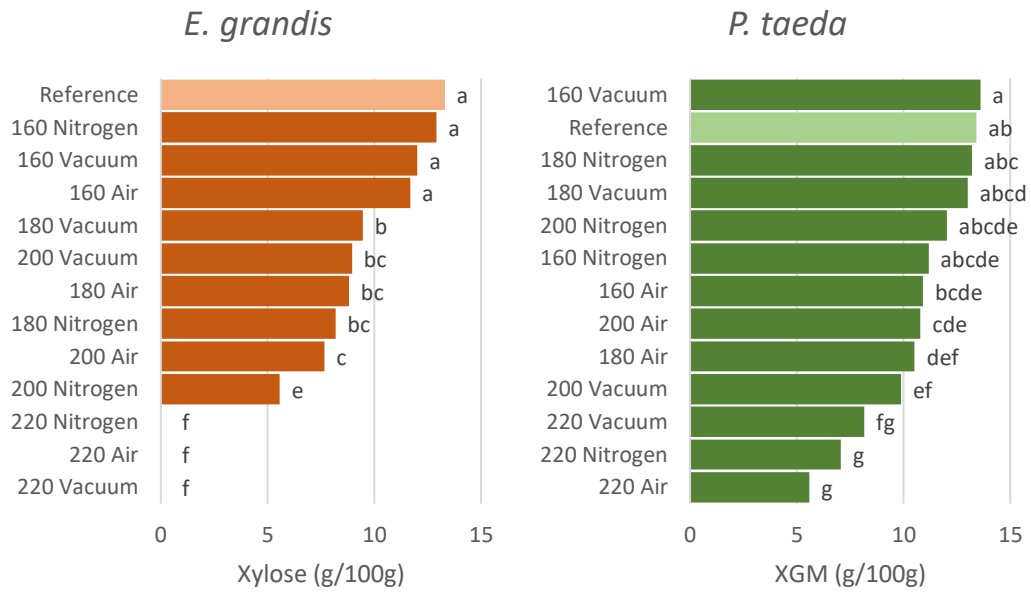

Figure 4.7. Analysis of variance and Tukey test for xylose content of E. grandis *and XGM content of* P. taeda*. Each letter means a statistically different group.*

While in the case of *E. grandis* degradation of xylan was total at the temperature of 220°C, *P. taeda* did not show heavy degradation until that temperature. This represents an advantage for Eucalypt wood in comparison to Pine from the perspective of the energy needed for an industrial production of thermally modified wood, as thermally modified *E. grandis* needs lower temperatures, and therefore less energy than *P. taeda*.

Mass loss is partially caused by depolymerization of hemicelluloses. Therefore, it is expected for these two variables to be closely correlated. In

the case of *E. grandis*, it appears to be a plateau in the depolymerization of the cell wall between mass losses of 3% to 6% (Figure 4.8), whilst after that, degradation takes place at a much higher rate.

In the case of *P. taeda*, mass loss of up to 5% are not easily explained by the reduction in XGM content, some samples presented almost no reduction in the XGM content, while rendering a mass loss of between 3% and 5%. Only after the threshold of 6%, the loss of mass also came with a reduction in XGM content.

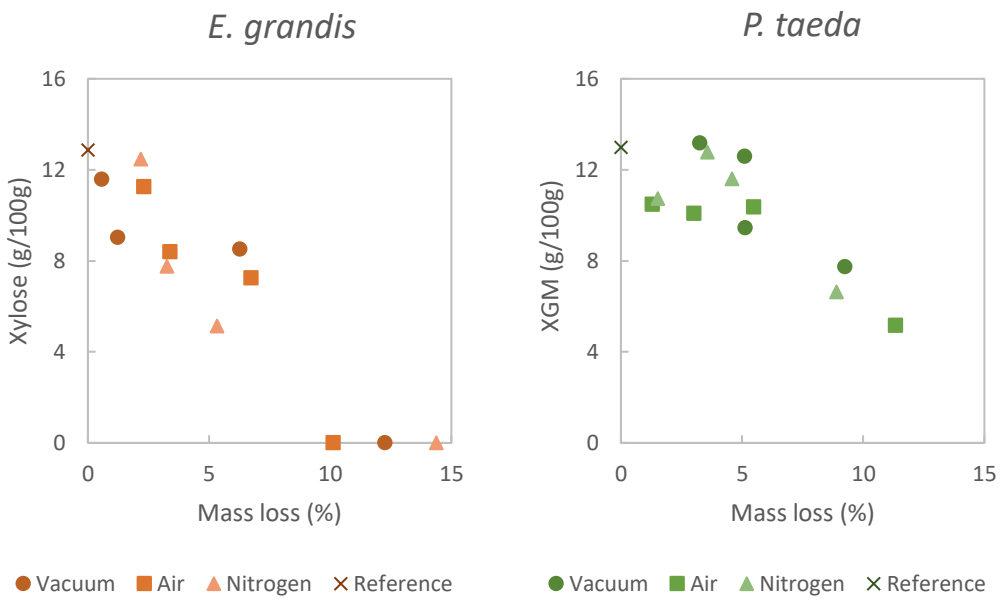

Figure 4.8. Mass loss vs. xylose content for E. grandis *and mass loss vs. XGM for* P. taeda*.*

If the process is studied independently of the modification atmosphere, that is, if only temperature is accounted as a variable that determines the relationship between mass loss and xylose content (*E. grandis*) and XGM (*P. taeda*), then there is good correlation between the variables, as it can be seen in Table 4.5. In this sense, mass loss might be

a good proxy for the prediction of polymer degradation, though more data ought to be collected to establish a proper relationship between them.

Table 4.5. Pearson correlation coefficients between mass loss and xylose for E. grandis*, and between mass loss and XGM for* P. taeda*. [1]Statistically significant correlations (p<0.05).*

	Xylose	XGM
E. grandis	-0.765[1]	-
P. taeda	-	-0.815[1]

4.3.3 GLUCOSE

One of the limitations of the method used for the determination of structural carbohydrates is that these are measured in the form of monomers, regardless of their origin within the polymer structure of the cell wall (cellulose or hemicellulose). This inevitably constrains the analysis of cellulose and hemicellulose degradation, since both macro-components contain the monomer glucose.

In spite of that, glucose content can be taken as an indirect indicator of cellulose content, but the fact that its determination includes the portion of hemicelluloses conformed by this monomer must be considered. Still, glucose monomers are usually part of the backbone of hemicelluloses chains and tend to be less susceptible to degradation than other monomers located in the side chains. Therefore, they are less susceptible to degradation than the side chains of hemicelluloses.

Glucose content of thermally modified *E. grandis* and *P. taeda* is shown at the beginning of section 4.2, in Table 4.3 and Table 4.4, respectively. In both cases, glucose content stays relatively constant

throughout the different conditions tested. Nonetheless, degradation of xylose, galactose and mannose affect the relative content of glucose in thermally modified samples that suffered from heavy depolymerization. Table 4.6 shows glucose content corrected by mass loss, that is, expressed as grams per 100 g of dry wood *before* thermal modification. In this way, changes in the other chemical constituents do not affect the analysis of the results in glucose content.

In the case of *E. grandis*, Table 4.6 shows that glucose content tends to be reduced with thermal modification, but no trend was observed, except for the fact that for all temperatures (except 220°C, which has been already discussed that the conditions at said temperature were too severe), glucose content was lower in the modifications that were done in air. Oxidation reactions due to oxygen present in air could be the reason behind the lower content of glucose when modified in air, as it is known that degradation tends to start at lower temperatures when oxygen is present (Shafizadeh & Bradbury, 1978).

Table 4.6. Glucose content of E. grandis *and* P. taeda *expressed as grams per 100 grams of dry wood before thermal modification.*

Temperature	Environment	*E. grandis*	*P. taeda*
(°C)		(g/100g before treatment)	
-	-	49.3	41.9
160	Vacuum	44.3	41.8
	Air	41.0	42.2
	Nitrogen	42.2	39.3
180	Vacuum	48.2	42.1
	Air	44.6	40.9
	Nitrogen	45.4	40.9
200	Vacuum	43.3	42.2
	Air	40.8	43.0
	Nitrogen	43.0	44.0
220	Vacuum	50.8	42.9
	Air	42.7	40.2
	Nitrogen	40.7	43.3

Glucose content in *P. taeda* samples did not present significant variations due to thermal modification. This result is in alignment with the fact that degradation of hemicelluloses was lower, and the cleavage of its side chain monomers occurs first, followed by degradation of the main chain constituents, which include glucose (Bobleter & Binder, 1980; Fengel & Wegener, 1989).

4.3.4 LIGNIN

Table 4.7 and Table 4.8 show the insoluble, soluble and total lignin content of unmodified and thermally modified *E. grandis* and *P. taeda*, respectively.

Table 4.7. Insoluble lignin, soluble lignin and total lignin content of thermally modified E. grandis *Results presented as mean ± standard deviation.*

Temperature (°C)	Environment	Insoluble lignin	Soluble lignin	Total lignin
		(g/100 g dry)		
-	-	26.34 ± 0.16	0.853 ± 0.014	27.19 ± 0.18
160	Vacuum	26.12 ± 0.38	0.83 ± 0.12	26.96 ± 0.45
	Air	25.21 ± 0.99	0.812 ± 0.034	26.02 ± 0.99
	Nitrogen	28.98 ± 0.91	0.785 ± 0.053	29.76 ± 0.86
180	Vacuum	27.0 ± 1.8	0.702 ± 0.060	27.7 ± 1.8
	Air	30.2 ± 1.1	0.58 ± 0.10	30.8 ± 1.0
	Nitrogen	24.78 ± 0.26	0.777 ± 0.079	25.56 ± 0.27
200	Vacuum	25.35 ± 0.64	0.51 ± 0.12	25.86 ± 0.54
	Air	29.89 ± 0.34	0.65 ± 0.12	30.54 ± 0.22
	Nitrogen	24.69 ± 0.37	0.53 ± 0.13	25.22 ± 0.46
220	Vacuum	35.16 ± 0.17	0.322 ± 0.014	35.48 ± 0.16
	Air	35.3 ± 4.1	0.42 ± 0.15	35.7 ± 3.9
	Nitrogen	27.73 ± 0.51	0.258 ± 0.040	27.99 ± 0.47

Table 4.8. Insoluble lignin, soluble lignin and total lignin content of thermally modified P. taeda*. Results presented as mean ± standard deviation.*

Temperature (°C)	Environment	Insoluble lignin	Soluble lignin	Total lignin
		(g/100 g dry)		
-	-	27.0 ± 1.6	1.515 ± 0.086	28.5 ± 1.7
160	Vacuum	27.71 ± 0.46	1.16 ± 0.24	28.87 ± 0.26
	Air	30.0 ± 1.6	1.45 ± 0.10	31.4 ± 1.5
	Nitrogen	29.4 ± 1.4	1.55 ± 0.20	31.0 ± 1.6
180	Vacuum	27.90 ± 0.67	1.453 ± 0.074	29.35 ± 0.66
	Air	27.3 ± 1.8	1.35 ± 0.16	28.7 ± 1.9
	Nitrogen	27.99 ± 0.87	1.514 ± 0.095	29.51 ± 0.91
200	Vacuum	30.19 ± 0.35	1.446 ± 0.082	31.64 ± 0.42
	Air	29.29 ± 0.37	1.367 ± 0.081	30.66 ± 0.42
	Nitrogen	28.09 ± 0.24	1.56 ± 0.18	29.65 ± 0.40
220	Vacuum	31.52 ± 0.73	1.440 ± 0.036	32.96 ± 0.76
	Air	39.99 ± 0.88	1.496 ± 0.067	41.48 ± 0.82
	Nitrogen	36.6 ± 6.5	1.523 ± 0.023	38.1 ± 6.5

Table 4.9 shows lignin content corrected by mass loss (expressed as grams per 100 g of dry wood *before* thermal modification). As previously explained, lignin is regarded as the most thermally stable macro-component

of wood, and similarly to what was explained in the case of glucose content, degradation of other cell wall constituents affects the relative content of lignin, which is expected to degrade to a much lower extent than other macro-components.

As it can be seen for both species, the corrected lignin content stayed relatively unchanged up to the modification temperature of 220°C, where it increased reaching a maximum of 32.4 g/100g and 37.3 g/100g for samples of *E. grandis* and *P. taeda* modified in vacuum, respectively. However, as shown in Table 4.7 and Table 4.8, no significant changes are seen regarding soluble lignin of these samples, even showing a decreasing trend in the case of thermally modified *E. grandis*. Hence, the increase in total lignin is due to an increase in the solid residue of the determination of insoluble lignin. Said apparent increase is most probably a result of hemicelluloses modification, which leads to humification and condensation products as acid insoluble residues (Tjeerdsma, et al., 1998; Wikberg & Maunu, 2004). Moreover, the more cleavage products the hemicelluloses produce due to high temperature degradation, the more reactive intermediates are produced, namely, 5-Hydroxymethylfurfural (HMF) and furfural. Eventually, said degradation products cause cross-linking reactions that increase the lignin polymer network (Boonstra & Tjeerdsma, 2006). This might also be an explanation for the diminishing content of soluble lignin with the increase of temperature in the case of *E. grandis*, as it has been proven that soluble lignin is a product of lignin degradation due to acid

hydrolysis and not necessary a portion of lignin that is inherently acid-soluble (Kaar & Brink, 1991). The more condensed form that lignin takes after high temperature modification can make it less prone to acid degradation.

Table 4.9. Lignin content of E. grandis *and* P. taeda*, expressed as grams per 100 grams of dry wood before thermal modification.*

Temperature (°C)	Environment	*E. grandis* (g/100g before treatment)	*P. taeda* (g/100g before treatment)
-	-	27.2	28.5
160	Vacuum	26.8	28.0
	Air	25.4	31.0
	Nitrogen	29.1	30.5
180	Vacuum	27.3	27.9
	Air	29.8	27.9
	Nitrogen	24.8	28.5
200	Vacuum	24.3	30.1
	Air	28.6	29.1
	Nitrogen	23.9	28.4
220	Vacuum	31.6	30.2
	Air	32.4	37.3
	Nitrogen	24.5	35.0

4.4 EQUILIBRIUM MOISTURE CONTENT

Table 4.10 shows the EMC of thermally modified *E. grandis* and *P. taeda*, measured at 20°C and 65% RH. Interestingly, in both species all modified samples showed a significant difference when compared against unmodified wood (Figure 4.9), and a consistent decrease in EMC is seen with the increase in treatment temperature, reaching a minimum of 4.11% in the case of *E. grandis* modified at 220°C in air and 4.93% in the case of *P. taeda* modified at the same temperature, but in vacuum. These maximum

values mean a reduction in EMC of more than 50% in relation to the references.

Table 4.10. Equilibrium moisture content at 20°C and 65% relative humidity of thermally modified E. grandis *and* P. taeda*. Results presented as mean ± standard deviation.*

Temperature (°C)	Environment	*E. grandis* (%)	*P. taeda* (%)
-	-	10.368 ± 0.054	10.66 ± 0.10
160	Vacuum	8.01 ± 0.45	8.53 ± 0.32
	Air	7.25 ± 0.65	7.722 ± 0.052
	Nitrogen	7.75 ± 0.32	7.765 ± 0.094
180	Vacuum	7.14 ± 0.53	7.28 ± 0.17
	Air	6.50 ± 0.84	7.16 ± 0.55
	Nitrogen	6.60 ± 0.45	7.09 ± 0.22
200	Vacuum	6.78 ± 0.26	7.2 ± 1.3
	Air	5.5 ± 1.1	6.35 ± 0.48
	Nitrogen	5.52 ± 0.87	6.352 ± 0.069
220	Vacuum	4.72 ± 0.91	4.93 ± 0.70
	Air	4.11 ± 0.42	5.21 ± 0.84
	Nitrogen	4.63 ± 0.84	5.58 ± 0.52

When it comes to the comparison between different heating environments of samples modified at the same temperature, even though Eucalypt samples modified in the presence of air appear to have had lower EMC when compared against samples modified in vacuum and nitrogen at the same temperature, the difference is not statistically significant (Figure 4.9). Only *E. grandis* modified at 200°C in vacuum had a statistically higher EMC than the samples of the same specie modified in air and nitrogen. Samples of *P. taeda* modified at the same temperature fall into the same group (Figure 4.9).

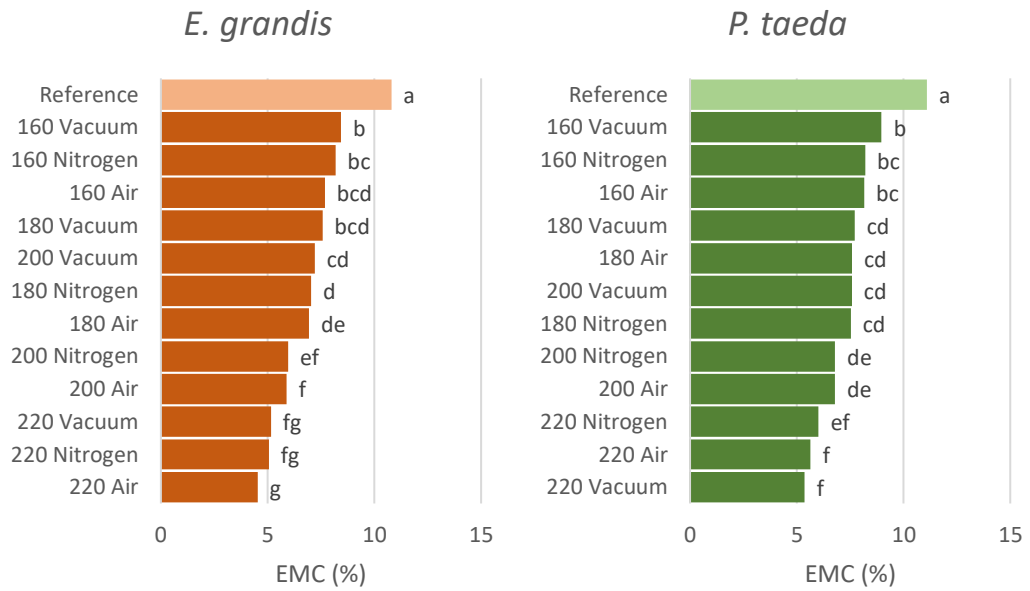

Figure 4.9. Analysis of variance and Tukey test for EMC of E. grandis *and* P. taeda*. Each letter means a statistically different group.*

As explained before, hemicelluloses are the most hygroscopic macro-component of wood, as they contain the greatest amount of water-accessible OH groups of the cell wall. Because of hemicelluloses' degradation, the concentration of those OH groups in wood is greatly reduced, which is thought to affect the EMC of thermally modified wood. However, as stated before, mild conditions are enough to significantly reduce EMC, and at those conditions, depolymerization of the cell wall was relatively low.

Figure 4.10 shows the relationship between EMC and mass loss for both species, between EMC and xylose content for *E. grandis* and between EMC and XGM for *P. taeda*.

In the case of *E. grandis*, samples modified at 160°C, which presented a mass loss lower than 2.5% (Table 4.1) and degradation of xylose of less than 15% (Figure 4.6), reached a reduction in the EMC of around 2%, from 10.37% (untreated sample) to 8.01%, 7.25% and 7.75% in vacuum, air and nitrogen, respectively, which accounts for reduction in relative terms of more than 20% in all three cases.

On the other hand, a comparison between samples modified at 200°C and 220°C present the opposite behavior. While mass loss increased from less than 6% to more than 10% in all three environments, and xylose content was not detected in samples modified at 220°C (reduction in relative terms of 66%, 56% and 40% remaining xylose in vacuum, air and nitrogen, respectively – Figure 4.6), EMC was again reduced by around 2% or less (2,1%, 2,3% and 0,9% in vacuum, air and nitrogen, respectively).

P. taeda showed a stronger ratio of EMC reduction to reduction in XGM at lower treatment temperatures (Figure 4.10). For example, while the XGM content stayed practically unchanged when comparing samples modified at 160°C in vacuum to the reference, EMC was reduced from 12.98% to 8.53%, which accounts for reduction in relative terms of more than 30%.

Besides the reduction in water-accessible OH groups of thermally modified wood, another reason for the reduction in EMC is related to the anatomical changes due to exposure to high temperature and low MC,

which leads to increased stiffness that reduces water uptake (Altgen & Militz, 2016; Endo, et al., 2016). Also, the formation of irreversible hydrogen bonds within hemicelluloses or the amorphous parts of cellulose, which can be denoted as hornification, can be associated with reductions in MC (Borrega & Kärenlampi, 2010).

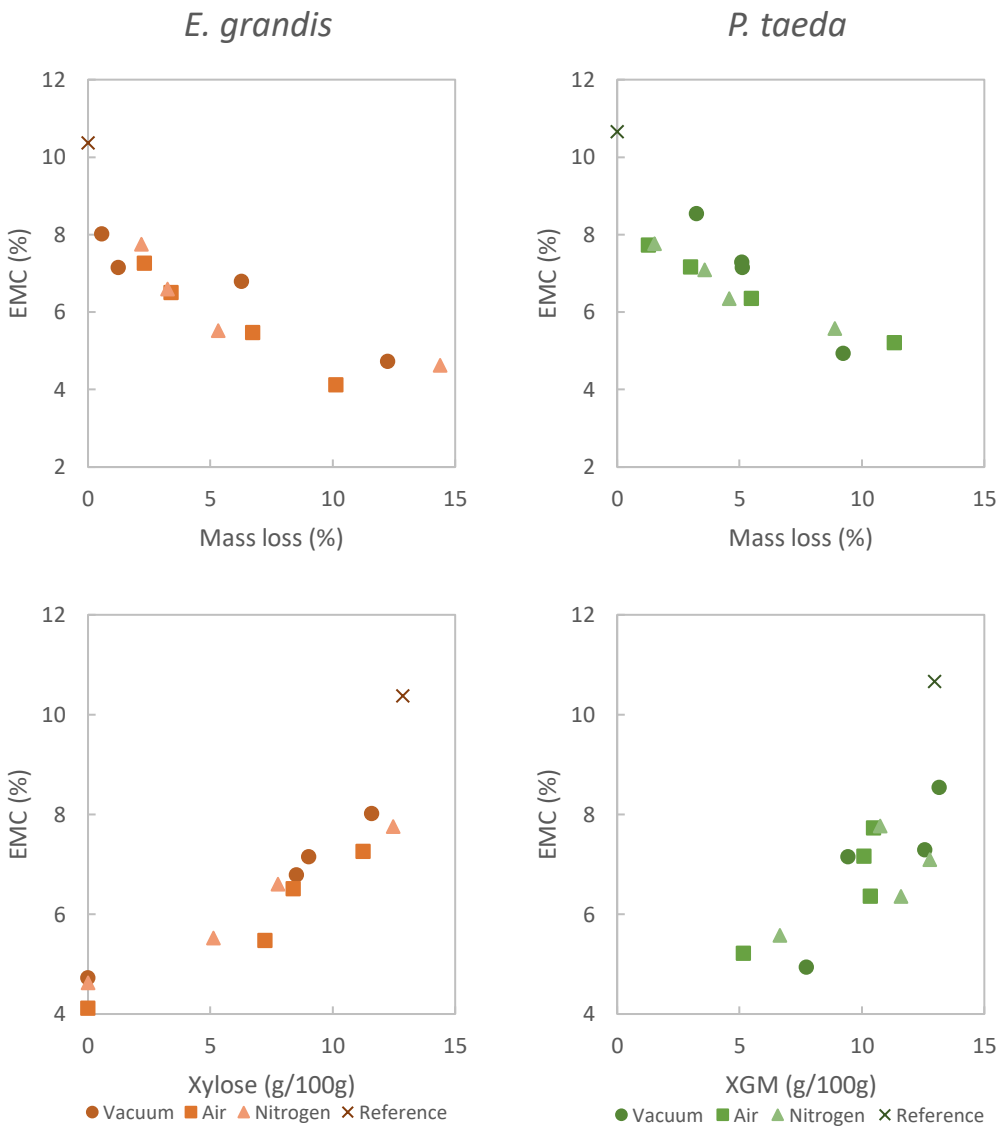

Figure 4.10. 1) EMC vs. mass loss of thermally modified E. grandis*. 2) EMC vs. mass loss of thermally modified* P. taeda*. 3) EMC vs. xylose content of thermally modified* E. grandis*. 4) EMC vs. XGM of thermally modified* P. taeda*.*

Table 4.11 shows the Pearson correlation coefficients between EMC and the variables mass loss and xylose in the case of *E. grandis*, and mass loss and XGM for *P. taeda*. It is expected for both hemicelluloses content and mass loss to be strongly correlated to EMC, as the former accounts for one of the reasons for EMC reduction (less water-accesible OH groups), and the latter is tightly related to the former. Nonetheless, and similarly to what has been discussed earlier, more data is needed to establish proper relationships.

Table 4.11. Pearson correlation coefficients between EMC and the following variables: 1) mass loss and xylose content of E. grandis*, and 2) mass loss and XGM of* P. taeda*. [1]Statistically significant correlations (p<0.05).*

EMC	Mass loss	Xylose	XGM
E. grandis	-0.850[1]	0.900[1]	-
P. taeda	-0.867[1]	-	0.752[1]

4.5 MECHANICAL PROPERTIES

Table 4.12 and Table 4.13 show the modulus of elasticity (*E*) and bending strength (*f*) of unmodified and thermally modified *E. grandis* and *P. taeda*, respectively.

Table 4.12. Modulus of elasticity (E) and bending strength (f) of thermally modified E. grandis*. Results presented as mean ± standard deviation.*

Temperature	Environment	*E*	*f*
(°C)		(GPa)	(MPa)
-	-	12.8 ± 1.7	101 ± 10
160	Vacuum	16.2 ± 2.2	86 ± 16
	Air	16.30 ± 0.86	89.0 ± 6.5
	Nitrogen	12.1 ± 1.5	84 ± 10
180	Vacuum	17.1 ± 1.6	94.5 ± 5.5
	Air	12.36 ± 0.80	66.3 ± 4.6
	Nitrogen	15.43 ± 2.9	66.8 ± 8.3
200	Vacuum	12.47 ± 0.58	60.0 ± 5.9
	Air	11.93 ± 0.25	52.7 ± 5.0
	Nitrogen	15.4 ± 1.9	54.1 ± 9.2
220	Vacuum	12.22 ± 0.96	32.0 ± 4.2
	Air	11.3 ± 1.0	38.9 ± 6.2
	Nitrogen	13.5 ± 1.1	71 ± 26

Table 4.13. Modulus of elasticity (E) and bending strength (f) of thermally modified P. taeda*. Results presented as mean ± standard deviation.*

Temperature	Environment	*E*	*f*
(°C)		(GPa)	(MPa)
-	-	11.31 ± 0.72	96.4 ± 4.1
160	Vacuum	8.0 ± 1.5	56.0 ± 9.5
	Air	6.99 ± 0.92	62.2 ± 7.0
	Nitrogen	8.6 ± 2.4	69 ± 17
180	Vacuum	9.3 ± 2.1	78.6 ± 9.2
	Air	8.10 ± 0.87	53 ± 11
	Nitrogen	9.6 ± 1.9	71 ± 12
200	Vacuum	10.6 ± 1.6	60.9 ± 7.2
	Air	9.62 ± 0.73	54.9 ± 4.7
	Nitrogen	11.3 ± 1.2	64 ± 20
220	Vacuum	7.85 ± 0.93	53.9 ± 4.7
	Air	5.88 ± 0.96	38 ± 12
	Nitrogen	7.88 ± 0.78	53 ± 15

4.5.1 BENDING STREGNTH

A reduction in the bending strength was observed for both species, which increased with treatment severity, reaching a minimum of 32.0 MPa at 220°C in vacuum (68% of reduction) for *E. grandis* (Table 4.12) and 38 MPa at 220°C in air in (61% of reduction) the case of *P. taeda* (Table 4.13).

Figure 4.11 shows the relationship between *f* and mass loss for both species, between *f* and xylose content for *E. grandis* and between *f* and XGM for *P. taeda*.

At a relatively low mass loss, *E. grandis* presents a reduction in its bending strength, as it can be seen in the samples modified at 160°C, which presented mass loss values of 0.57%, 2.32% and 2.18%, while bending strength was reduced by 15%, 12% and 17% (relative to the reference) in vacuum, air and nitrogen, respectively. However, an analysis of variance (Figure 4.12) shows that those differences are not statistically significant. This is due to the high variance observed in the results of bending strength. Still, results are conclusive in the sense that all samples presented a reduction in their bending strength when compared against the reference. Similar results were presented by De Cademartori et al. (2012) for Brazilian *Eucalyptus grandis*, where bending strength of modified wood was lower than that of unmodified samples in all cases, ranging from 22% up to 50% of reduction.

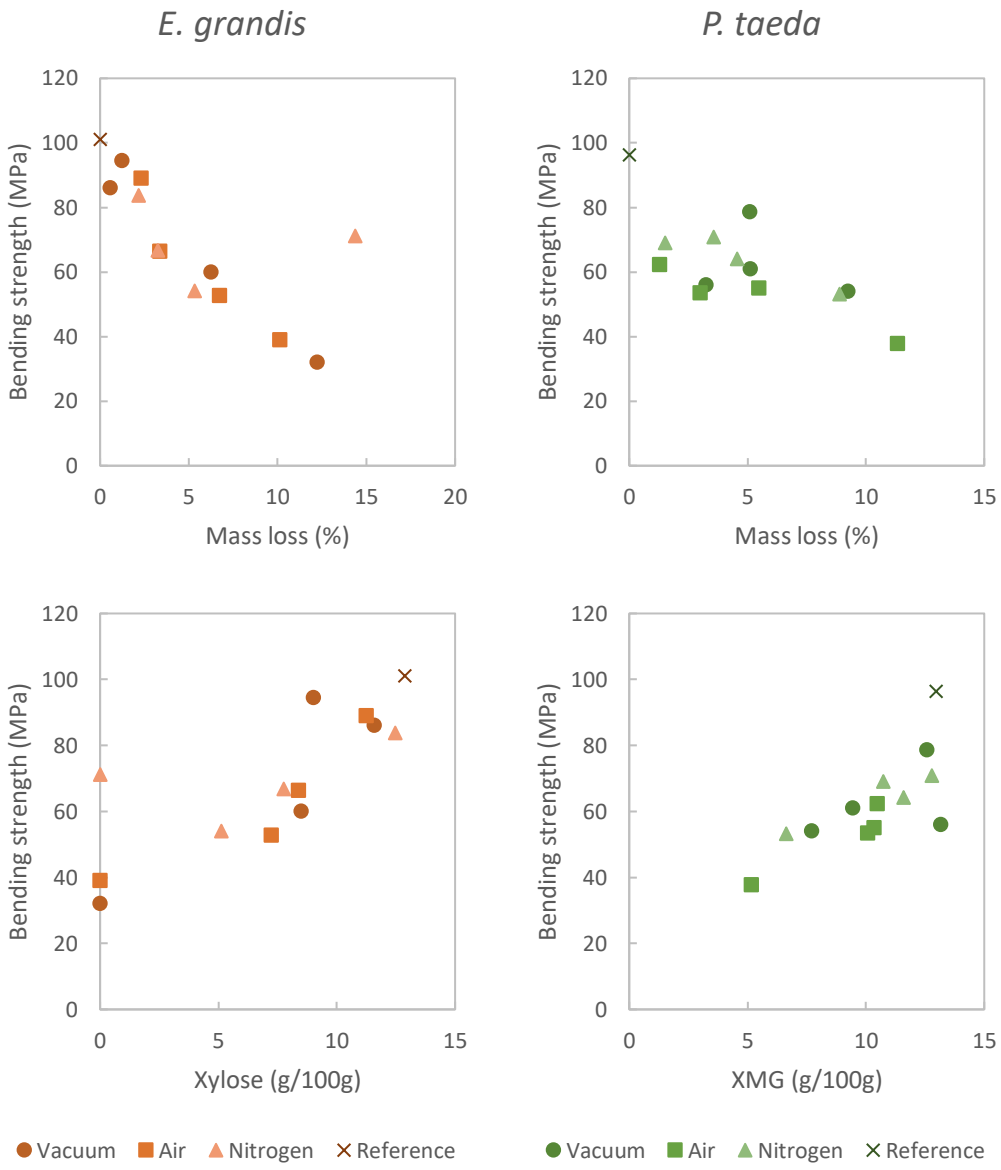

Figure 4.11. 1) Bending strength vs. mass loss of thermally modified E. grandis*. 2) Bending strength vs. mass loss of thermally modified* P. taeda*. 3) Bending strength vs. xylose content of thermally modified* E. grandis*. 4) Bending strength vs. XGM of thermally modified* P. taeda*.*

Similarly, samples of *P. taeda* modified at 160°C showed a reduction in bending strength with relatively low mass loss. While mass was reduced by 3.25%, 1.29% and 1.52%, bending strength reduction accounted for 42%, 36% and 28% (relative to the reference) in vacuum, air and nitrogen, respectively. In this case, almost all samples (except samples

subjected to 180°C in Vacuum) presented a significantly lower bending strength when compared against the unmodified sample. Esteves (2008) found similar behaviors for Portuguese *Pinus pinaster*, already reaching a 40% reduction with mass losses of 3%, and reaching a maximum of around 60%.

When comparing bending strength of *E. grandis* and *P. taeda* modified at lower temperatures (160°C and 180°C), it appears that Pine wood is more easily affected by thermal treatment.

In the case of *E. grandis* modified at 220°C in nitrogen, despite the fact of being the condition that presented higher mass loss, it also presented the highest bending strength among samples modified at the same temperature (71 MPa of that of nitrogen against 32 MPa for vacuum and 39 MPa for air). However, there is a relatively high standard deviation in said sample. Those boards modified at 220°C in vacuum or air did not show the same dispersion. It is possible to propose the hypothesis that, while 220°C is a severe condition for the thermal modification of *E. grandis*, an environment filled with nitrogen instead of air tends to be more protective for the wood.

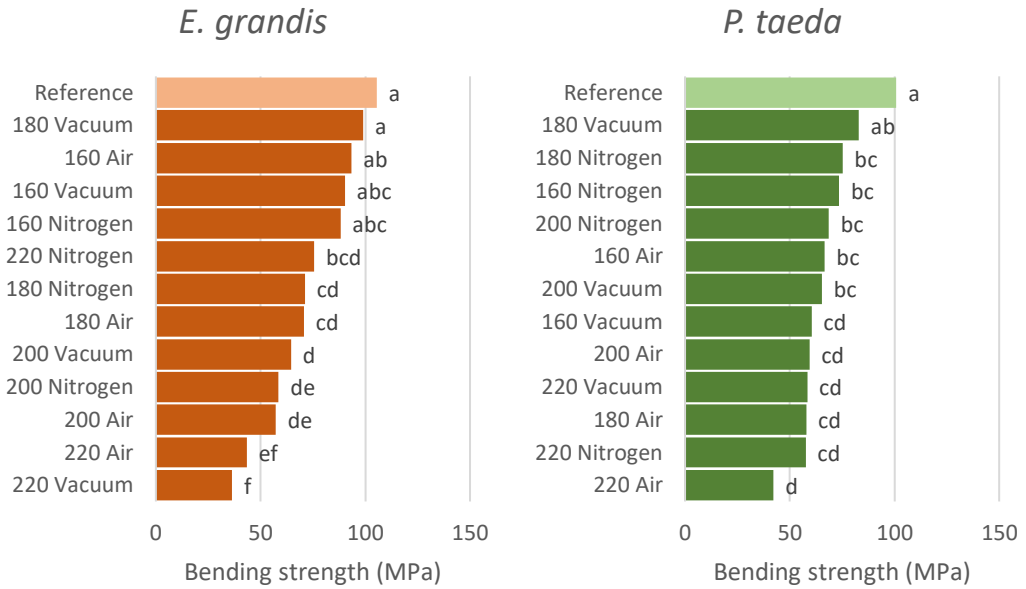

Figure 4.12. Analysis of variance and Tukey test for bending strength of E. grandis *and* P. taeda*. Each letter means a statistically different group.*

Table 4.14 shows the Pearson correlation coefficients between bending strength and the variables mass loss and xylose in the case of *E. grandis*, and mass loss and XGM for *P. taeda*. As it can be visually interpreted in Figure 4.11, the relationship between the aforementioned variables is rather erratic at low mass loss and degradation of hemicelluloses' sugars. However, and with the exception of the already discussed sample of *E. grandis* modified ta 220°C in nitrogen, the relationship between variables tends to be stronger as mass loss and hemicelluloses degradation increases.

Table 4.14. Pearson correlation coefficients between bending strength and mass loss, and bending strength and xylose content of E. grandis *and XGM of* P. taeda*. [1]Statistically significant correlations (p<0.05).*

Bending strength	Mass loss	Xylose	XGM
E. grandis	-0.741[1]	0.839[1]	-
P. taeda	-0.707[1]	-	0.740[1]

This is a particularly interesting correlation, as mass loss can be easily measured in an industrial environment, acting as a predictor of the deterioration of bending strength. Again, more data must be collected in order to get a proper correlation coefficient that can serve predictive purposes.

4.5.2 MODULUS OF ELASTICITY

As shown in Table 4.12 and Table 4.13, modulus of elasticity (*E*) did not present a clear trend with temperature increase or modification environment. In the case of *E. grandis*, some modified samples presented an increase in *E* when compared against the unmodified reference, indicating increased rigidity, particularly at low temperatures in vacuum and air (Figure 4.13).

The minimum value was obtained with samples modified at 220°C in air, reaching only an 11.49% reduction compared to the reference, similarly to what was reported by Calonego et al. (2012), where thermal modification of Brazilian *E. grandis* in air showed a reduction in *E* of only 8.4% when modified at 220°C.

On the other hand, only the modification of *P. taeda* at 200°C in nitrogen showed a slightly higher *E* than the reference, although not significantly meaningful (Figure 4.13). All other samples showed slight decreases in modulus of elasticity.

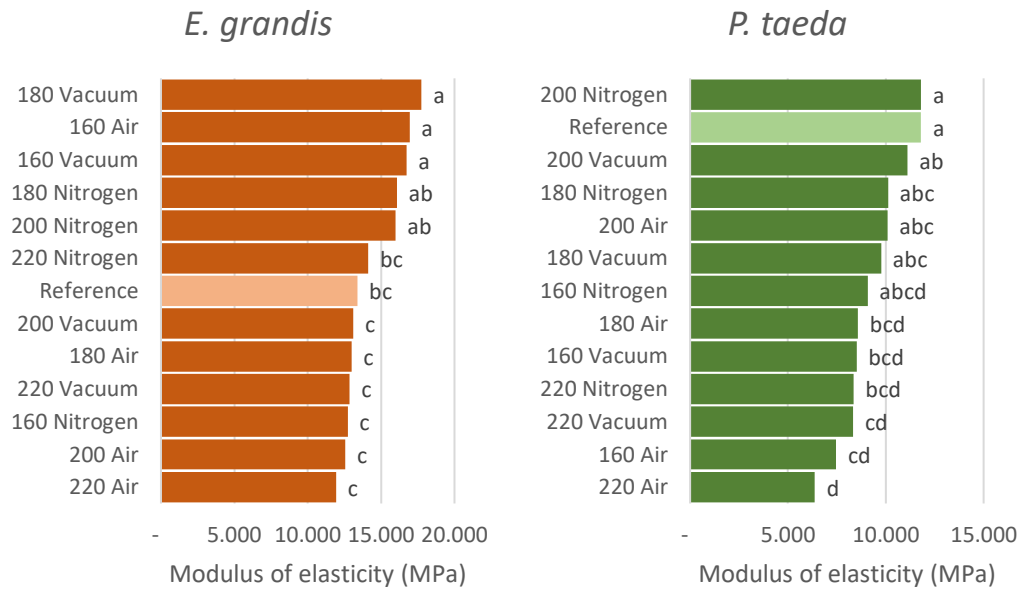

Figure 4.13. Analysis of variance and Tukey test for modulus of elasticity of E. grandis *and* P. taeda*. Each letter means a statistically different group.*

A possible explanation for the relatively unchanged elasticity of thermally modified wood of both species is the compromise between cell wall degradation, which is expected to hinder it, and the already described cross-linking reactions between lignin and the products of thermal degradation as well as the demethoxylation of lignin, which derives in a more condensed lignin structure that might enhance mechanical properties (Wikberg & Maunu, 2004).

4.5.3 ANALYSIS OF COEFFICIENT OF VARIATION OF BENDING STRENGTH AND MODULUS OF ELASTICITY

Table 4.15 and Table 4.16 show the coefficient of variation (CV) of the measurements, as well as the number n, which is the ideal sample size required for a precision of 15% and a confidence level of 90% for the

modulus of elasticity and the bending strength of *E. grandis* and *P. taeda*, respectively.

Table 4.15. Coefficient of variation (CV) and sample size required (n) according to standard deviation for variables bending strength (f) and modulus of elasticity (E) of E. grandis*.*

Temperature	Environment	*f*		*E*	
		CV	n	CV	n
(°C)		(%)			
-	-	10.06	2	12.93	3
160	Vacuum	18.17	4	13.63	3
	Air	7.27	1	5.25	1
	Nitrogen	12.29	2	12.16	2
180	Vacuum	5.82	1	9.52	2
	Air	6.91	1	6.49	1
	Nitrogen	12.47	2	18.51	5
200	Vacuum	9.86	2	4.61	1
	Air	9.56	2	2.10	1
	Nitrogen	16.92	4	12.66	2
220	Vacuum	13.19	3	7.88	1
	Air	16.01	4	9.21	2
	Nitrogen	36.56	17	8.15	1

In relation to the bending strength of *E. grandis*, modifications performed in nitrogen presented the biggest CV among the three treatment environments in all temperatures except for 160°C. At 220°C, CV tends to increase in all environments. as it has been already discussed, heavy degradation of the cell wall took place at said temperature. Therefore, intrinsic variability of wood among the three boards used in each treatment could be responsible for greater variations in the results.

Based on the ideal sample size (n), generally, 3 boards per treatment were enough to overcome the intrinsic variability in wood's properties, except for samples modified in nitrogen at 200°C and 220°C, in

air at 200°C and in vacuum at 160°C. However, future experiments could benefit from an increase in the sample size.

On the other hand, the CV of the modulus of elasticity of untreated *E. granids* is relatively high, which evidences the intrinsic variability that this property has in this specie. The lower CV found at temperatures of 220°C might indicate a homogenization of wood's rigidity. Although *E* did not show a clear trend in its variation with temperature and modification environment, the ideal sample size (n) indicates that 3 boards per treatment condition was a large enough sample (except for the condition modified at 180°C in nitrogen). Thus, variability in the properties of wood is not expected to be the reason for the lack of a clear trend.

Table 4.16. Coefficient of variation (CV) and sample size required (n) according to standard deviation for variables bending strength (f) and modulus of elasticity (E) of P. taeda*.*

Temperature	Environment	*f*		*E*	
		CV	n	CV	n
(°C)		(%)			
-	-	4.26	1	6.34	1
160	Vacuum	16.96	4	19.14	2
	Air	11.24	2	13.13	3
	Nitrogen	24.30	8	28.22	10
180	Vacuum	11.64	2	22.50	7
	Air	19.71	5	10.68	2
	Nitrogen	17.46	4	19.72	5
200	Vacuum	11.83	2	15.11	3
	Air	8.60	1	7.59	1
	Nitrogen	30.71	12	10.88	2
220	Vacuum	8.66	1	11.79	2
	Air	32.50	13	16.34	4
	Nitrogen	28.97	11	9.91	2

The CV of *P. taeda*'s bending strength is significantly increased with thermal modification, in any case it is more than doubled when compared against that of the untreated reference. When compared against *E. grandis*, it shows higher variability in its CV. In this case, it would have been useful to increase the number of boards used per condition.

In relation to the modulus of elasticity of *P. taeda*, similarly to *E. grandis*, at higher temperatures the CV tends to be lower, which might also indicate a homogenization of this property.

4.6 REVERSIBILITY OF CHANGES IN EMC AND DIMENSIONAL STABILITY

The reversibility of the changes in hygroscopicity was studied through the analysis of the sorption isotherm, the EMC and the maximum volumetric swelling (S_{max}) of *E. grandis* subjected to thermal modification at 200°C in the three environments, along with an unmodified reference.

In all tests, a certain degree of reversibility in the enhancement of properties due to thermal modification was observed. EMC increased after the wood was in contact with water, either by Soxhlet extraction or by being soaked in water. Also, maximum swelling of thermally modified wood showed an increase after the water-soaking cycles.

4.7 SORPTION ISOTHERMS

4.7.1 CHANGE IN MASS DUE TO SOXHLET EXTRACTION

Table 4.17 shows the mass loss due to Soxhlet extraction. When compared to the extractive content of both unmodified and modified wood presented in section 4.2 (also presented in Table 4.17), it becomes evident that extraction was not complete. Only a fraction of the extractive content was removed. Firstly, because extraction was performed only with water, not followed by ethanol, with the main objective of resembling what would happen to timber during service, and secondly, because of the lower extraction rate of solid wood when compared against milled wood.

Table 4.17. Extracted mass due to Soxhlet extraction with water and total extractive content of E. grandis *modified at 200°C.*

	Extracted mass	Total extractive content
	(%)	
Reference	0.94	3.93
Vacuum	1.23	7.88
Air	0.85	8.64
Nitrogen	1.09	8.41

4.7.2 FIRST SORPTION ISOTHERM

Figure 4.14 shows the first sorption isotherm at 20°C of the samples tested. As it can be seen in the first portion of the isotherm (from 0% RH to 30% RH), curves do not show the typical sigmoid shape of sorption isotherms (shown in Figure 2.8). This is due to the fact that it was not possible to perform measurements at lower RH than 30% and therefore the first portion of the curve is not accurately represented.

All three samples, both non-extracted and extracted, presented sorption isotherms with lower EMC than that of the reference over all the RH conditions tested.

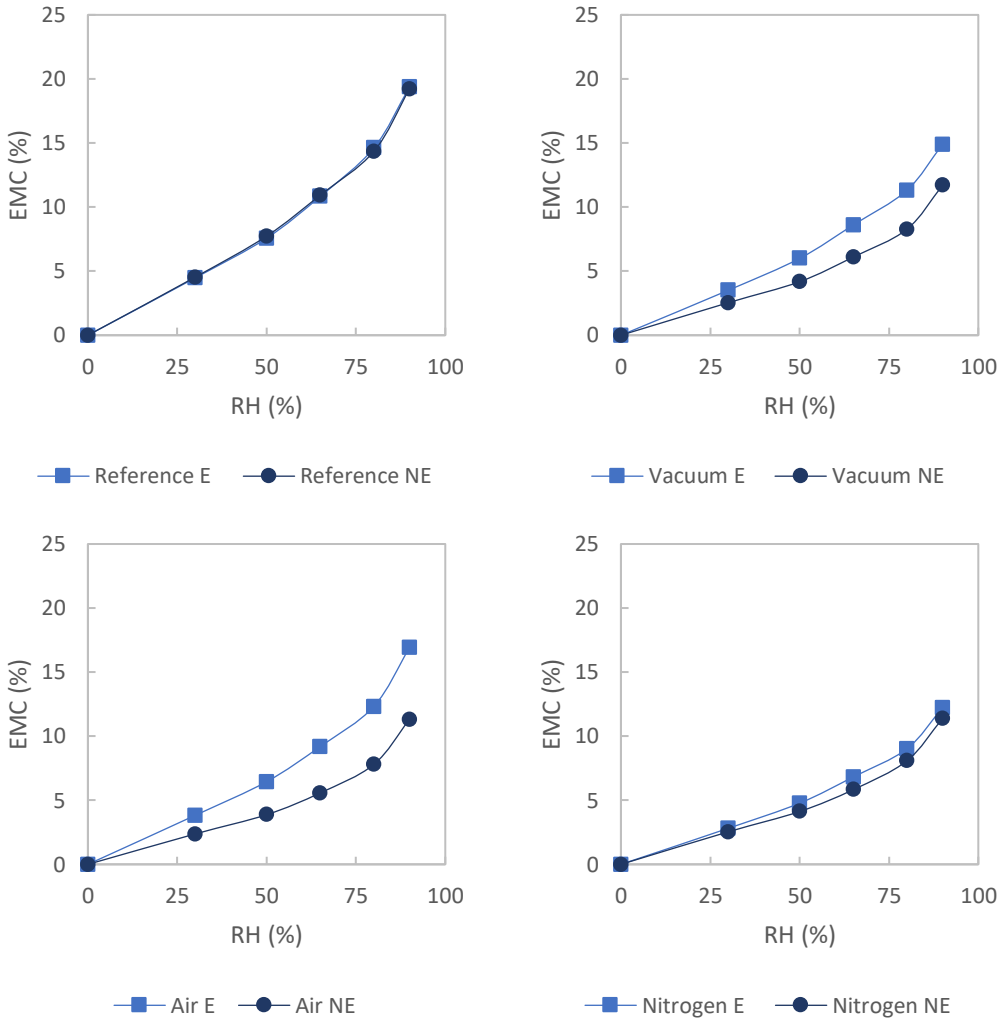

Figure 4.14. First adsorption isotherm at 20°C. ***E****: extracted.* ***NE****: non-extracted.*

The unmodified sample did not show a change in its hygroscopicity after extraction, meaning that the extraction process had no effect on its hygroscopicity. A very similar behavior was observed in the non-extracted samples modified in the three different atmospheres. As it can be seen in

Figure 4.15, the EMC ratio between modified sorption isotherm and that of the reference falls between 0.5 and 0.6. At 90% RH, EMCs of 11.7%, 11.3% and 11.4% were reached when modified in vacuum, air and nitrogen, respectively.

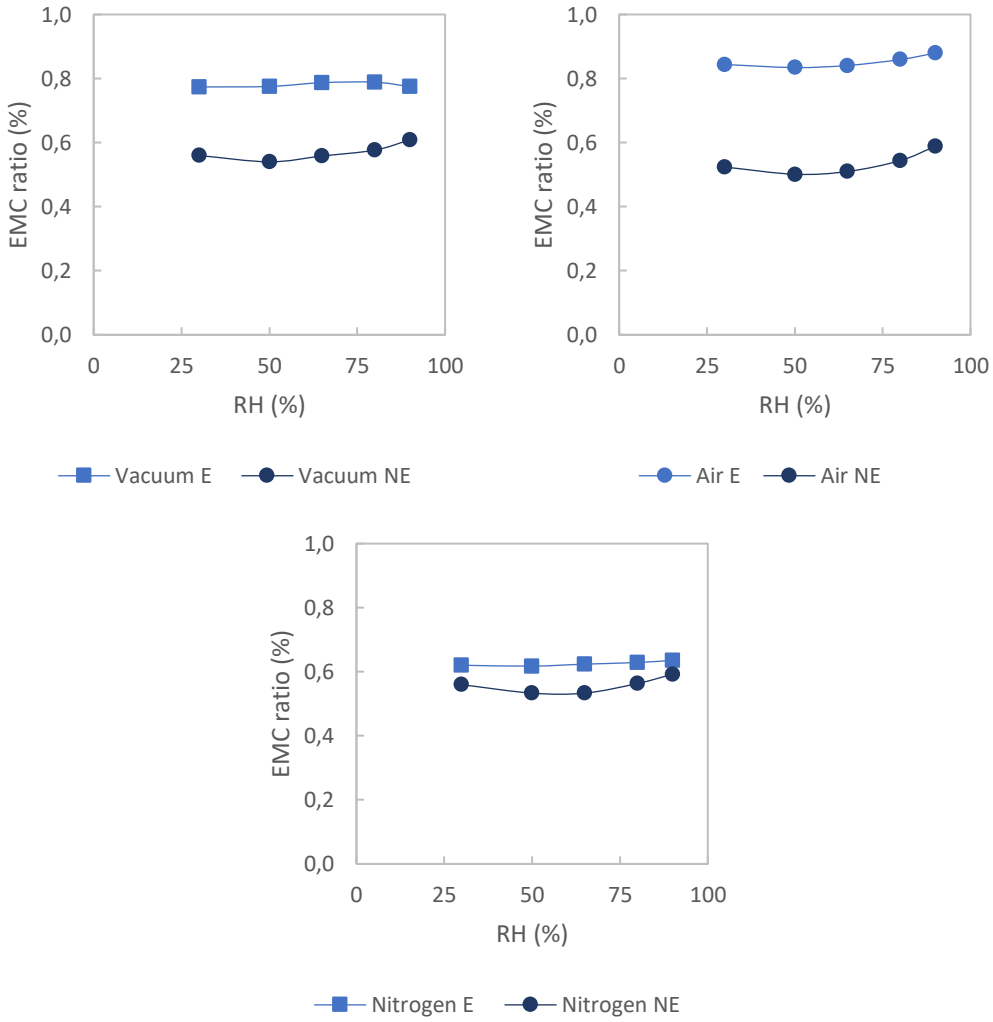

Figure 4.15. Ratio between the EMC of thermally modified samples and non-extracted reference. ***E****: extracted.* ***NE****: non-extracted.*

However, in all three cases, the extraction process had negative effects on the improvements in hygroscopicity observed in non-extracted samples. The condition tested in air presented the most reversibility, in all

measured points, the EMC ratio was above 0.8, reaching an EMC of 17% at 90% RH. The condition tested in vacuum also presented a high degree of reversibility, consistently increasing the EMC ratio all through the sorption isotherm (between 0.77 and 0.79 in all RH tested). The most consistent behavior when comparing non-extracted to extracted samples was presented by the samples modified in nitrogen, where EMC increased less than 2% throughout the sorption curve, reaching only 12.2% at 90% RH.

The lower xylose content showed by the sample modified in nitrogen (5.13% in nitrogen compared to 8.51 in vacuum and 7.23 in air - Table 4.3) can be regarded as a possible reason for the more permanent reduction of the EMC in said sample. Higher reduction of water-accessible OH groups in the polymer matrix can lead to a more permanent reduction of wood's hygroscopicity.

4.7.2.1 HAILWOOD-HORROBIN MODEL

Table 4.18 shows the main equilibrium constants and results of the Hailwood-Horrobin model. Parameter W (the weight of a wood molecule capable of adsorbing a water molecule) confirms the trend observed in Figure 4.14 and Figure 4.15. Similar results were seen in both references (225 and 238 for non-extracted and extracted samples, respectively), and the condition modified in nitrogen was the one that presented the higher W among the extracted specimens (379). In the case of the non-extracted samples, W was 2.26, 2.68 and 2.46 times bigger than the reference when modified in vacuum, air and nitrogen, respectively. These results are aligned

with what has been reported by Amilivia (2017), where this parameter increased 2.37 times (from 306 in the case of the reference to 728) when *E. grandis* was modified at 200°C for 3 hours in vacuum.

When compared against the reference, both $M_{h,100\%}$ (moisture content associated with the monomolecular layer of water at 100% RH) and $M_{d,100\%}$ (moisture content related to the successive layers of water at 100% RH) were reduced after thermal modification, regardless of being extracted or not.

In the case of non-extracted samples, $M_{h,100\%}$ was reduced to a further extent than $M_{d,100\%}$, in relative terms. This means that the monomolecular layer was more affected than the successive ones, indicating that the amount of water molecules bonded to wood decreased at a higher rate.

In the case of thermally modified and extracted samples, $M_{100\%}$ increased due to extraction, both the monomolecular and polymolecular layers were able to retain more water after extraction. However, reversibility was higher for the monomolecular layer, this is an evidence that the weakening of the chemical bonding between water and wood was not exclusively due to irreversible changes associated with reduction of water-accessible OH groups or hornification of cell wall polymers.

*Table 4.18. Results from the Hailwood-Horrobin model. Equilibrium constants **K_h**, **K_d** and parameter **W** are defined in section 3.12. **$M_{h,100\%}$** is the moisture content associated to the monomolecular layer (hydrate). **$M_{d,100\%}$** is the moisture content associated to the polymolecular layer (dissolved). **$M_{100\%}$** is the total moisture content calculated by the model. **r** is the correlation between the experimental data and the modeled isotherm. **E**: extracted. **NE**: non-extracted.*

Treatment	Extraction	K_h	K_d	W	$M_{h,100\%}$	$M_{d,100\%}$	$M_{100\%}$	r
Reference	**E**	2.02	0.74	238	4.516	21.111	25.626	0.9996
Vacuum	**E**	1.70	0.70	271	3.605	15.395	19.000	0.9993
Air	**E**	2.31	0.76	300	3.814	18.862	22.675	0.9991
Nitrogen	**E**	2.04	0.73	379	2.848	13.119	15.967	0.9990
Reference	**NE**	1.95	0.71	225	4.662	19.937	24.599	0.9990
Vacuum	**NE**	2.78	0.80	509	2.439	14.230	16.669	0.9991
Air	**NE**	3.44	0.83	603	2.213	14.941	17.153	0.9993
Nitrogen	**NE**	3.47	0.81	554	2.399	14.147	16.546	0.9995

4.7.3 DYNAMIC VAPOR SORPTION

Figure 4.16 shows a two-cycle sorption and desorption curve of non-extracted and extracted *E. grandis* modified in nitrogen at 200°C, as well as the hysteresis of each cycle. The first sorption curve of both samples is comparable to the results presented in the preceding section, with a maximum EMC at 95% of 11% and 12% for the non-extracted and extracted samples, respectively.

Interestingly, a big difference in the sorption curve between the first and the second cycle of the non-extracted sample is observed, particularly at RH content between 55% and 85% (peaking at 75%). Although EMC at 95% RH stayed practically unchanged, hysteresis was strongly reduced, going from 3.5% to 2.1% at 75% RH. The hysteresis curve of the second cycle is comparable to those of the two cycles of the extracted sample, where almost no difference in hysteresis was found between the first and second cycle.

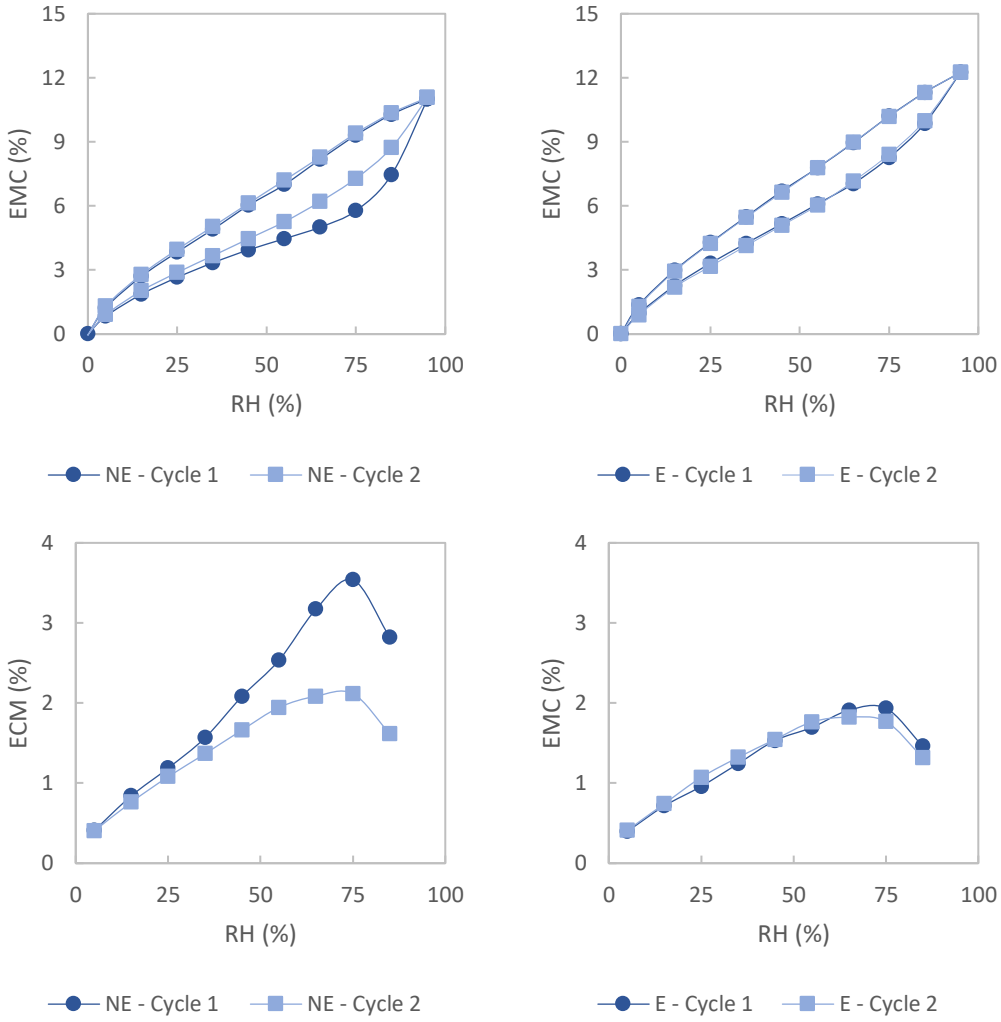

Figure 4.16. Sorption isotherm and hysteresis at 20°C of thermally modified E. grandis *at 200°C in nitrogen.* ***E****: extracted.* ***NE****: non-extracted.*

As the non-extracted sample did not suffer any further processing between thermal modification and the measurement of the sorption isotherm (the sample was never in contact with a high humidity environment after it was taken out from the treatment oven), any stiffness related to the high temperatures and low RH conditions during treatment were still present. Curiously, the high moisture environment of the first sorption and desorption cycle was enough to reverse this behavior, so there was no need

to soak the sample in water to bring about an increase of 1.2% in EMC at 65%. Nonetheless, maximum EMC (at 95% RH) remained constant, thus said high humidity environment was not enough to induce the same changes observed after extraction.

4.8 WATER-SOAKING CYCLES

Table 4.19 shows the mass loss after the water-soaking cycles. When compared against the total extractive content, it is evidenced that most of the extractable compounds still remained in wood after the water-soaking cycles, similarly to what was observed after the water extraction performed for the previous test (Table 4.17).

Table 4.19. Mass los after the three water soaking cycles and total extractive content of E. grandis *midified at 200°C.*

	Dry mass loss	Total extractive content
	(%)	
Reference	0.90	3.93
Vacuum	0.75	7.88
Air	1.15	8.64
Nitrogen	1.14	8.41

Figure 4.17 shows the changes in EMC and S_{max} of the samples in each of the cycles. In all cases, including the reference, EMC and S_{max} increased because of the water-soaking cycles. The reference reached a maximum EMC of 14% at 65% RH in cycle 3, after almost not increasing (0.51%) from cycle 1 to cycle 2. On the contrary, all modified samples greatly increased their EMC from cycle 1 to cycle 2, further increasing in cycle 3, but to a much lower extent. An analogous behavior was observed

in the case of S_{max}, with the reference showing a rise from 17.9% on cycle 1 to 18.8% and 20.6% on cycles 2 and 3, again increasing less from cycles 1 to 2, than from cycles 2 to 3.

Specimens modified in vacuum were the only ones that reached the same EMC as the reference (11.9% in the third cycle of samples modified in vacuum, same as the reference in the second cycle, and 0.5% higher than in cycle 1). All other conditions, either when measuring EMC or S_{max}, samples did not reach the same values of the unmodified and non-soaked reference, meaning that the reversibility was not total, at least after 3 cycles.

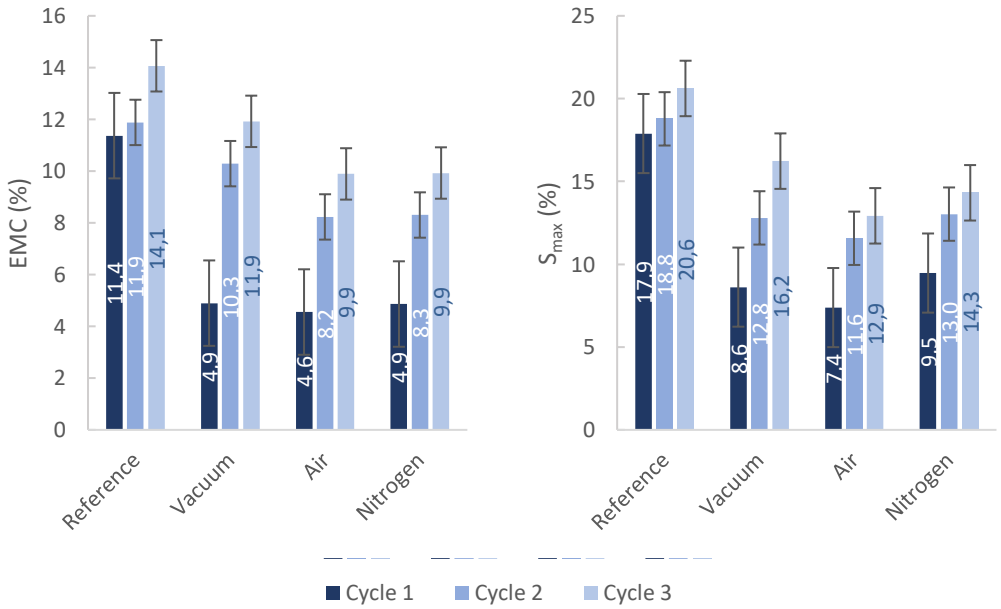

Figure 4.17. EMC measured at 20°C and 65% RH and maximum volumetric swelling (S_{max}) of E. grandis *unmodified and thermally modified at 200°C in vacuum, air and nitrogen.*

In Figure 4.18, EMC and S_{max} values from cycle 1 were fixed to 100 and changes in cycles 2 and 3 are expressed relative to cycle 1. This allows to compare the relative changes that took place in EMC and S_{max} in

comparison to the first cycle between the different modification conditions tested. As expected, the reference fell well below the modified samples. As it was not subjected to any modification whatsoever, properties were not expected to change much after being water-soaked. In both EMC and S_{max}, specimens modified in nitrogen performed better than the other two conditions, as they presented lower reversibility. This goes in alignment with what was observed after Soxhlet extraction.

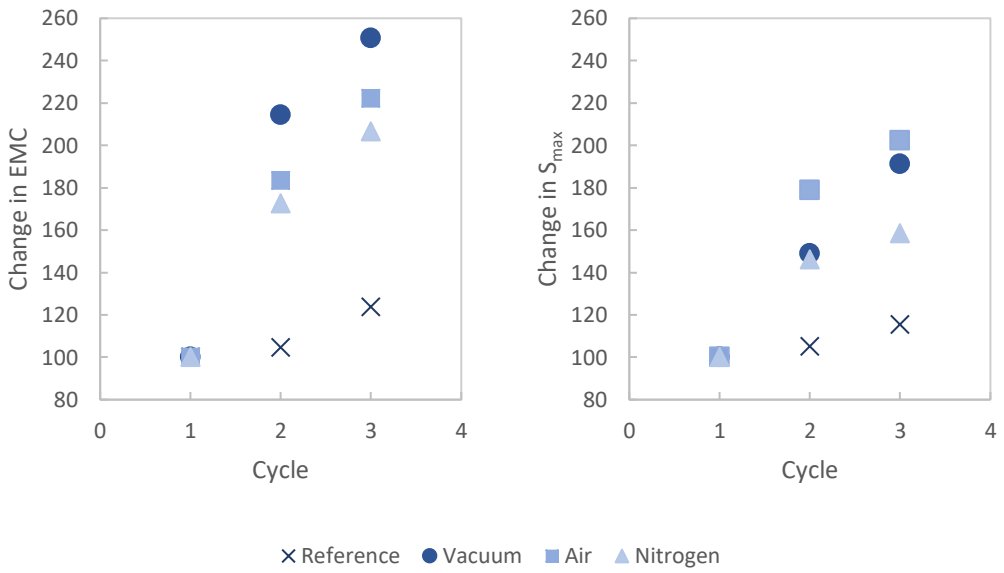

Figure 4.18. Relative changes in EMC measured at 20°C and 65% RH and in maximum swelling (S_{max}) of E. grandis *unmodified and thermally modified at 200°C in vacuum, air and nitrogen. EMC and S_{max} of cycle 1 were fixed to 100.*

Regarding their EMC, specimens modified in vacuum performed worse than those modified in air, showing a 31% and 29% higher increase in the second and third cycles, respectively. This somehow differs with the results of the previous test, where reversibility in EMC at different RH content was greater for samples modified in air. This evidences that different leaching or extracting processes can yield varying results.

In the case of S_{max}, vacuum and nitrogen performed similarly in cycle 2 (increases of 46% and 49%, respectively), while air increased its maximum volumetric swelling by 79%. However, in cycle 3, vacuum kept increasing and located just below air (91% and 102% increase relative to cycle 1, respectively), while wood modified in nitrogen showed much less reversibility, only 13% increase from cycle 2 to cycle 3 (59% increase overall).

5 CONCLUSIONS

Thermal modification changed wood properties, with temperature being a more relevant parameter than heating environment on the effects they had on wood. Overall, higher temperatures led to increased changes in most properties, irrespective of the treatment atmosphere, with lower temperatures being necessary to bring about similar changes in *E. grandis* than in *P. taeda*. In most cases there was no significant difference between the different heating environments tested, so the differences between them were not conclusive.

This technology is an effective method for the modification of the chemical structure of the cell wall, being evidenced by the degradation of the constituents of the hemicelluloses. Cellulose and lignin appear to resist degradation at the temperatures tested in this work, even though some indications of lignin modification were seen.

Significant reduction in the equilibrium moisture content was achieved. Also, dimensional stability of heat-treated wood was increased. However, both properties present certain degree of reversibility, meaning that some changes in these properties are expected if the product is in contact with water or very high humidity environments during its service life. This must be considered when assessing thermally modified wood, as overestimations of the improvements in these properties can be misleading.

Reduction in bending strength cannot be overseen, as even relatively mild conditions derived in a reduction in strength. Nonetheless, this has already been considered by the industry and the applications of thermally modified wood rarely need to withstand heavy loads.

Correlation between mass loss and several other properties, namely degradation of hemicelluloses, equilibrium moisture content and bending strength, was strong, making it a good indicator for intensity of treatment, which can be used at industrial scale for quality control. However, these correlations cannot be used irrespectively of the species being modified, as differences between *E. grandis* and *P. taeda* are of relevance.

5.1 FUTURE WORK

There is need for further work in order to completely understand the effects that this technology has on the wood species currently cultivated in Uruguay for construction purposes, *P. taeda* and *E. grandis*.

A large-scale modification process, or at least one with lower heating rates that emulates the longer heating and cooling times in industrial processes might help uncover some differences between heating atmospheres, as the total duration of the process performed in this work significantly differs from industrial-scale processes.

Even though quantitative analysis suggests that lignin and cellulose are not degraded due to thermal modification, changes are expected to

occur in their chemical structure. The degree of polymerization of cellulose as well as the crystallinity index can help further understand the consequences of the application of this technology in said macro-component. Also, the chemical study of lignin, with determinations such as the molecular weight or the Syringyl to Guaiacyl ratio in *E. grandis* lignin, would help shed some light on the changes on reactivity that lignin undergoes as a result of thermal modification.

Although both degradation of hemicelluloses and reduction in EMC are strong indicators of increased durability of wood against rotting fungi, studies on decay resistance should be performed to validate this hypothesis.

The mechanical tests in this work where performed on small samples, and while results are of high relevance and provide important guidance, they might differ from those of full-scale samples. Also, the measurement of properties like hardness and dynamic strength could be of great value.

As surface properties are expected to change after thermal modification, its wettability will be affected, which will also affect the behavior with adhesives. Testing the performance of different adhesives might help understand the necessary developments that should be made in the adhesives and the gluing process for them to be more applicable to the changes in surface properties.

Finally, most wood properties are expected to change with time. Long term field tests would be of great value to understand the relevance of the changes in performance of thermally modified wood during service.

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