
Doctoral Program in Engineering

Doctoral thesis

# Development of a high-performance structural material from reforested wood of the *Brosimum utile* (Kunth) Oken species from the department of Chocó

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**To my children, siblings, and parents**

**A mis hijos, hermanos y padres**

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# Abstract

The development of high-strength wood-based materials is one of the main challenges facing the wood industry in the face of the growing demand for sustainable materials for advanced engineering applications. Wood is a material derived from forests and in many cases its extraction is a selective and excessive activity that exerts great pressure on the most desirable forest species, since their properties provide better conditions for its use. This would represent a high potential to contribute from an environmental approach to the technological development of the wood industry as a strategy to reduce dependence on the use of threatened forest resources and promote the use of other forest resources that are currently underutilized, such as lesser-known woods of low density and durability.

In current practice, various strategies to increase the strength of low-density wood have been the subject of considerable research, through methods such as densification, although they still face certain limitations in terms of development. These densification methods improve the mechanical properties of wood by first reducing the cell wall strength by physical or chemical methods and then applying mechanical compression. The most significant advances have been achieved by combining treatments such as delignification and densification.

This thesis has focused on the development of a high-performance structural material from low density reforested wood as a strategy to improve woods with low properties and to reduce the compression of the best-known woods. The improvement of woods with low properties would allow the research of new materials with potential applications in different technological sectors. The proposed method consists of a two-stage densification of wood materials, called Hot Isostatic Pressing (HIP), which includes two important areas of research. In the first stage of the study, the material is prepared by partial removal of lignin and hemicellulose, thereby reducing the

compressive strength of the anatomical wood structure. In the second stage, high densification is achieved by hot isostatic pressing in an argon atmosphere. The results obtained indicate that the delignification treatment is a process with non-uniform effects on the removal of lignin/hemicellulose and accumulated minerals due to the anatomical structure of the wood. The results show that the method can achieve almost complete densification of the wood, reaching values up to 1.47 g/cm$^3$, which exceeds the density increases achieved with previous densification methods and any density increase ever recorded for a hardwood species. In comparison, this method can also preserve approximately 35% of the original volume of the wood, compared to other methods that can typically only maintain 20% of the volume. It also shows homogeneous density patterns, stable densification without shape recovery and improved mechanical properties. This research also examines the effect of densification on the natural decay processes of HIP-densified Sande wood in comparison with non-densified Sande, Andiroba and Choiba specimens, demonstrating its effectiveness in achieving higher natural durability of densified wood in low adverse climates (temperate - dry).

Ultimately, the two-stage densification process proposed in this thesis contributes to the improvement of low-density woods by developing a high-performance structural material from the partial delignification and isostatic densification of wood. This suggests a promising potential for new HIP processed wood materials.

# Resumen

El desarrollo de materiales de alta resistencia a base de madera es uno de los principales retos que afronta la industria de la madera ante la creciente demanda de materiales sostenibles para aplicaciones de ingeniería avanzada. La madera, es un material derivado de los bosques y en muchos casos su extracción es una actividad selectiva y desmedida que ejerce gran presión sobre las especies forestales más deseables, ya que sus propiedades brindan mejores condiciones para su uso. Esto representaría un alto potencial para contribuir desde un enfoque medioambiental al desarrollo tecnológico de la industria de la madera como estrategia para reducir la dependencia del uso de recursos forestales amenazados y promover el uso de otros recursos forestales que actualmente son poco aprovechados como las maderas menos conocidas, de baja densidad y durabilidad.

En la práctica actual, varias estrategias para aumentar la resistencia de la madera de baja densidad han sido objeto de considerable investigación, a través de métodos como la densificación, aunque todavía se enfrentan a ciertas limitaciones en términos de desarrollo. Estos métodos de densificación mejoran las propiedades mecánicas de la madera reduciendo primero la resistencia de la pared celular por métodos físicos o químicos y aplicando después compresión mecánica. Los avances más significativos se han conseguido combinando tratamientos como la deslignificación y densificación.

Esta tesis se ha centrado en el desarrollo de un material estructural de alto desempeño a partir de madera reforestada de baja densidad como estrategia que contribuye a potenciar maderas con bajas propiedades y reduce la presión que se ejerce sobre las maderas más conocidas. Potenciar las maderas de bajas propiedades permitiría trabajar en la investigación de nuevos materiales con posibilidades potenciales de aplicación en diferentes sectores tecnológicos. El método propuesto

consiste en la densificación en dos etapas para materiales de madera denominado prensado isostático en caliente (HIP), el cual abarca dos importantes áreas de investigación. La etapa inicial del estudio prepara el material mediante la eliminación parcial de lignina y hemicelulosa, lo que permite reducir la resistencia a la compresión de la estructura anatómica de la madera. En la segunda etapa, se consigue una alta densificación mediante prensado isostático en caliente en una atmósfera de argón. Los resultados obtenidos indican que el tratamiento de deslignificación es un proceso con efectos no uniformes sobre la eliminación de lignina/hemicelulosa y los minerales acumulados debido a la estructura anatómica de la madera. Los resultados demuestran que el método puede lograr la densificación casi completa de la madera, alcanzando valores de hasta 1.47 $g/cm^3$, lo que supera los incrementos de densidad alcanzados con los métodos de densificación anteriores y cualquier incremento de la densidad jamás registrado para una especie de madera dura. En comparación, este método también puede preservar alrededor del 35% del volumen original de la madera, en comparación con otros métodos que normalmente sólo pueden mantener el 20% del volumen. Además, muestra patrones de densidad homogéneos, densificación estable sin recuperación de la forma y propiedades mecánicas mejoradas. Esta investigación también revisa el efecto de la densificación en los procesos de descomposición natural de la madera de Sande densificada mediante HIP en comparación con especímenes no densificados de Sande, Andiroba y Choiba, demostrando su eficacia para obtener una mayor durabilidad natural de la madera densificada en clima poco adverso (templado – seco).

En definitiva, el método de densificación de dos pasos propuesto en esta tesis contribuye a potenciar maderas de baja densidad mediante el desarrollo de un material estructural de alto desempeño a partir de la deslignificación parcial y densificación isostática de la madera. Lo que sugiere un potencial prometedor para los nuevos materiales de madera procesados con HIP.

# List of Products

The following papers and conferences are the main products of this doctoral thesis:

## Journal papers.

1. J.C. Maturana, P. Guindos, J. Lagos, C. Arroyave, F. Echeverría and E. Correa. Two-step hot isostatic pressing densification achieved non-porous fully-densified wood with enhanced physical and mechanical properties. Scientific Reports, (2023) 13:14324.

## Oral presentations at conferences

J.C. Maturana. “Desarrollo de un material estructural de alto desempeño a partir de madera reforestada de la especie Brosimum Utile (Kunth) Oken del departamento del Chocó” in Encuentro Internacional de Educación en Ingeniería ACOFI (2022), Cartagena, Colombia.

J.C. Maturana, C. Arroyave, F. Echeverria, A. Hurtado, E. Correa. “Desarrollo de un material estructural de alto desempeño a partir de madera reforestada de la especie Brosimum Utile (Kunth) Oken del departamento del Chocó” in Once Congreso Internacional de Materiales “Materiales para la vida” (XI CIM 2022), Santa Marta, Colombia.

J.C. Maturana, E. Correa, C. Arroyave, F. Echeverria. “Desarrollo de un material estructural de alto desempeño a partir de madera reforestada de la especie Brosimum Utile (Kunth) Oken del departamento del Chocó” in 2do Encuentro de Ingeniería, Innovación y Sostenibilidad, Medellín, Colombia.

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# Nomenclature

Acronyms and abbreviations

| | |
|---|---|
| % | Percentage |
| °C | Degrees celsius |
| ATR | Attenuated total reflectance. |
| C1 | Condition 1 |
| C2 | Condition 2 |
| cm | Centimeter |
| CR | Compression ratio |
| DC | Durability class |
| DDW | Densified-delignified wood |
| DI | Deionized water |
| DNW | Densified natural wood |
| DW | Delignified wood |
| EMC | Equilibrium moisture content |
| Fig. | Figure |
| FT-IR | Fourier transform infrared |
| g | Gram |
| h | Hour |
| HIP | Hot isostatic pressing |
| HP | High-pressure |
| L | Longitudinal |
| M | Molar mass |
| MC | Moisture content |
| mm | Millimeter |
| MOE | Modulus of elasticity |
| MOR | Modulus of rupture |
| MPa | Megapascal |
| NTC | Colombian Technical Standard |
| NW | Natural wood |
| Psi | Pounds per square inch |
| R | Radial |
| RH | Relative humidity |
| Sande-D | Densified Sande |
| Site 1 | L1-Medellín |
| Site 2 | L2-Quibdó |
| SEM | Scanning electron microscopy. |
| T | Tangential |
| $T_o$ | Initial time |
| $T_1$ | Final compression |
| $T_F$ | Final time |
| TH | Thermohydro |
| THM | Thermo-hydro-mechanical |
| $T_i$ | Initial compression |
| TM | Thermo-mechanical |
| TS | Thickness swelling |
| VTC | Viscoelastic thermal compression |
| WA | Water absorption |
| WL | Weight loss |
| µg | Microgram |

# Chapter 1

## 1 Introduction

This chapter provides the necessary background for this research, followed by a statement of the thesis objectives and key contributions. It then outlines the thesis framework, clearly defining the scope of the research.

## 1.1 Background

Throughout history, our relationship with materials has evolved. Initially, we relied solely on naturally occurring materials. Later, we developed transformation techniques like ceramics and metalworking to create materials with superior properties, such as a high strength-to-weight ratio or improved resistance to corrosion. In modern society, the focus has shifted towards designing materials with specific functions in mind. This approach leverages the well-understood connection between a material's structure and its properties. Wood exemplifies this concept perfectly. As a natural material with a long history of use in construction, furniture, and tools, wood has also been subjected to various modification techniques. These modifications unlock properties and functionalities not typically found in unmodified wood. Recent research efforts have yielded exciting advancements in wood modification, such as densified wood for improved strength (Song et al. 2018), transparent wood for unique visual applications (Wang et al. 2023), superflexible wood for innovative building materials (Song et al. 2017), mesoporous and hydrophobic biocomposites (Fu et al. 2018), and the development of a multifunctional building material that blocks sound and retards heat loss in buildings (Zhao et al. 2023). The driving force behind these innovations is the growing demand for wood-derived materials that address contemporary concerns like carbon footprint reduction and sustainable industrial growth (Chen et al. 2020a).

The properties of wood significantly influence its suitability for various applications. For each property, there is a stimulus capable of eliciting a response. For example, mechanical properties describe how wood deforms under load (William D. Callister 2009). Applying a compressive force to wood increases its density by reducing the spacing between wood fibers (Samuel J. Record, M.A. 1914). This demonstrates a relationship between wood's structure and its properties. Understanding this structure-property relationship is crucial for designing modern engineered wood products, as wood's physical and mechanical properties stem from its hierarchical cellular structure.

Wood's ultrastructure consists of the cell wall, primarily composed of cellulose, hemicellulose, lignin, and pectin (Gibson 2012). Cellulose forms microfibrils – the main structural element – whose orientation within the cell wall matrix influences wood's strength and stiffness (Gibson 2012; Chen et al. 2020a). These properties are key determinants of a wood's behavior from the nanoscale to the macroscale (Gibson 2012; Stokke et al. 2014). At the cellular level, density variations occur due to differences in cell wall thickness and composition. Softwoods generally have simpler cellular anatomy than hardwoods, with two main cell types: tracheids and parenchyma. Hardwoods have a more complex structure with fibers, vessels, and parenchyma. Fibers, with their thick cell walls, provide mechanical strength. This structural difference often results in lower densities in softwoods compared to hardwoods. Wood density is classified as: low (<0.40 g/cm$^3$), medium (0.40-0.75 g/cm$^3$), and high (>0.75 g/cm$^3$) (Ruffinatto and Crivellaro 2019), the limit being the cell wall density (=1.5 g/cm$^3$) (Gibson 2012). The anatomical composition and density of wood can be altered through ultrastructural modification (J.M.Dinwoodie 2004; Rowell 2005; Gibson 2012; Stokke et al. 2014).

Wood, in this context, is a non-homogeneous material with a complex structure, as shown in Figure 1.1. Due to its natural variability, wood undergoes modification processes to achieve more standardized features and properties. This approach aims to develop new bio-based materials that meet society's growing demand (Callum Hill 2006; Navi and Sandberg 2012). Materials that contribute to the preservation of forest ecosystems that host a large part of the planet's biodiversity and motivate the reduction of the pressure exerted on the best-known woods, by promoting the use of lesser-known timber species, such as lower-density woods. However, lesser-known timbers have limitations of use associated with low density and durability (Skyba et al. 2009; Frey et al. 2018). Density is one of the most important properties of materials and, in particular, in wood, because it is closely related to most of the physical and mechanical properties that determine their application and performance. Therefore, in order to achieve the high-performance materials demanded by modern society, low density wood species must be modified.

One of the great advantages of wood is that its properties can be designed to suit application conditions (Ashby and Jones 2013), especially, starting from density (Dömény et al. 2018). Modification methods that improve the limitations of wood properties by increasing density are mechanical compression, chemical densification by filling the space in the cell structure with a chemical substance, or by a combination of mechanical and chemical methods (Luan et al. 2022). Densified wood, also known as high-density wood or modified wood, is a type of engineered wood that has been treated with a combination of heat, pressure, and/or chemicals to increase its density, strength, and durability. Densified wood has several advantages over traditional wood and other building materials, such as strength, durability, and resistance to fire and moisture.

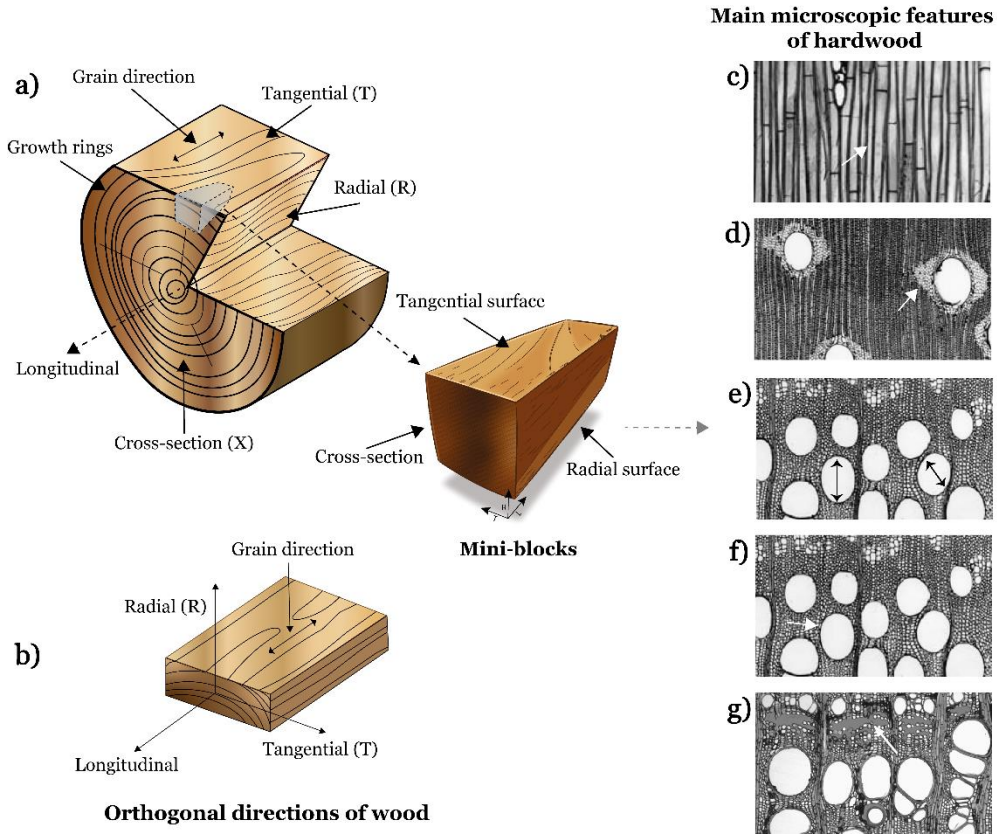


*Figure 1-1 Schematic illustration of the main anatomical features observed in some woods. a) and b) scheme showing the three main planes recognized in wood, cross-section, or transverse (X), radial (R) and tangential (T) planes or surfaces. Main anatomical characteristics of the woods studied c) fibers, d) parenchyma, e) lumens, f) vessels, g) intercellular canals.*

Thermo-hydro-mechanical (THM) compression is the most widespread technique to modify wood by mechanical compression, it is carried out by different stages including softening of the cellular structure, transverse compression, and blocking of the deformed structure (Sadatnezhad et al. 2017; Cabral et al. 2022). This method resorts to the effects of temperature, humidity, and mechanical action to increase the wood density reaching partial values up to 1.29 g/cm$^3$ (Kutnar et al. 2021). Through this method, with the increase in density, several studies were able to increase properties such as hardness by more than 90% or three times with respect to the control sample, and compressive strength increased between 3 and 20 times (Skyba et al. 2009; Rautkari et al. 2013; Bao et al. 2017). Resistance to rotting by biological agents (white and brown rot fungi) has also been increased by combining densification with thermal post-treatment, achieving higher rotting effects in control woods between 24.90 and 31.32% concerning densified and thermally post-treated samples (Pelit and Yalçın 2017). Thermomechanical compression (TM) is another thermal compression technique, usually performed by preheating, conditioning, and hot pressing at temperatures reaching up to 180 °C, and subsequent cooling below 100 °C. These procedures include the use of modified uniaxial presses to raise the temperature (Navi and Girardet 2000). Viscoelastic thermal compression (VTC) uses a continuous pressing machine (Sadatnezhad et al. 2017) to compress the softened wood using heat and steam (Luan et al. 2022). With this method, densities up to 1.4 g/cm$^3$ (Kamke and Rathi 2011) are achieved; however, limitations prevail such as non-uniform density patterns (Kutnar et al. 2009), the porosity of the wood does not disappear completely and is limited to the treatment of laminated wood (Kutnar et al. 2009; Kamke and Rathi 2011; Standfest et al. 2013). An increase in wood density has also been demonstrated by combining two wood treatment processes: 1) plasticization by electromagnetic irradiation and, 2) hydraulic press with heating plates. He succeeded in modifying the density in European beech samples, achieving an increase between 41 and 55% for radially and tangentially densified samples (Dömény et al. 2018). However, the cell wall collapse was partial, so elastic recovery effects were present. Densification processes combined with a thermal modification treatment have been

shown to increase the density of Scots pine wood up to a 50% compression factor and double the hardness while reducing the shape recovery of densified wood to below 1% (Laine et al. 2016).

Another method of densification of wood is by isostatic compression technique. Trenard Y., (1977) studied isostatic compressibility in hardwoods (beech) and softwoods (spruce and Scots pine), using a mercury medium for compression of the wood anatomical structure, allowing an increase in density and improving mechanical properties. Similarly, high-pressure (HP) densification can compress the wood structure at room temperature in a short time using isostatic pressure generated by water (Li et al. 2016; Luan et al. 2022). However, densification with this method is limited to 1.0 g/cm$^3$, thus showing limited increases in mechanical properties (Li et al. 2016; Yu et al. 2017). Blomberg, J., and Persson (2004) used the semi-isostatic compression technique, to densify Scots pine (softwood) using oil as the compression medium, achieving an increase in density of up to 70% and thus an improvement in mechanical properties (Blomberg 2005; Blomberg et al. 2006). However, the density increase has been limited up to 1.0 g/cm$^3$ (Blomberg 2005; Blomberg et al. 2006).

Recognizing the limitations of single-approach densification – such as non-uniform density and incomplete cell wall collapse – researchers have shifted their attention to combined techniques. Integrating chemical pretreatment with mechanical modification offers a promising alternative (Cabral et al. 2022). Specifically, chemicals aid in softening the wood by removing lignin, making wood more pliable for compression (Frey et al. 2018). This enhances the effectiveness of densification, improving not only mechanical strength but also addressing durability concerns (Shams et al. 2005; Frey et al. 2018; Shi et al. 2020; Jakob et al. 2020).

Densified wood holds immense promise for the future, but overcoming challenges like scaling up production cost-effectively will be key for widespread adoption. With its strength, durability, sustainability, and aesthetic appeal, densified wood has the potential to revolutionize the construction industry, replacing less sustainable materials in structural applications and offering

innovative solutions in other diverse scenarios. Figure 1.2 presents an illustration of specimens during mechanical testing.

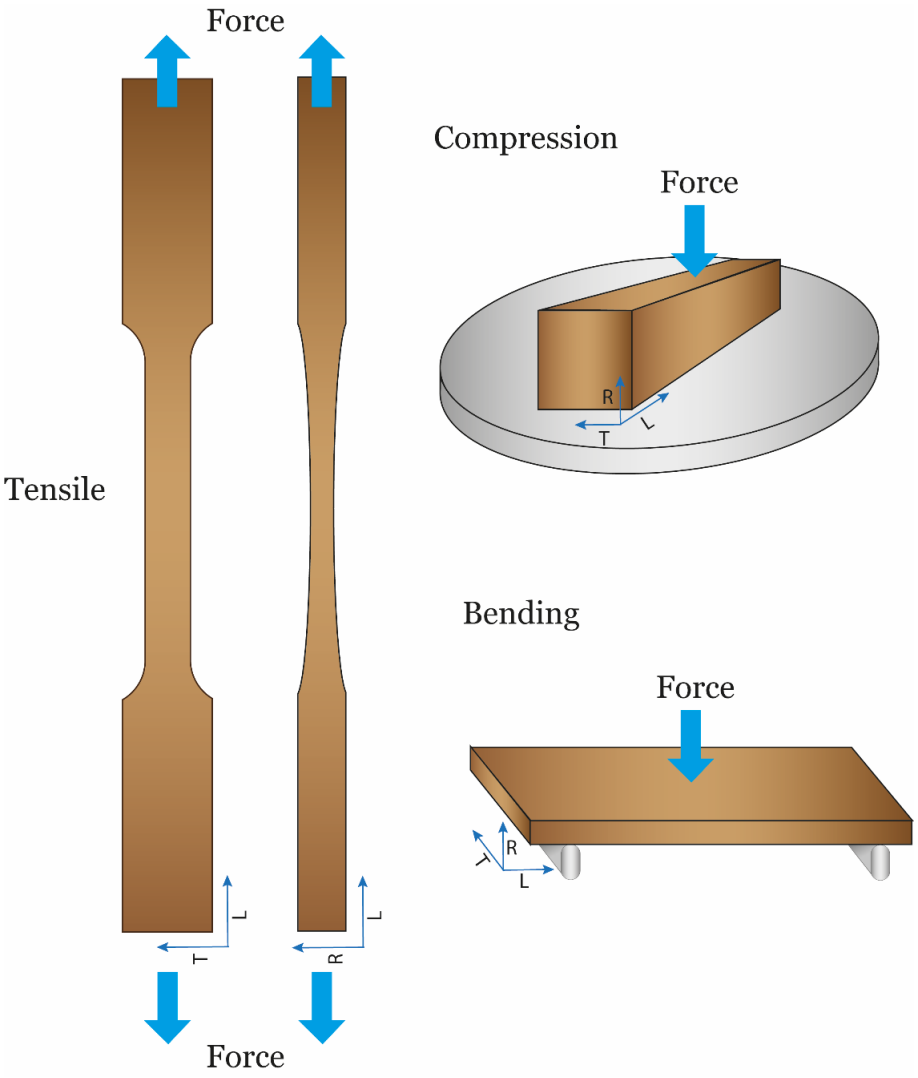


*Figure 1-2 Schematic illustration of specimens during mechanical tests.*

## 1.2 Objectives

### 1.2.1 General objectives

The main objective of this thesis is to develop a set of processes to obtain a natural structural material with improved physical, chemical and mechanical properties from the equiaxial densification of reforested wood of the *Brosimum utile* (Kunth) Oken species from the Department of Chocó.

### 1.2.2 Specific objectives

In order to achieve the main objective mentioned above, a set of three specific objectives has been defined.

- To define a delignification procedure for *B. utile* samples based on the identification of their main ultrastructural components as a pre-treatment for their subsequent densification.
- To establish an equiaxial pressure procedure under temperature, pressure, and time parameters to improve the mechanical properties of partially or totally delignified *B. utile* samples.
- To evaluate the physical and mechanical properties, as well as the resistance against to the attack of biological degradation agents of the obtained structural material.

## 1.3 Main contributions

In today's world, the focus on environmentally friendly materials like wood is fueling research for novel applications. Wood, one of the most abundant biomaterials, offers vast potential for the development of high-performance, functional wood-based products. Densification, a process that modifies wood structure to enhance its properties, is a particularly promising area of study for structural materials. However, further research is needed to fully optimize this technology. This thesis explores the development of a high-performance structural wood-based material using a novel densification strategy. It combines mechanical compression with a chemical pre-treatment to remove lignin, a component that hinders compression. Chapter 2 investigates how the unique pore structure and hierarchical organization of wood (i.e., arrangement of cells and cell walls) affect the efficiency of this pre-treatment. Chapter 3 introduces a two-step densification process involving partial delignification followed by hot isostatic pressing (HIP) in an argon atmosphere. This innovative approach offers several advantages, including a completely densified non-porous wood with values close to those of the cell wall density. Chapter 4 then evaluates the biological resistance of the densified wood under simulated decay conditions representing two distinct climates. The results demonstrate enhanced decay resistance, particularly in drier temperate environments, suggesting potential applications for outdoor construction, landscaping, and agriculture, among others.

## 1.4 Outline

This Ph.D. thesis explores the development of advanced bulk wood densification techniques for creating high-performance, sustainable structural materials. My research focuses on selected tropical hardwoods. I investigate how various treatment conditions influence the densification process and how to optimize the resulting material properties. Detailed analysis of the collected data, along with key experimental findings and conclusions, are presented in the following chapters.

This doctoral thesis comprises five sequential chapters, each addressing specific aspects and objectives related to my research focus:

- **Chapter 1**: this initial chapter provides essential background information on wood modification, outlines the research objectives, and highlights the thesis's primary contributions. Additionally, it presents a detailed outline of the full thesis structure.
- **Chapter 2**: Alkaline Delignification for Sustainable Tropical Hardwood Modification: This chapter explores the potential of using alkaline delignification as a sustainable pre-treatment method to enhance the properties of tropical hardwoods for materials development.
- **Chapter 3**: Enhancing Properties Through Two-Step Hot Isostatic Pressing: In this chapter, I investigate an innovative two-step densification approach that combines hot isostatic pressing with a unique pre-treatment. My findings demonstrate significant improvements in the wood's physical and mechanical properties.
- **Chapter 4**: Assessing Natural Durability of Densified Wood: This chapter focuses on evaluating the resistance of densified B. utile wood to decay organisms in real-world conditions. The results will offer insight into its potential service life in outdoor environments.
- **Chapter 5**: Conclusions and Future Directions: This final chapter integrates the findings from the previous chapters to evaluate the overall success of my research objectives. I will present key conclusions, reflect on the broader implications of this work, and provide recommendations for future avenues of research. Additionally, this chapter will include a merits section highlighting publications and conference presentations resulting from this thesis.

# Chapter 2

## 2 Alkaline Delignification of Tropical Hardwoods: A promising Approach for Sustainable Material Development

The content of this chapter corresponds to the author's version of the article submitted for publication under the same name. In this chapter, the study of the delignification procedure corresponding to the first partial objective is carried out.

# Alkaline Delignification of Tropical Hardwoods: A Promising Approach for Sustainable Material Development

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## 2.1 Abstract

Wood delignification is a promising approach for developing sustainable materials from tropical hardwoods. This study investigated the uniformity and efficiency of partial alkaline delignification of three commercially important tropical hardwoods (Andiroba, Sande, and Choiba) using a mixed aqueous solution of sodium hydroxide and sodium sulfite ($NaOH/Na_2SO_3$) as a pretreatment for densification. The effects and distribution of the solution under the influence of the anatomical features of each hardwood were analyzed using FT-IR, optical microscopy, and SEM. The process resulted in the partial removal of lignin and hemicellulose in varying proportions between the center and ends of the wood. This reduction in lignin and hemicellulose content led to a decrease in MOE, MOR, and hardness of the delignified wood. Additionally, the results suggest that sodium accumulation in the wood structure may also modify its mechanical properties. The relationship between the chemical treatment and the anatomical characteristics of the wood species was found to influence delignification, which in turn affected the effectiveness of densification and subsequent compression. The findings of this study suggest that alkaline delignification is a promising approach for developing new materials from tropical hardwoods, but further research is needed to optimize the process and minimize the negative impact on mechanical properties.

**Keywords:** Partial delignification, wood chemistry, tropical hardwoods, wood modification, anatomical structure.

## 2.2 Introduction

It is well known that anatomical features of wood (cell length, cell wall thickness, vessel diameter, ray type and frequency, among others) are closely related to its density, mechanical properties, and therefore, its industrial applications (Luan et al. 2022; Cabral et al. 2022; Jakob et al. 2022b). For instance, longer cells and thicker cell walls result in denser wood, while shorter cells and

thinner cell walls result in less dense wood. In addition, larger vessels result in weaker and less stiff wood, while smaller vessels result in stronger and stiffer wood. Regarding its industrial applications, dense woods with straight grain are often used for structural applications, such as beams and posts. In contrast, woods with open pores and low density are often used for decorative applications, such as veneer and flooring (Luan et al. 2022; Cabral et al. 2022; Jakob et al. 2022b). In addition to the above, it is common to carry out different technological processes with the aim of improve the durability, strength, workability, and dimensional stability of wood. Among these processes is the densification of wood which is a process that increases the density of wood by removing voids and compressing the cell walls through different techniques, such as compression, use of heat and steam, or a combination of all of these (Chen et al. 2020a; Cabral et al. 2022; Jakob et al. 2022b).

Within the densification process, delignification is used as a pretreatment technique for softening the cell wall of the wood (Jakob et al. 2022b). The pretreatment removes part of the lignin in wood by accessing the polymeric matrix of lignin, hemicellulose, and cellulose in the ultrastructure (Maturana et al. 2023). In the process of extracting lignin from the wood cell wall to disintegrate the lignocellulosic structure into its fibrous components, the process of depolymerization of wood is complex due to the high variability in their chemical composition (Kumar et al. 2021). Industrially, the most used methods for removing lignin are impregnation with sulfite and alkaline solutions, both of which are classified as chemical solvents that reduce the rigidity of the lignocellulosic structure (Jamaldheen et al. 2022). For example, in the major chemical pulping process used in the world today, about 90% of lignin is removed in the Kraft process which involves the digestion of wood chips (Brännvall 2017). Alkaline reagents derived from the hydroxyl of sodium, potassium, calcium, and ammonium salts are also used (Kumar and Sharma 2017). The most used alkaline reagent for the pretreatment is sodium hydroxide, this is an effective chemical agent as it can expose cellulose to a greater degree (Rabemanolontsoa and Saka

2016), is selective to dissolve lignin and hemicellulose, retains cellulose, and increases wood porosity (Kim et al. 2016). Sodium hydroxide has been widely used to develop different versatile materials and products (Song et al. 2018). The effects of minerals impregnation within wood cell walls, associated with the ions and water uptake at molecular, originate mechanical damage by the accumulation of ions that are crystallization (Mi et al. 2020).

On the other hand, in the mixed aqueous solution of sodium hydroxide and sodium sulfite, lignin removal is achieved by complex chemical reactions generated by the encounter of $NaOH/Na_2SO_3$ aqueous solution with the monomeric lignin units (Li et al. 2021). Sodium hydroxide breaks the ether and ester linkages of lignin-carbohydrate complexes (LCC) and the ester and carbon-carbon (C-C) linkages of lignin molecules (Kim et al. 2016). $Na_2SO_3$ contributes to lignin and hemicellulose dissolution, decreasing the process duration (Kim et al. 2020b).

Recently, it was reported that a reduction of 45% of lignin is optimal for the densification process since an excess of lignin removal generates collapsed wood cell walls as the wood becomes more porous and less rigid. By contrast, with the deficient or partial remotion of lignin, there is elastic recovery after the densification process (Song et al. 2018). However, to the best of our knowledge, there are few studies about the effect of non-uniform removal of the lignin components and its relation to the anatomical structure of wood during the delignification process. It is expected that insufficient impregnation conducts to non-uniform delignification, with the wooden piece surface being delignified to a higher extent than the wood center, which can generate that the solution unreacted or partially reacted with wood (Brännvall 2017). Pretreatment with chemicals followed by densification has led to improved mechanical performance of natural wood (Song et al. 2018). Hence, pretreatment is necessary before densification to ease the compression process (Gondaliya et al. 2023). Nevertheless, chemical pretreatment being heterogeneous, can lead to non-uniform densification, and the densified wood is less mechanical stable (Jakob et al. 2022b; Maturana et

al. 2023; Gondaliya et al. 2023). Most existing methods result in incomplete densification and lack dimensional stability, particularly in response to humid environments (Song et al. 2018).

There is a lack of information about the non-homogeneous delignification ratio in relation to the type of the anatomical structures as vessels, rays, and fibers that influence wood species in the delignification process (Brännvall 2017). Even less information is available on the non-homogeneous delignification ratio with the type of anatomical structure. Although few reports address the influence of the vessels, rays, and fibers in the delignification, it is not is related to the delignified wood used in the densification process. The effect of heterogeneous delignification rate and levels have been detected from wood chips on Kraft pulping process (Brännvall 2017). Despite the use of chemical delignification to improve wood's mechanical properties, the materials science and engineering community has not focused on how wood's structure affects the movement of fluids (chemical solvents) through its tissues, penetration into ray cell channels, and the resulting variation in delignification across wood pieces.

In this work, three selected tropical hardwood species *Brosimum utile* (Sande), *Carapa guianensis* (Andiroba), and *Dipteryx oleifera* (Choiba) different densities were compared. This study compares the anatomical features, chemical composition, and delignification process of three types of wood. It also examines the ash content and partial removal of lignin and hemicellulose from the natural wood at the ends and center of each specimen. Delignification was performed using an alkaline chemical treatment with a mixed aqueous solution of $NaOH/Na_2SO_3$ by digesting the wood. This caused the collapse of the cell walls, so it is necessary to investigate its effect on the underlying relationship between the structure and mechanical properties of these three wood species after lignin removal.

## 2.3 Materials and methods

### 2.3.1 Materials and chemicals

Sande (*Brosimum utile*), Andiroba (*Carapa guianensis*), and Choiba (*Dipteryx oleifera*) tropical wood species were used for the delignification process. The dimensions of the three specimens were set at 30 × 30 × 100 $mm^3$ (radial × tangential × longitudinal) and they were kiln-dried at a constant weight at 103 °C for 24 h before use. Sodium hydroxide (≥ 99,0%) and sodium sulfite (≥ 97%) were purchased from Merck (Canada). Deionized (DI) water was used as the solvent to process the wood. All chemicals were used as received.

### 2.3.2 Analysis of delignified wood

Firstly, the delignification process with alkaline solution reported by Song et al. (2018) was carried out. The specimens were immersed in a boiling mixed aqueous solution of 2.5 M, NaOH and 0.4 M $Na_2SO_3$ at 90 °C for 7 h, followed by immersion in boiling DI water several times to remove the excess of chemical reagents. Next, the delignified wood (DW) was oven-dried at 50 °C for one week at constant weight. Then, the DWs were evaluated from specimens divided into two sections: *ends* and *center,* respectively, as shown in Figure 2.1. The limits were established as the perimeter area of the center of the cross-sectional bulk wood. From the specimen in longitudinal direction, the 15 mm thick ends were extracted. The center was calculated as the excess material from the end removal.

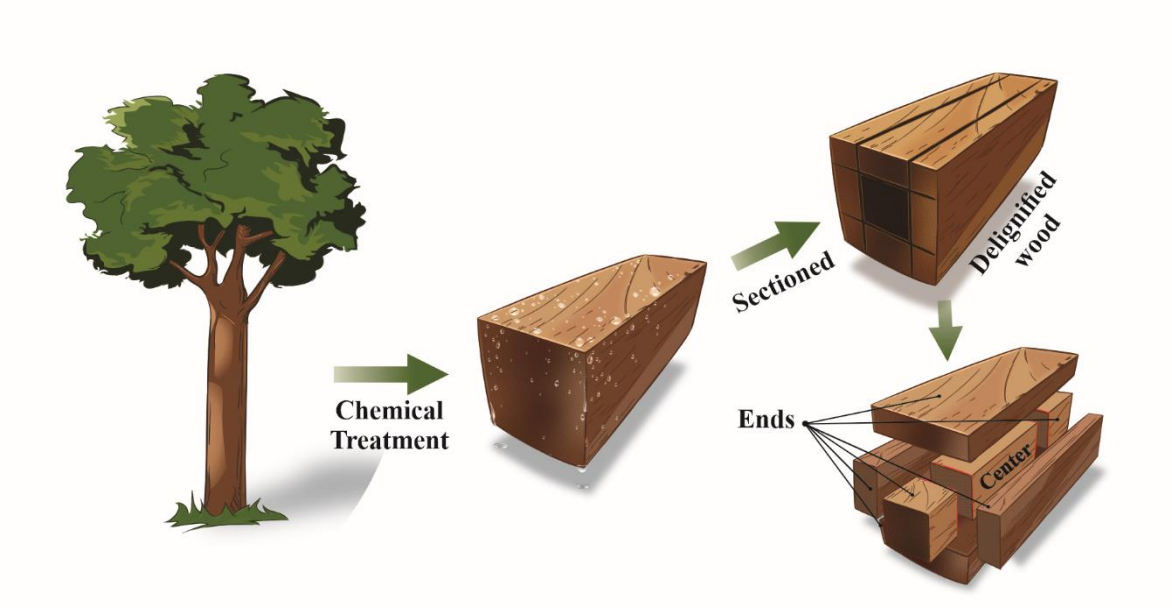


*Figure 2-1 Schematic illustration of delignified wood sectioning. The process involves studying delignified wood by comparing the differences observed between the ends and the center of each specimen.*

### 2.3.3 Measurements and characterizations

The FT-IR spectrum were collected on the three specimens using an FTIR spectrometer (Spectrum Two, PerkinElmer, MA, USA) equipped with an ATR module, recording over a range of 4000-450 $cm^{-1}$ at a resolution of 4.0 $cm^{-1}$ and taking the average of 24 scans for each specimen. The natural wood (NW) and DW were prepared as thin sections, with thicknesses lower than 1 mm. One measurement was performed per specimen. The spectra were recorded as transmittance versus wavenumber to find the effect of the delignification process on the pieces and identify the presence of functional groups that could be present in the specimens. The partial removal of the chemical components of the specimens was quantitatively examined according to Van Soest et al. (Van Soest et al. 1991). Ash composition was determined by the volatilization losses method according to the NTC 5167 standard. The microstructure of the NW and DW was observed under the optical microscope (Olympus BX50F4), and the anatomy of the detected fibers, vessels, and rays was described using the International Association of Wood Anatomists List of Features for

Hardwood Identification (IAWA 1989). The surfaces of the specimens were prepared in cross-section, and the generated images were analyzed using Motic Images Plus 3.0 software. Twenty-five lumen and fiber wall thickness measurements were counted from different cross-sectional areas. Then, scanning electron microscope (SEM, JEOL JSM-6490LV) at 20 kV was used to reveal the morphologies of the wood specimens. The observed characteristics were measured by SEM analysis and using the image analysis ImageJ software (Schneider et al. 2012). The basic specific weight (density) was measured in 5 wood samples for each specimen before and after the delignification process. The apparent volumetric mass density of the specimens was calculated using the following equation: $\rho_{Wood} = m/V$, where $m$ is the weight and $V$ is the volume of the specimens before and after the delignification process, respectively. The porosity of the specimens was calculated based on the dried sample mass and solid wood before and after delignification. Porosity was calculated with the following equation:

$$\text{Porosity } (\%) = \left(1 - \frac{\rho_{\text{wood}}}{\rho_s}\right) \times 100$$

Where $\rho_{wood}$ and $\rho_s$ are the volumetric mass densities of the wood and solid wood, respectively. According to the previous study, the density value of solid wood (cell wall) of 1500 kg $m^{-3}$ was used (Gibson 2012). The absorption capacity of the specimens was determined by measuring the increase in weight relative to their dry state. The NW specimens were cut into cubes with dimensions of 30 × 30 × 30 $mm^3$ (radial × tangential × longitudinal) and dipped in a water container for 30 min. At least five replicates were measured to calculate the average value. The absorption capacity (g/g) was calculated as follows:

$$\text{Absorption } (g/g) = \frac{m_1 - m_0}{m_0}$$

Where $m_o$ and $m_1$ are the sample's dry mass and final mass during water absorption, respectively.

The mechanical properties of the natural and delignified specimens were evaluated using a Tinius Olsen testing machine. The modulus of rupture (MOR) and modulus of elasticity (MOE) in compression parallel to the grain were measured according to the NTC 784 standard (Icontec-NTC-784 1974), using three specimens from each species, prepared with the dimensions of the cross-section of 30 x 30 x 100 $mm^3$ in longitudinal direction. Janka's hardness method was used to measure the hardness before and after the delignification according to NTC 918 (Icontec - NTC 918 1975). Three specimens were analyzed with 30 x 30 x 100 $mm^3$ cross-section and longitudinal dimensions.

### 2.3.4 Statistical analysis

Data from this study were analyzed using Statgraphics Centurion 19. A correlation analysis was performed between the lumen diameters of the wood fibers and the degree of delignification of the treated woods.

## 2.4 Results and discussion

### 2.4.1 Analysis of alkaline solution effects on delignification process

In the delignification process by digestion with chemicals, a key factor on the wood structures is its cellular chemical composition since lignin is a complex amorphous polymer (Boerjan et al. 2003; Maturana et al. 2023). Chemical removal of lignin was achieved by complex chemical reactions generated by the interaction of $NaOH/Na_2SO_3$ aqueous solution with the monomeric lignin units (Li et al. 2021). Indicative of these chemical changes is the loss of the natural luster of delignified wood.

Delignification process was performed similarly in all specimens using the mixed aqueous solution of $NaOH/Na_2SO_3$. However, it had different removal effects of chemical components in NW of the three specimens (Kim et al. 2020b). For all three species after chemical treatment, no

significant reduction in the intensity of the bands located at 1593 and 1505 $cm^{-1}$ for the aromatic skeleton in lignin was observed. This lack of reduction in the intensity of the peaks at 1593 and 1505 $cm^{-1}$ is because only a partial amount of lignin was removed. In the three species of woods, the intensities of the band at 1028 $cm^{-1}$ (Figure 2.2b) were similar after alkaline treatment, which indicates that the cellulose was not removed (Da Costa et al. 2021).

In comparative FT-IR spectrums of hardwood samples, some spectral differences are observed between NW and DW samples (Figures 2.2a, b). Bands located at 1736 and 1235 $cm^{-1}$ for carbonyl stretching and C–O stretching are significantly reduced for Sande and Andiroba. This is an effect that has been reported in other studies (Guan et al. 2018; Yang et al. 2020), and it is attributed to the breaking of chemical bonds and removal of extractives (Shi et al. 2018), as well as to the removal of chromophores from the lignin (Meng et al. 2020). FT-IR spectroscopy of hardwood samples shows that lignin has been partially removed by the alkaline treatment. In the case of Choiba, no bands were observed at 1736 and 1235 $cm^{-1}$, neither in natural nor in delignified wood. The spectra band at 1736 $cm^{-1}$ is attributed to acetyl-xylan when tentatively assigned to xylan (hemicellulose) and ρ-coumaric acids of lignin (Md Salim et al. 2021). The band centered at 1235 $cm^{-1}$ was assigned to the C-O stretching of the guaiacyl unit in lignin (Zhuang et al. 2020). The decrease in band intensities in the two species after heating with alkali solution was likely caused by cleavage of the β-O-4 bond, the primary bond in lignin, and removal of acetyl groups from galactoglucomannan. (Horikawa et al. 2019). When delignified at 90°C for 7 hours in an alkali solution, Sande and Andiroba showed partial lignin removal, with 47.4% and 73.7% removal, respectively. However, Choiba showed no significant lignin removal (Figure 2.2c-e). Although this strategy has shown to be effective for Sande and Andiroba, different degrees of lignin removal were obtained. Based on this, we suggest that besides the chemical composition of wood, the anatomical structures of the studied woods is an important factor that may influence both, the heterogeneous distribution, and the effects of the alkaline chemical solution on the anatomical

structure of the wood. A chemical pre-treatment is very important regarding delignification followed by densification, which leads to the enhanced mechanical performance of natural wood. In fact, according to Song et al. (2018), wood densification with 45% lignin removal results in the best mechanical properties. Furthermore, wood with lower lignin removal, such as Choiba, experiences less structural collapse, while wood with high lignin removal, such as Andiroba, recovers its elasticity. Delignification can affect the polysaccharides, causing larger deformations in the wood, and the plastic flow deformation of the cell (Seki et al. 2022).

SEM images (Figure 2.3j-l) showed that the cellular structure of the DW preserved the morphology and microscopic features of the honeycomb structure of NW. After partial removal of lignin and hemicellulose, the fibers, and vessels in the dry state of the DW cross-section in the three specimens retained their round or oval shape (Figure 2.3j-l). However, partial lignin removal in the middle lamella caused a separation between adjacent cell walls (Wu et al. 2019) (yellow arrows in Figure 2.4a-d). At the same time, microcracks were observed in some fiber cells of Sande (Figure 2.4a), due to the partial removal of lignin from the cell wall.

The relationship between wood morphological features and the delignification process is not well understood. Lignin removal is not uniform, or heterogeneous (Brännvall 2017), because it depends on how well the chemical solvents can move through the wood tissue and penetrate the ray cell channels. In this study, the impregnation of the alkaline solution was analyzed in the delignification process of each wood. Wood specimens were sectioned between the center and the end (Figure 2.1). Figure 2.2c-e shows the relative chemical composition after chemical treatment of the center and the ends of the three types of wood, respectively. The results indicated that the delignification was different between the center and the ends in Sande (Figure 2.2c). Despite the morphological similarities between Sande and Andiroba, the percentage of delignification was not similar in these species. The difference in the efficiency of the delignification process between Sande and Andiroba is due to the wood structure of Andiroba. This is because Andiroba, among

its anatomical features, has common vessel clusters and traumatic resin canals (intercellular canals) (Wheeler 2011) (Figure 2.4e, f). Resin channels are common in the Meliaceae species family to which Andiroba belongs (Dünisch and Baas 2006). These channels allow movement of the alkaline fluid to be more homogeneous in the wood, providing additional openings for a longitudinal flow of the solution (Brännvall 2017; Wagih et al. 2021). Thus, the resin canals in Andiroba wood may have allowed the alkaline solution to flow more easily, which may explain why more lignin was removed from Andiroba wood than from other types of wood. Rays may also be a beneficial morphological factor for delignification in Sande and Andiroba because the rays in both species are similar, with 4 to 10 serial rays visible to the naked eye on the tangential surface. In contrast, Choiba has rays of 1 to 3 cells, which are not visible to the naked eye on the tangential surface. The characteristics of the fibers showed the same pattern of vessels and rays. While Sande and Andiroba had thin to thick-walled fibers with a large lumen (Figure 2.3d). Choiba wood fibers had very thick-walled, with a small lumen (Figure 2.3f). The fiber luminaire's mean diameter of the three tropical hardwoods is shown in Table 2.1. Specifically, the pattern of reduced lumens in Choiba wood's main anatomical features suggests that delignification is difficult in this wood, requiring different delignification parameters than those used for Sande and Andiroba specimens. The fibers in Sande and Andiroba were thin-to-thick-walled, ≤ 3 μm. Meanwhile, fibers in Choiba wood were very thick-walled, ≥ 5 μm, which is associated with a smaller fiber lumen with higher density wood as the Choiba (Mamoňová and Reinprecht 2020). This is in line with the observations that Choiba is the wood with the highest density and presents the highest cell wall thickness in fiber cells (Table 2.1). Then, after comparing the anatomical features of the three species, we observed that the structure plays a pivotal role in the efficiency of the delignification process.

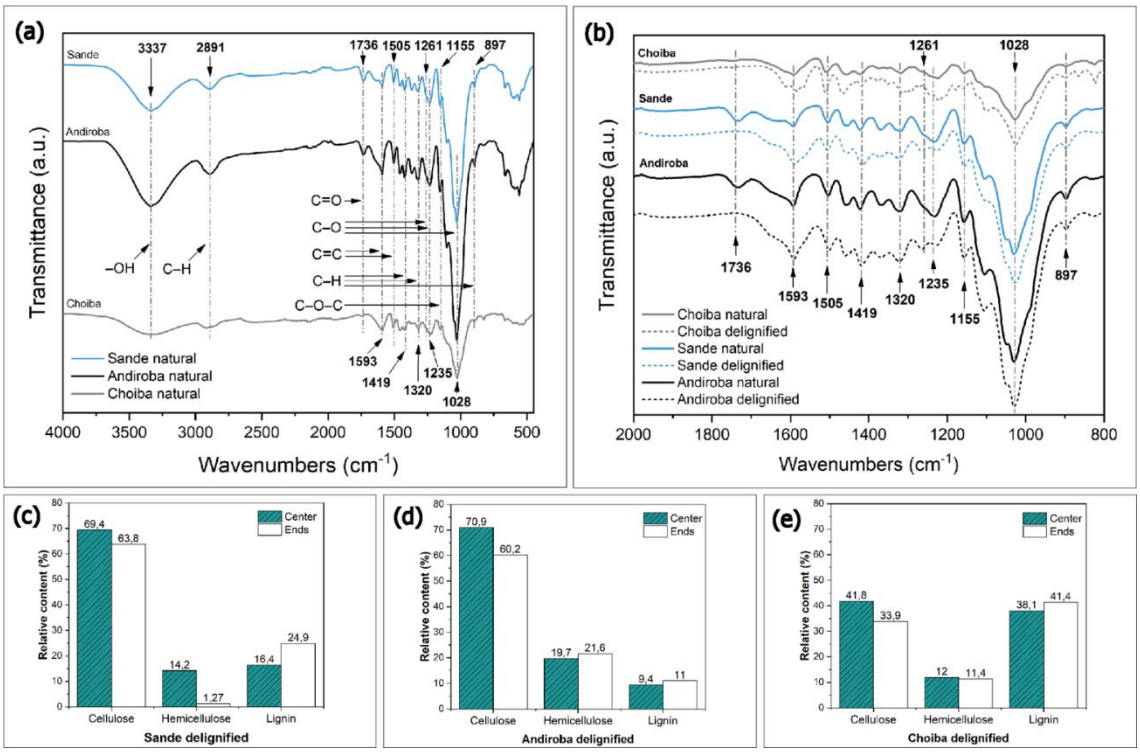


*Figure 2-2 FT-IR spectra of (a) natural wood and (b) delignified wood. (c-e) Comparison of the relative content of cellulose, hemicelluloses, and lignin in different wood specimens obtained from the chemical composition of the ends and centers of delignified wood.*

*Table 2-1 Chemical composition, density, and absorption capacity of natural woods.*

| Specimen | Family | Cellulose (%) | Hemicellulose (%) | Lignin (%) | Basic density (g/cm³) | Absorption capacity (g/g) | Fiber luminaire's diameter (µm) |
|---|---|---|---|---|---|---|---|
| **Sande** | Moraceae | 47.6 ± 0.7 | 12.1 ± 0.2 | 31.2 ± 0.9 | 0.44 ± 0.01 | 0.14 ± 0.009 | 41.24 ± 9.02 |
| **Andiroba** | Meliaceae | 34.0 ± 1.0 | 12.13 ± 0.06 | 35.7 ± 0.7 | 0.50 ± 0.01 | 0.08 ± 0.009 | 40.96 ± 9.30 |
| **Choiba** | Fabaceae | 32.0 ± 2.0 | 10.6 ± 0.8 | 34.8 ± 0.2 | 0.94 ± 0.04 | 0.03 ± 0.003 | 5.12 ± 3.36 |

Mineral content within wood is another important factor that can affect the chemical delignification process. For example, wood with a high calcium content can be difficult to delignify

(Saltberg et al. 2009). Thus, mineral content could have had a negative effect on the removal of lignin in Choiba, where the calcium content was higher than in Sande and Andiroba (Table 2.2). Calcium ions ($Ca^{+2}$) can form an intermolecular bond with homogalacturonan (HG) molecules to form rigid structures known as the “egg crate model” (Siedlecka et al. 2008). Thus, creating rigid structures of pectin-calcium-pectin that stabilize the pectin network, influencing wall elasticity. Less methylated lignin formation of "eggshell" structures influences the plasticity of the wall (Siedlecka et al. 2008). In Choiba, the spectra bands located at 1028 and 897 $cm^{-1}$ are attributed to demethylated lignin (M Sain 2013), increasing cell wall rigidity and controlling cell wall mechanical properties (Dewhirst et al. 2020). The anatomical results indicated that the coarse fibers impede the flow of the alkaline solution into the interior of high-density woods such as Choiba. Which is related to the low efficiency of the delignification process in Choiba hardwood.

### 2.4.2 Mechanical and physical properties

Partial or complete removal of hemicellulose from wood modifies its mechanical properties, as shown by the decreasing trend in the three tropical hardwoods in Table 2.2 and by previous research (Kumar et al. 2021). In the present study it was possible to observe a direct relationship between the decrease in mechanical properties and the disappearance of the infrared band located at 1736 $cm^{-1}$ for those woods with anatomical features that allow a higher degree of delignification. For Sande, after the delignification process, significant reductions in both MOR and MOE of about 46 and 80%, respectively, are observed, while for Andiroba, these reductions are observed to be 24 and 31%, respectively. As for Choiba wood, MOE was reduced by 49%. The surface hardness of DW compared to that of the NW decreases by 12, 38%, and 42% for Sande, Andiroba, and Choiba respectively. Also, the hardness at the ends of the DW was reduced by 34% in all specimens. Chemical degradation weakens wood by breaking down its structural components, which reduces its mechanical properties. Another relevant factor that can affect the mechanical properties is foreign inorganic components (such as sulfur, calcium, sodium, and chlorine), which

can cause hydrolysis of some carbohydrates and the formation of minerals crystals resulting in mechanical changes (Mi et al. 2020), because salts cause an increase in water absorption (Var and Kardaş 2019). It has been reported that salt ions alter the bonding between water molecules and amorphous fibers, causing an increase in free water, which affects the structure by reducing the bonding between fibers and leading to a decrease in wood strength (Gao et al. 2024). In addition, the hydration of the salts in the solid state increases the volume of the salts, deforming the main tissues and causing breakage and severe mechanical damage to the wood (Mi et al. 2020). According to the ash composition results Andiroba, Sande, and Choiba significantly increased their inorganic elements (Table 2.2). Comparing NW with DW the sodium showed increases of 237.8, 266.3, and 190.0 times for Sande, Andiroba, and Choiba, respectively. Considering that the ions can diffuse inside the wood, this could lead to an accumulation of sodium.

Accumulation of minerals can deform tracheid and ray cells and burst wood cell walls due to macroscopic swelling, which affects the mechanical performance of wood (Mi et al. 2020), thus chemical pretreatment with mineral accumulation alters the properties of delignified wood. Sodium ion accumulation can be removed from wood by soaking it in an aqueous acid solution (e.g., dilute acetic acid) followed by several immersions in boiling DI water to remove excess acid. This procedure was not used in this study. However, it should be a priority for future research. The non-uniform impregnation of the center and ends of the wood with the $NaOH/Na_2SO_3$ aqueous solution explains the differences in sodium content distribution between Sande, Andiroba, and Choiba hardwoods. This is mainly due to the variations in their anatomical features.

The physical properties (density and porosity) of the hardwoods remained largely unchanged after delignification, as the mass loss was insignificant. Delignification softens the wood's anatomical structure by removing lignin and hemicellulose, facilitating densification. These conditions are ideal for subsequent treatments such as densification (Song et al. 2018).

*Table 2-2 Results of partial delignification on the mechanical and physical properties and chemical components of natural wood.*

| Specimen | Parameter | Natural wood | Delignified wood | Rate D/N |
|---|---|---|---|---|
| **Sande** | Wood density (g/cm³) | 0.55 ± 0.002 | 0.59 ± 0.015 | |
| | Porosity (%) | 63.5 ± 0.16 | 60.7 ± 0.98 | |
| | Total ash content (%) | 0.55 | 7.26 | 13.2 |
| | Center ash content (%) | | 1.7 | |
| | Ash content at the ends | | 8.09 | |
| | Total Calcium (CaO) (%) | 0.184 | 0.1452 | |
| | Magnesium (MgO) (%) | 0.0552 | 0.048 | |
| | Sodium (Na) (%) | 0.009 | 2.14 | 237.8 |
| | Potassium ($K_2O$) (%) | 0.103 | 0.0351 | |
| | Sulfur (S) (%) | 0.090 | 0.303 | |
| | Strength MOR (MPa) | 44.4 ± 2.4 | 19.6 ± 4.6 | |
| | Strength MOE (MPa) | 5244.5 ± 719.6 | 985.6 ± 223.6 | |
| | Hardness (sides) (N) | 2790.4 ± 523.6 | 2464.3 ± 257.7 | |
| | Hardness (ends) (N) | 3434.5 ± 539.6 | 2249.7 ± 242.2 | |
| **Andiroba** | Wood density (g/cm³) | 0.55 ± 0.007 | 0.59 ± 0.016 | |
| | Porosity (%) | 63.6 ± 0.47 | 60.4 ± 1.04 | |
| | Total ash content (%) | 1.02 | 8.34 | 8.2 |
| | Center ash content (%) | | 0.98 | |
| | Ash content at the ends | | 4.98 | |
| | Total Calcium (CaO) (%) | 0.3835 | 0.338 | |
| | Magnesium (MgO) (%) | 0.0416 | 0.0429 | |
| | Sodium (Na) (%) | 0.0086 | 2.29 | 266.3 |
| | Potassium ($K_2O$) (%) | 0.0471 | 0.0353 | |
| | Sulfur (S) (%) | 0.096 | 0.184 | |

| Specimen | Parameter | Natural wood | Delignified wood | Rate D/N |
|---|---|---|---|---|
| **Choiba** | Strength MOR (MPa) | 44.4 ± 2.4 | 33.6 ± 3.1 | |
| | Strength MOE (MPa) | 5244,5 ± 719.6 | 3621.6 ± 1478.8 | |
| | Hardness (sides) (N) | 4544 ± 401.5 | 2810.7 ± 383 | |
| | Hardness (ends) (N) | 5943.7 ± 642.9 | 3909.5 ± 355.8 | |
| | Wood density (g/cm$^3$) | 1.06 ± 0.006 | 1.05 ± 0.011 | |
| | Porosity (%) | 29.6 ± 0.42 | 30.3 ± 0.76 | |
| | Total ash content (%) | 1.23 | 9.69 | 7.9 |
| | Center ash content (%) | | 1.33 | |
| | Ash content at the ends | | 3.12 | |
| | Total Calcium (CaO) (%) | 0.5306 | 0.399 | |
| | Magnesium (MgO) (%) | 0.0497 | 0.051 | |
| | Sodium (Na) (%) | 0.00821 | 1.56 | 190.0 |
| | Potassium ($K_2O$) (%) | 0.0452 | 0.0202 | |
| | Sulfur (S) (%) | 0.079 | 0.066 | |
| | Strength MOR (MPa) | 78.5 ± 1.6 | 76.8 ± 8.8 | |
| | Strength MOE (MPa) | 21102.1 ± 2680.3 | 10706.9 ± 2087.8 | |
| | Hardness (sides) (N) | 14045.8 ± 1355.9 | 8087.3 ± 900.5 | |
| | Hardness (ends) (N) | 15297.9 ± 2320.8 | 7929 ± 524.7 | |

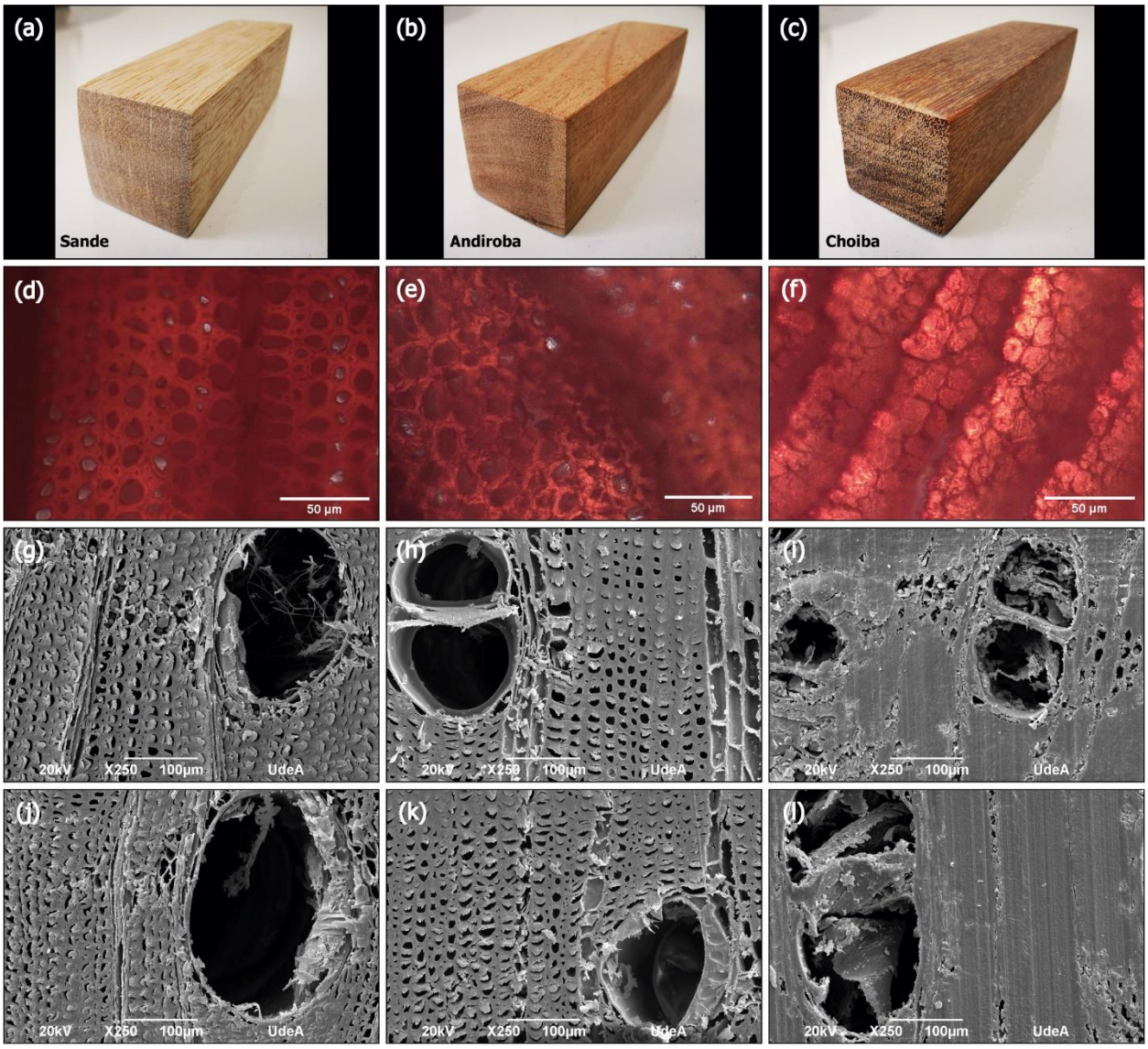


*Figure 2-3 Anatomical and structure of different wood specimens: (a-c) photographs of natural wood showing cross-section, radial, and longitudinal section of specimens; (d-e) cross-sectional optical images showing lumen structure and wood fibers; (g-i) SEM images showing the honeycomb-like structure of natural wood; (j-l) SEM images showing the preserved structure of the woods after delignification treatment.*

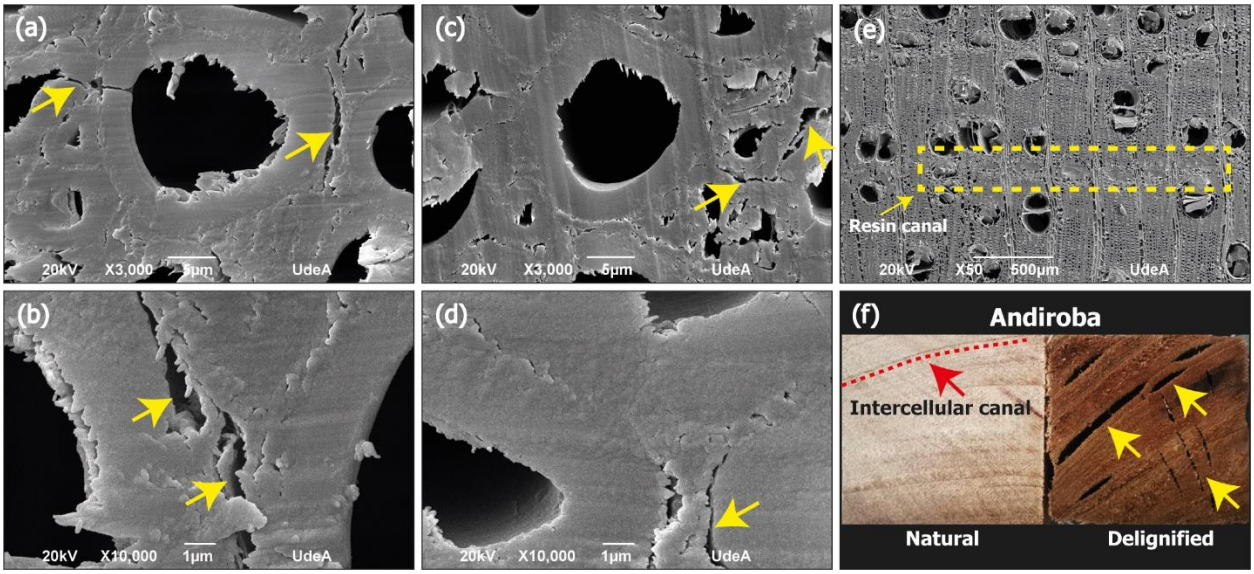


*Figure 2-4 Effects of partial delignification on wood structure: a) and b) SEM images showing the preserved structure of delignified Sande; c) and d) SEM images showing the preserved structure of delignified Andiroba; e) photograph showing a band of traumatic intercellular canals (tangential line of axial resin canals) in Andiroba wood; f) photograph showing delamination effects in traumatic channels of delignified andiroba cross-section.*

## 2.5 Conclusions

Of the three tropical hardwood specimens evaluated, the two least dense species, Andiroba and Sande, were partially delignified using a mixed aqueous solution of sodium hydroxide and sodium sulfite ($NaOH/Na_2SO_3$) as a pretreatment for densification. Lignin removal was greater in the center of the delignified hardwoods than at the ends. The anatomical results showed that the coarse fibers in the high-density wood Choiba hindered the flow of the alkaline solution, preventing delignification. Conversely, the intercellular resin channels in Andiroba and Sande wood facilitated the removal of lignin and hemicellulose. Alkaline chemical treatment of hardwood reduces the lignin and hemicellulose content, which can lower the modulus of elasticity (MOE), modulus of rupture (MOR), and hardness of the delignified wood. However, the results of this study suggest that mineral accumulation, such as sodium, can also contribute to changes

in the mechanical properties. This confirms that alkaline chemical treatment is a process with non-uniform effects on lignin/hemicellulose removal and accumulated minerals due to the anatomical structure of the wood.

# Chapter 3

## 3 Two-step hot isostatic pressing densification achieved non-porous fully-densified wood with enhanced physical and mechanical properties.

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The content of this chapter is the author's version of the article published under the same title. In this chapter, an equiaxial compression process has been established to improve the physical and mechanical properties of wood.

# Two-step hot isostatic pressing densification achieved non-porous fully-densified wood with enhanced physical and mechanical properties.

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## 3.1 Abstract

A new two-step densification method for wooden materials entitled hot isostatic pressing (HIP) is proposed. This method has the advantage over previous densification methods that can

achieved almost the full densification of wood, reaching values up to 1.47 g/cm$^3$, which exceeds any value ever reported for a hardwood species. Furthermore, it can preserve about 35% of the original volume, in comparison to other methods which typically can preserve only 20% of the volume. Although not tested in this investigation, in principle, the HIP method should be capable of densifying any shape of wood including circular and tubular cross sections because the main densification mechanism is based on gas pressure that is equally exerted in the entire surface, rather than localized mechanical compression, which can only be effective with rectangular cross sections. In the first stage of the two-step proposed method, the compressive strength of the anatomical wood structure is reduced by delignification, and, in the second, a full densification is achieved by hot isostatic pressing under argon atmosphere. Three tropical hardwood species with distinct anatomical characteristics and properties were used to test the method. The HIP-densified wood's microstructural, chemical, physical, and mechanical properties were assessed. Apart from the high densification values and volume preservation, the results indicate that proposed method was effective for all the tested species, showing homogenous density patterns, stable densification without noticeable shape recovery, and enhanced mechanical properties. Future research should test the HIP method in softwoods and consider the ring orientation in order to enhance the control of the densified geometry.

## 3.2 Introduction

Two-step densification is a process that improves the mechanical properties of wood by first reducing the cell wall strength by physical or chemical methods (softening of the anatomical structure) and subsequently applying mechanical compression (Kamke and Rathi 2011; Song et al. 2018). Softening facilitates the wood's densification (Frey et al. 2018) and avoids problems such as shape recovery in densified wood (Laine et al. 2016; Xiang et al. 2020). Mechanical densification of wood typically comprises the application of one of the following processing

methods: viscoelastic thermal compression (VTC), thermo-mechanical (TM), thermo-hydro (TH), or thermo-hydro-mechanical (THM). All these methods commonly include a densification process of at least two steps, as they firstly soften the structural components of wood with heat or moisture, taking advantage of the viscoelastic properties of the wood, before subsequently applying mechanical compression (Jakob et al. 2022a). However, a drawback these methods share is that the densified wood tends to swell back (shape recovery) when it is subjected to moisture after the process has been completed. Therefore more than two steps are normally necessary to reduce shape recovery, such as additional heating or cooling treatment after pressing, which increases the cost and time of the processing (Yu et al. 2020; Albert and Liew 2022).

Multiple physical and mechanical properties improve with densification (Kutnar et al. 2008), some of them showing great increases depending on the compression system used, the wood species, and the processing parameters. Some of the most highly-sought improvements include higher density and dimensional stability, stronger modulus of rupture and modulus of elasticity, and increased compression perpendicular to the grain strength (Shi et al. 2020; Cabral et al. 2022). Despite such improvements, the aforementioned densification processes show some disadvantages or limitations in addition to swelling back, such as limited increases in density as well as partial and non-homogeneous densification. For example, it is typically acknowledged that wood cell wall density amounts to 1.5 g/cm$^3$ (Gibson 2012); however, THM processing, despite having been shown to improve wood's density and mechanical strength (Sandberg et al. 2013), only achieves partial densification up to 1.29 g/cm$^3$ (Kutnar et al. 2021), while the density achieved via TM processing has been reported as only 1.10 g/cm$^3$ (Laskowska et al. 2021). These typical mechanical compression methods show limitations in removing the empty lumens of the wood in the weakest regions of the structure, and may cause micro-fractures in the cell wall of vessels and fibers (Bekhta et al. 2016; Laine et al. 2016). Regarding VTC densification, this method has been capable of reaching densities up to 1.4 g/cm$^3$ (Kamke and Rathi 2011), however, it does not

completely remove wood porosity and it is limited to the processing of thin wood laminates (Kutnar et al. 2009; Kamke and Rathi 2011; Standfest et al. 2013). Besides, the VTC method yields non-uniform density patterns (Kutnar et al. 2009). Another limitation of the previously-mentioned mechanical densification methods is that, although wood can be densified in all different directions (radial, tangential, or longitudinal), these techniques reach top densification values only when applied in the radial direction (Luan et al. 2022; Cabral et al. 2022). For these reasons, wood treated with any of these methods has limitations in its use.

In this context, new wood densification methods have been researched in recent years with a view to reducing HERE the aforementioned drawbacks, achieving full densification, and further improving wood properties. Equiaxial or isostatic densification may be an alternative method for achieving a more efficient densification. One equiaxial densification technique, high-pressure (HP) treatment, densifies wood in the absence of heat treatment (Luan et al. 2022) by applying hydrostatic pressure to vacuum-sealed wood in a polymer bag inside a chamber filled with pure water (Li et al. 2016; Sun et al. 2016). HP densification can process low-density softwood in a brief time while preserving a significant volume of the treated wood because the material is not only pressed in one direction. However, densification with this method is limited up to 1.0 g/cm$^3$, which represents a relatively low increase in mechanical properties (Li et al. 2016; Yu et al. 2017). On the other hand, semi-isostatic compression technology - so-called since compression is not perfectly isostatic-, applies pressure to wood laying on a rigid surface through a flexible oil-filled rubber diaphragm (Blomberg and Persson 2004). This rapid, non-thermal processing technique has demonstrated increases in wood density up to approximately 1.0 g/cm$^3$ (Blomberg 2005; Blomberg et al. 2006). Even higher increases have been reported, but the density of the modified wood decreases because of the compression set recovery effect (Blomberg et al. 2006). This technique is only used to process low-density softwood, and it has a significant disadvantage in that does not reduce compression set recovery unless additional treatments are included. A study by Boonstra and Blomberg (Boonstra and Blomberg 2007) reported a reduction of the shape

recovery effect in densified wood by including a heat treatment process before the semi-isostatic compression. More recently, the study by Song et al. (2018) proposed a new two-step densification process, which densified both softwood and hardwood up to a density of 1.3 g/cm$^3$, significantly improving their mechanical properties, inhibiting the shape recovery effect, and providing excellent resistance to wet conditions without the need to include a post-treatment phase. As a first step, they softened the anatomical structure of the wood by chemical lignin removal (delignification), a process that has been extensively researched in combination with other wood modification treatments (Frey et al. 2019; Kumar et al. 2021; Li et al. 2021; Jamaldheen et al. 2022). The aim of the lignin removal was to expose the cellulose chains in order to subsequently modify the material (Li et al. 2021; Gullo et al. 2023). Although this process is typically focused on the removal of the lignin, it typically leads to also some hemicellulose removal, therefore may be more accurate to refer it as lignin/hemicellulose removal. The disadvantage of the densification process of the aforementioned study was that it still was unable to achieve full densification by vanishing porosity (density of 1.3 g/cm$^3$), and also that a significant volume loss of about 79% CR in the radial direction was obtained due to uniaxial densification being found (Sikora et al. 2021). Finally, it also required a time-consuming process. Other recent works on this densified wood development process achieved similar results (Shi et al. 2020; Jakob et al. 2022a).

In this article, a new two-step densification method consisting of delignification followed by hot isostatic pressing (HIP) is proposed. HIP has been traditionally used for the densification of metals and ceramics by simultaneously heating and applying high isostatic pressure (Weddeling and Theisen 2017), customarily using argon as the compression gas (Eklund and Ahlfors 2018), which allows for equiaxial pressing (Atkinson and Davies 2000). This method has the advantage of allowing equal pressure to be exerted on all surfaces while having control of processing temperature and pressure, as illustrated schematically in Fig. 3.1a. In this research we explored the applicability of the HIP technique after partial lignin/hemicellulose removal in the two-step process in order to achieve high-performance fully-densified wood with enhanced properties. The

effect of isostatic compression on the densified wood's physical/mechanical properties and post-mechanical fixation is evaluated in three hardwood species using compression ratio (CR), water absorption (WA) capacity, SEM imaging, and FTIR spectroscopy.

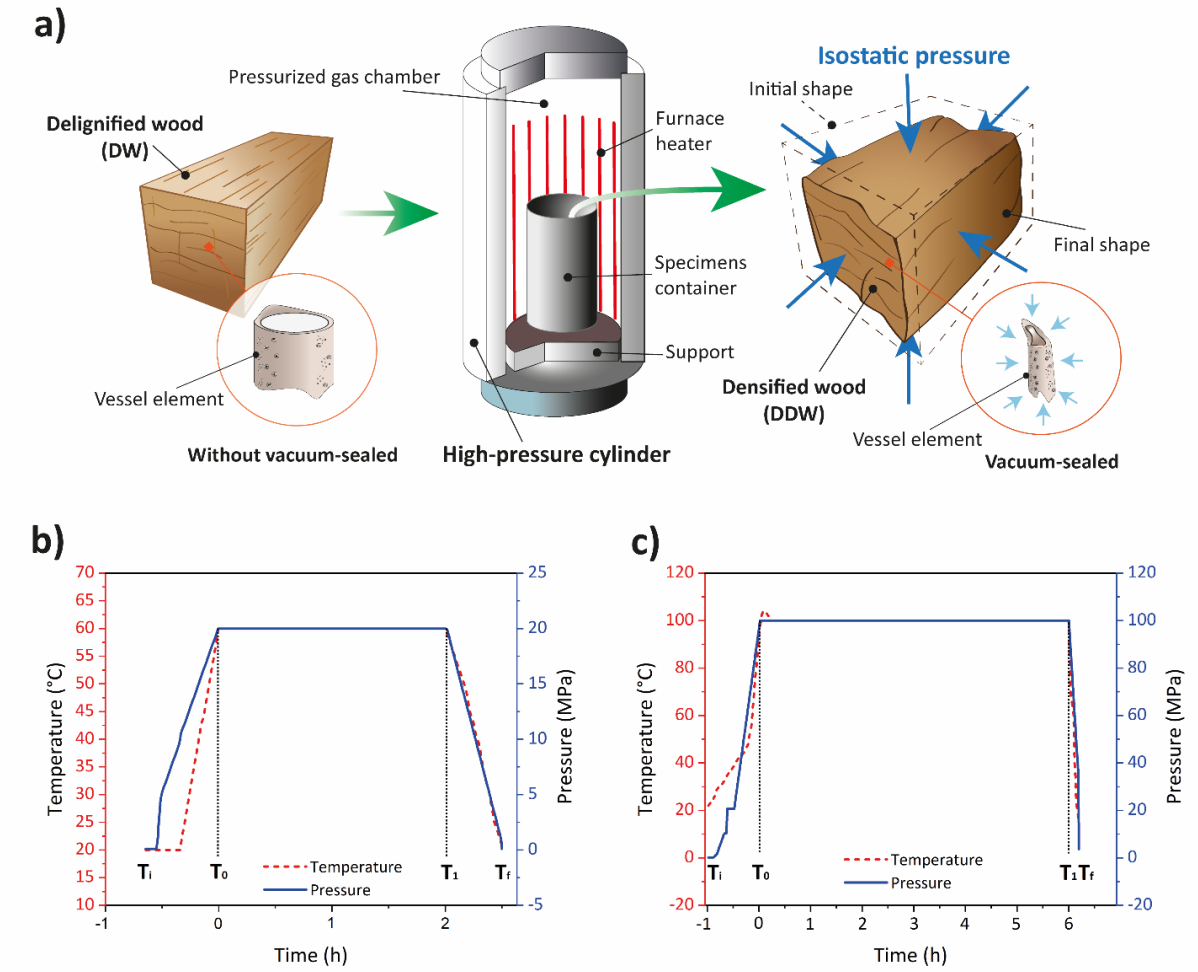


*Figure 3-1 Graphical illustration and parameters of the densification process. (a) Illustration of the densification process stages by chemical pretreatment and subsequent hot isostatic pressing. (b-c) Schematic diagram of the HIP process parameters: preheating (Ti ~ To), compression (To ~ T1), and release (T1 ~ TF). (b) Condition 1 (C1) simultaneously applies a pressure of 2900 psi (20 MPa) and a temperature of 60 °C for 2 h of treatment. (c) Condition 2 (C2) simultaneously applies a pressure of 14500 psi (100 MPa) at 100 °C for 6h of treatment.*

## 3.3 Materials and methods

### 3.3.1 Materials

Three tropical hardwood species namely: Sande (Brosimum utile), Andiroba (Carapa guianensis), and Choiba (Dipteryx oleifera) were considered in this research. The specimens were obtained from the trunks of different trees and measured 35 × 35 × 170 mm (radial × tangential × longitudinal). Before processing, all specimens were kiln-dried up to constant weight at 103 °C for 24 h. Sodium hydroxide (≥ 99.0%) and sodium sulfite (≥ 97%) were purchased from Merck (Canada). Deionized (DI) water was used as the solvent to process the wood. All chemicals were used as received.

### 3.3.2 Two-step process toward densified wood

The proposed method consists of a two-step processing. This entails a chemical pretreatment, which leads to partial lignin/hemicellulose removal, followed by a HIP process, in which wood becomes densified. In the first step, delignification is achieved by immersing the specimens in a boiling mixed aqueous solution of 2.5 M, NaOH and 0.4 M, $Na_2SO_3$ at 90 °C for 7 h, followed by immersion in boiling distilled water several times to remove the excess chemical reagents. Previous studies present more details of this process (Song et al. 2018; Li et al. 2021). Next, the delignified wood (DW) is oven-dried at 50 °C to 12% moisture content and prepared with dimensions of 30 × 30 × 150 mm (radial × tangential × longitudinal). That is, the ends of the DW were removed before densification process (Annex 4 Fig. S4). The DW specimens are then vacuum-sealed at room temperature and covered in a high-temperature-resistant, flexible aluminum bag. Finally, the HIP process is applied. In this research, the HIP system consisted of an HP830 machine, American Isostatic Presses, Inc., Ohio, USA, equipped with a crucible to contain the specimens. The HIP process used a high-purity (99.999%) argon atmosphere. The

schematic illustration of the preparation procedure of the HIP densified process is presented in Fig. 3.1a. The wood specimens were compressed by the HIP in an equiaxial direction. During the HIP process, the specimens were compressed using two different control parameter conditions (temperature, pressure, and time). The first condition (C1) consisted of simultaneously applying a pressure of 2900 psi (20 MPa) and a temperature of 60 °C for 2h of treatment (Fig. 1b). The second condition (C2) used a pressure of 14500 psi (100 MPa) at 100 °C for 6h of treatment (Fig. 3.1c). Subsequently, the pressure was gradually released over approximately 30 minutes to counteract shape recovery effects in both conditions. Fig. 3.1b and 1c illustrate the applied pressure and temperature as a function of time during the HIP process. Three replicates were performed for each group of specimens and pressure condition.

### 3.3.3 Measurements and characterization

A scanning electron microscope (SEM, JEOL JSM-6490LV) operating at 15 and 20 kV and 85 amperes was employed to evaluate the morphology and microstructure of the cross-section of the three densified wood specimens. The densified specimens were sectioned by the cryofracture technique. The observed characteristics were measured by SEM analysis and using the image analysis ImageJ software (Schneider et al. 2012). The Fourier transform infrared (FTIR) (Spectrum Two, PerkinElmer, MA, USA), using a device equipped with an attenuated total reflectance (ATR) module, was performed in range from 4000-450 $cm^{-1}$ at a resolution of 4.0 $cm^{-1}$ and taking the average of 24 scans for each specimen. The natural wood (NW) and densified wood were prepared as thin sections, with thicknesses lower than 1 mm. One measurement was performed per specimen. The spectra were recorded as transmittance versus wavenumber to find the effect of the HIP process in the specimen. The number of chemical components (carbohydrates and lignin) measured are not presented in this study.

Moisture content was measured before and after each process step by oven drying at 50 °C to constant weight. The bulk density of the three specimens was determined before and after the HIP process. Density was evaluated by directly measuring their volume with a Mitutoyo micrometer (precision of 0.001 mm) and their weight with a RAD WAG-AS 310.R2 electronic microbalance (accuracy of ± 0.1 μg). In addition, to visualize the homogeneity of the densification process, the optical density of the specimens was measured using microcomputed tomography with the SkyScan 1278 at the University of Chile, Santiago, Chile. The shrinkage ratio of the three specimens was evaluated before and after the HIP process. The compression ratio of the densified wood volume was measured from the ratio of the initial and final volume of the specimens in dry conditions before and immediately after densification, respectively. For dimensional stability (thickness swelling – TS), pre-cut specimens of the rectangular cross-section of specimens with dimensions of approximately 15 × 15 × 30 mm (radial × tangential × longitudinal) were fully immersed in DI water for 30 minutes at room temperature. Before the full immersion test, specimens were painted on all sides using commercial varnish for exteriors. The 30-day moisture absorption method for the species was also used. For this method, specimens were placed in a stable environment at 20 °C and 65% RH for 30 days. The dimensions and weight of the pieces before and after immersion and humidity conditions were recorded. The weight gain (g $g^{-1}$), denoted as the mass of water (g) adsorbed per unit mass of dry densified wood (g), was used to evaluate WA capacity. The mechanical properties of the NW and densified wood were evaluated using an Instron testing machine with a capacity of 10 and 150 kN. Three-point static bending tests were used to determine the bending properties using the modified standard procedure outlined in ASTM D143-21(ASTM D143-21 2021) with a specimen dimension of about 5 × 20 × 100 mm (radial × tangential × longitudinal). The compressive strength was measured according to the ASTM D143-21 (2021) standard, in which specimens for compressive testing should have dimensions of 10 × 10 × 30 mm (radial × tangential × longitudinal). Tensile properties were determined in specimens that were cut to the dimensions of 3 × 10 × 140 mm (radial × tangential

× longitudinal). The specimens were loaded at a constant loading rate until they failed. Before mechanical properties, specimens were conditioned at 65% RH and 20 °C until a constant mass was obtained. The tests were conducted at 20 °C and 55% relative humidity. At least three replicates were measured to calculate the mean value of the measurements. Origin Pro 2018 was employed to analyze all data and plot figures.

## 3.4 Results and discussion

### 3.4.1 Effect of the HIP on the microstructure of wood

Scanning electron images showing the cross-sections of Sande, Andiroba, and Choiba wood following a HIP process are displayed in Fig. 3.2. To establish a clear baseline, it was decided to study the effect of wood delignification on the HIP process. To this end, natural wood (NW) (this condition refers to wood that was neither densified nor delignified), densified natural wood (DNW) (this condition refers to natural wood that was densified without being previously delignified) and densified-delignified wood (DDW) (this condition refers to wood that was previously delignified and then densified) were analyzed. For NW (Fig 3.2a, 3.2d, and 3.2g), the surface and internal porosity of the three specimens were comprised of a structure of diffuse-porous vessels, visible to the naked eye. Andiroba wood showed gums in heartwood vessels (Dünisch and Baas 2006), see the yellow circle of dashed lines in Fig. 3.2d. The anatomical characteristics of the three non-densified specimens were consistent with the results of previous observations for each wood species (Wheeler 2011). The fibers of Sande wood consisted of non-septate, thin- to thick-walled fibers with a large lumen. The fibers in the Andiroba wood consisted of septate, thin- to thick-walled fibers with a broad lumen. In contrast, Choiba wood fibers consisted of non-septate, very thick-walled fibers with a small lumen. In Fig. 3.2b, 3.2e, and 3.2h, corresponding to the DNW following the HIP process, it was observed that the anatomical wood

structure had an obvious reduction in porosity. This effect was similar for the DDW (Fig 3.2c, 3.2f, and 3.2i). However, different degrees of fiber lumen reduction were obtained from the Sande specimen (Fig 3.2b and 3.2c). Although a more significant effect on fiber lumen decrease is observed in DNW than in DDW, this behavior is not generalized in the DDW structure and may be attributed, among other factors, to the difference between the lignin contents of DNW and DDW. In addition, in culture cells without cell-wall has been observed that upon equiaxial compression device for mechanical manipulation the cells decrease in cell cross-sectional area, however, increases in cell layer height (Peussa et al. 2022). Thus, there may be a possibility that heartwood vessels-DDW flexed at the beginning of compression since heartwood vessels from DDW have less lignin than DNW. Furthermore, it is known that the direction of the applied force affects cellular orientation. According to the morphological results, the densification process was effective for both Andiroba and Sande, and the densification was sensitive to previous delignification processes. This is consistent with the fact that wood deformation in compression depends on the specimens used (Blomberg et al. 2006), as the anatomical characteristics of the species influence delignification and subsequently compression. For example, the HIP process was less effective for Choiba than for the other species since the thick-walled fibers, being more difficult to compress, did not suffer significant alterations (Fig. 3.2h and 3.2i), and so a smaller reduction was achieved in the lumens of the anatomical structure of this species. In the SEM images of the DNW and DDW specimens, a marked reduction of the span volume of the cells can be observed, as well as a deformation of the cell walls of the densified wood specimens in the compression direction (in this case equiaxial). Other studies have reported similar behavior (Dömény et al. 2018). Both the vessel structure and fibers deformed irregularly. According to a previous report, fibers under isostatic compression acquire an irregular shape (Blomberg et al. 2006). Furthermore, the cell walls of DNW and DDW were not damaged and maintained their original integrity, indicating that most of the cell walls of the inner layers were softened by chemical and thermal pretreatment during the densification process (Xiang et al. 2022). In that

sense, the HIP process preserves one of the most important aspects of VTC densification since it modifies the wood in the absence of microfractures. This is considered an important factor in improving densified wood's physical and mechanical properties (Kutnar et al. 2009) because the integrity of the anatomical structure is preserved. In addition, it also demonstrates the importance of the partial removal of the basic chemical components of wood before the densification process.

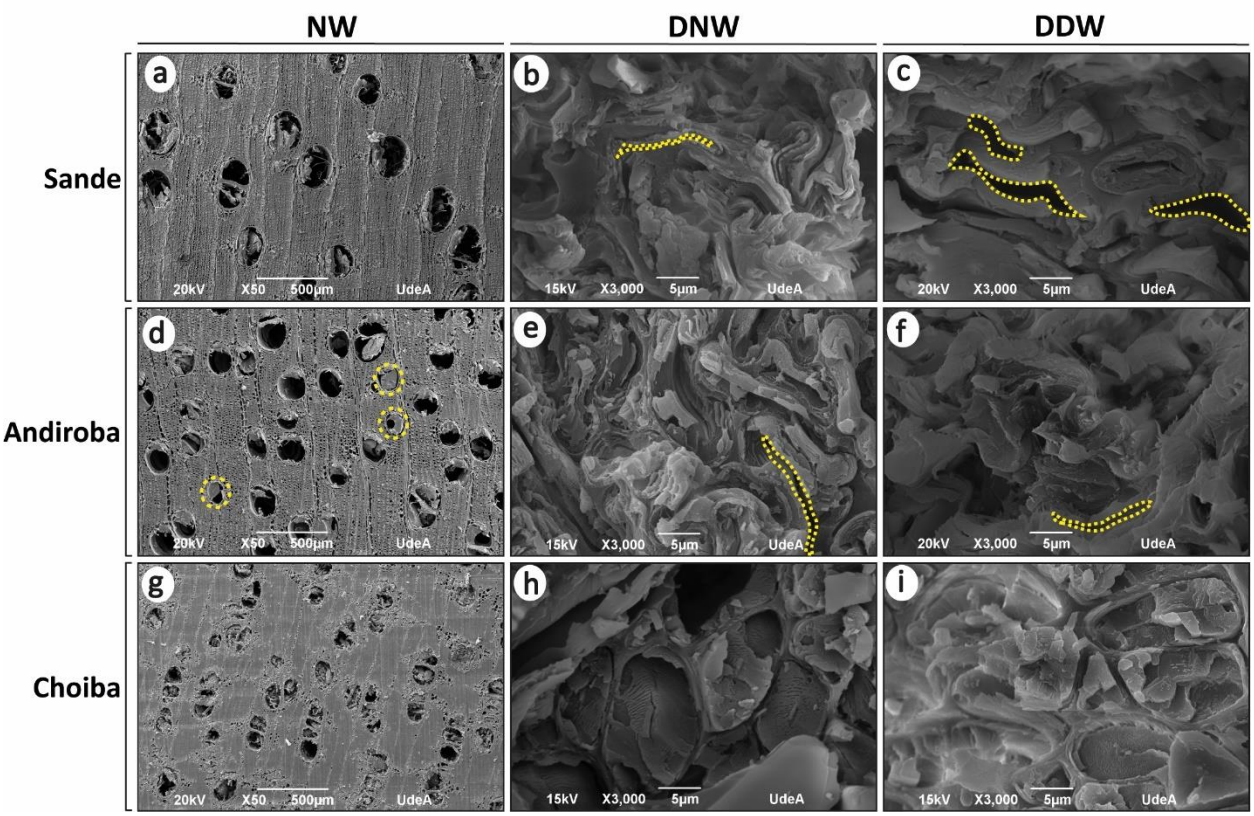


*Figure 3-2 Scanning electron images showing the cross-sections of Sande, Andiroba, and Choiba wood treated by hot isostatic pressure. NW = natural wood, DNW = densified natural wood, and DDW = densified-delignified wood. Heartwood vessels are highlighted in yellow.*

### 3.4.2 FTIR analysis

Lignin and hemicellulose were partially removed using a sodium hydroxide treatment before the densification process. This delignification procedure reduces cell wall strength and expands the lumens, improving both the interconnections between lumens (Frey et al. 2019) and the vacuum performance before the HIP process. By comparison the effect of lumen expansion in densified wood is shown in Fig. 3.2b and 3.2c. Fig. 3.3a shows the FT-IR spectra of wood specimens, which are compared for NW and delignified wood (DW). According to these results, the absorption of the bands located at 1736 and 1235 $cm^{-1}$ for carbonyl stretching and C-O stretching of the guaiacyl unit of lignin (Zhuang et al. 2020), is significantly reduced, which demonstrates the removal of lignin and hemicellulose (Chen et al. 2020b; Md Salim et al. 2021) in delignified Sande and Andiroba woods. For Choiba, this behavior was not observed. It should be noted that delignification was performed analogously in all specimens. Compositional analyses determined the relative lignin, hemicellulose, and cellulose in the specimens studied (Annex 1 Fig. S1). Lignin and hemicellulose reductions were shown to occur in the thin cell wall wood specimens. Although the fiber wall thickness is similar between Sande and Andiroba (Fig. 3.3b), the lignin removal in Andiroba was higher than expected (Annex 2 Fig. S2), even when Andiroba has a smaller vessel lumen diameter than Sande species. These differences in the effect of the delignification process between Sande and Andiroba can be explained by variations in the anatomical characteristics of the specimens, as well as by the reactions occurring during delignification, which have been described extensively in previous studies (Brännvall 2017). The decrease in lignin in the Sande specimen due to the delignification process was as expected. Song et al. (2018) demonstrated that a 45% reduction in lignin is ideal for the densification process. The typical absorbance at 1539 and 1506 $cm^{-1}$ for the aromatic skeleton in lignin (Chen et al. 2020b) showed no significant variation in lignin from the reduction of band intensity after treatment. This showed that the lignin component was partially preserved with delignification. The intensities of the bands at 1028 and 1740 $cm^{-1}$ (Fig. 3.3a) were observed to be similar in each wood specimen after alkaline treatment,

which indicates that the cellulose was not removed (Da Costa et al. 2021). In general, delignification treatment degrades some components of the wood cell wall (lignin/hemicellulose) and, as a consequence, generates pores in the anatomical structure that facilitate wood compression during the densification process (Yahyaee et al. 2022).

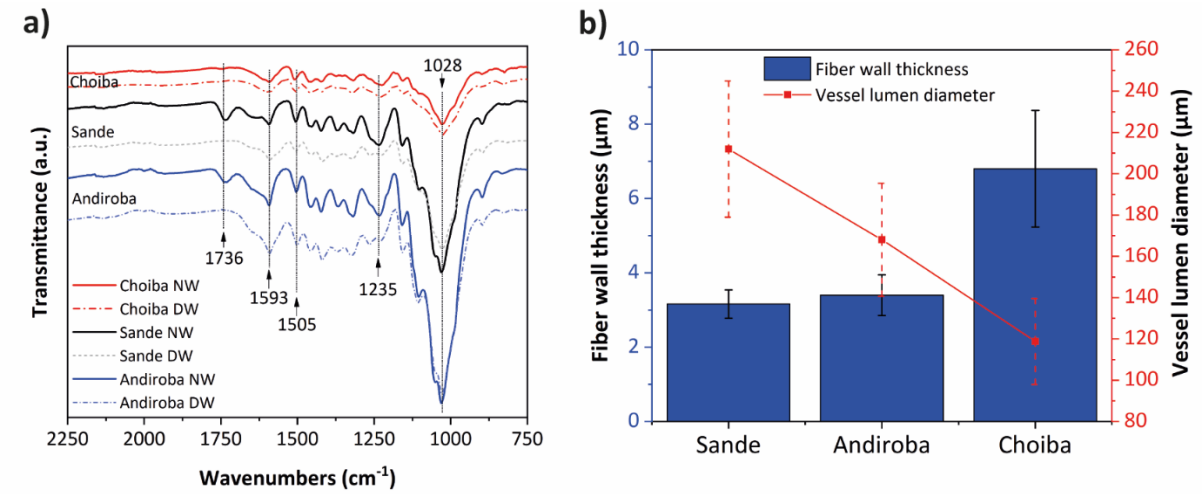


*Figure 3-3 Variations in chemical composition and anatomical aspects of the specimens studied. (a) FT-IR spectra of various wood specimens after alkaline chemical treatment (NW natural wood, DW delignified wood). (b) Some anatomical differences of the specimens studied.*

### 3.4.3 Physical properties

The physical properties and appearances of natural and delignified-densified wood are presented in Fig 3.4. The densities of NW vary in the range of 0.44 to 0.91 g/cm$^3$. After the HIP process, for any HIP condition (i.e., C1 or C2), and regardless of whether the delignification procedure was performed or not, the density of the hardwoods increased. For HIP process condition C1 (i.e., 20 MPa, 60 °C and 2 h), density increased in all three hardwood species. It is important to note that only DW was used for C1. The greatest increase occurred for the Sande species. The largest increase, about 2.6 times in comparison to natural wood, was for Sande (Fig 3.4a), while Andiroba

(Fig 3.4b) showed an increase of 1.5 times and Choiba (Fig 3.4c) 1.2 times. On the other hand, HIP process condition C2 (i.e., 100 MPa, 100 °C, and 6 h) led to a higher density increase. In C2, both NW and DW were densified. Comparing DNW with NW, the density showed increases of 2.7, 2.44, and 1.4 times for Sande, Andiroba, and Choiba, respectively. However, for DDW, even larger increases of 3.3 times 2.7, and 1.5 times were respectively obtained. Considering these effects on density, we believe that, among other aspects, thus, wood density increases with increases in HIP process parameters (pressure, temperature, and time); however, because only two sets of parameters were tested in this novel investigation, further processing parameters should be analyzed in the future to find the optimal processing parameters for HIP densification of each wooden species. Furthermore, it is noted that the increase in density was more positively affected in those specimens where delignification pretreatment was previously performed. Moreover, the greatest increase in density occurred in those specimens where a greater amount of lignin was removed, while the smallest increase in density was for Choiba. The last of these results may be due to the small fiber lumen and wall thickness hindering cell wall compression (Blomberg et al. 2006). In addition to the foregoing, the vacuum state of the fiber and vessel lumens during the HIP process allowed the cell wall of all three specimens to collapse (Annex 3 Fig. S3). During this step, the elevated gas pressure reduces the lumens of the anatomical structure by compressing the softened cell wall through both chemically and temperature effects during processing, allowing the cell wall not to fracture during deformation. The increased density of DNW and DDW specimens was mainly attributed to the decrease in cell lumen volume. As shown in Fig. 3.3b, Sande showed the highest vessel lumen and the lowest fiber thickness, while Choiba showed the inverse, that is, the lowest vessel lumen and the highest fiber thickness. Therefore, after the HIP process, the highest density value was reached in the specimen with the lowest density value, in which the previous delignification process had the most noticeable effect. Sande DDW reached a maximum density value of 1.49 g/cm$^3$ (~239% higher than that of the Sande NW).

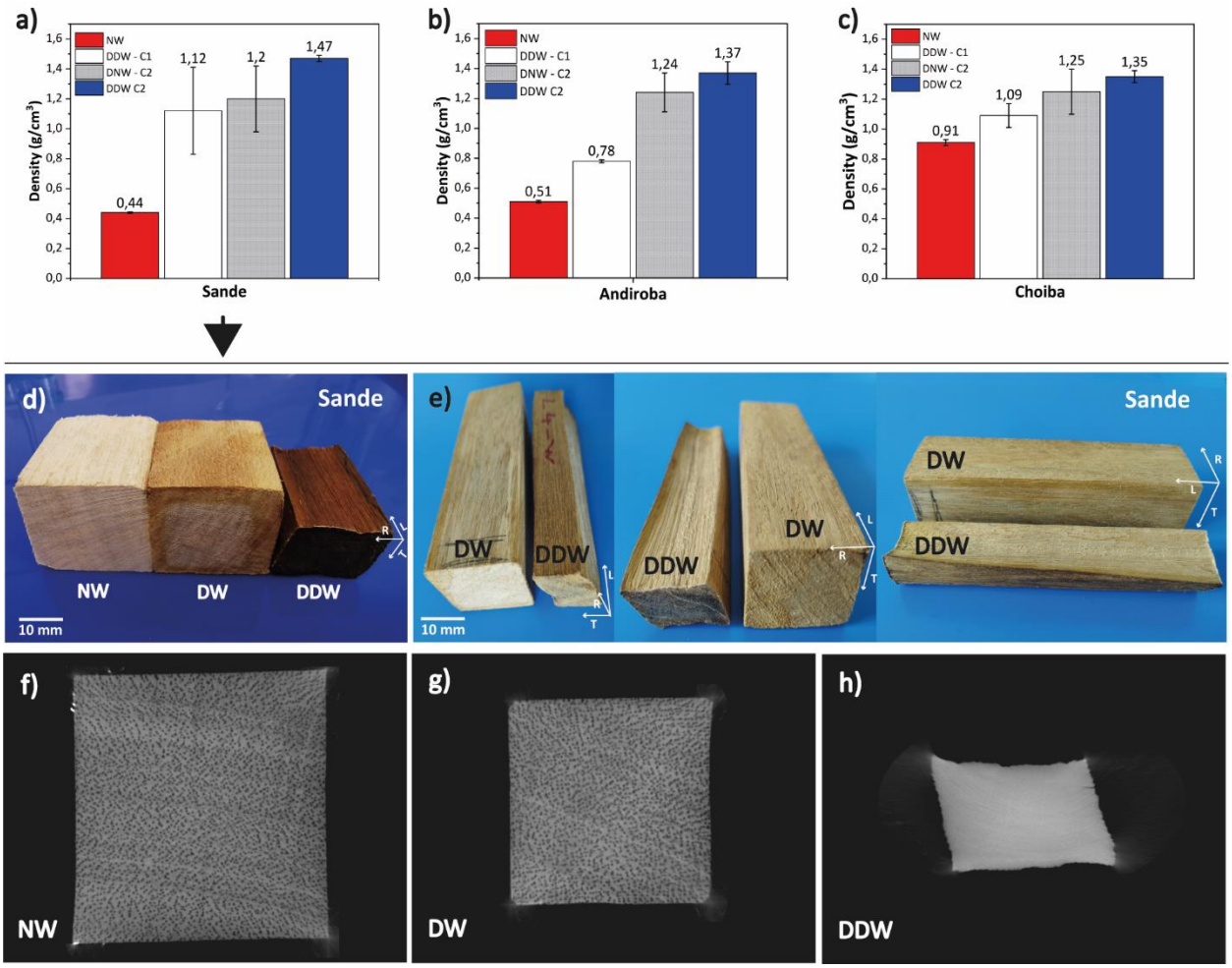


*Figure 3-4 Physical properties and appearances of natural and delignified-densified wood. Density evolution of a) Sande, b) Andiroba, and c) Choiba. NW = natural wood, DW = delignified wood, DNW = densified natural wood, DDW = densified-delignified wood, C1 = condition 1 for the HIP process, and C2 = condition 2 for the HIP process, d) and e) Physical of Sande following different treatments, f) NW, g) DW and h) DDW optical densities.*

It has been reported that the cell wall of this species shows a density value of 1.5 g/cm$^3$ (Gibson 2012); consequently, this result indicates that the combined effect of the chemical pretreatment (partial removal of lignin and hemicellulose) alongside the HIP process allows the wood to be densified almost up to its cell wall density, i.e. porosity is almost completely removed. SEM images confirmed that Sande DDW retained a small part of the lumens of the porous structure without

completely collapsing (Fig. 3.2c). This effect was even observed to a lesser extent in Sande DNW (Fig. 3.2b); however, it had no major effect on density. This conclusion is further reinforced when studying the homogeneity of density using optical density in Sande. While annual rings and other regions of different densities are clearly visible in the measurements of natural wood (Fig. 3.4f) and delignified wood (Fig. 3.4g), the optical density of delignified-densified wood (Fig. 3.4h) reveals a very homogeneous structure where only the annual rings are barely visible. This is evidence that HIP densification gives the modified wood a homogeneous density; especially with higher processing conditions (C2). It also demonstrates the effectiveness of the equiaxial pressure in densifying the wood equally throughout its entire structure.

Table 3.1 shows natural wood and CR shrinkage values after the HIP densification process. The CR values were derived from the HIP process (C2). Although the nature of the densification process is isostatic (or equiaxial), the compressibility of densified wood occurs mainly in the tangential direction (Fig. 3.4d and 3.4e). In this process, failure is radial and tangential, but selectively over the weaker direction (Blomberg et al. 2005). Compression tended to be greater in the tangential direction, as the rays tended to have a restraining effect on compression in the radial direction. This differs from Blomberg's predominance of compressibility in the radial direction (Blomberg and Persson 2004). However, this is the main reason why such a high density was obtained in the Sande species. This predominant increase in density due to compression in the tangential direction has been described elsewhere (Dömény et al. 2018). In the present case and considering that the HIP process acts on the region that gives less resistance to compression, this effect was because the natural wood under study had a higher incidence of tangential shrinkage. As shown in Fig. 3.4d, the result of the HIP process was dominated by the compression of the specimen in the tangential direction, followed by of the compression in the radial direction. In contrast, the longitudinal direction remains almost unaltered. This pattern was observed in all three specimens. According to the results, the highest CR was 65% in DDW Sande. Although Choiba NW presented higher shrinkage values, the effects of the HIP process were the opposite,

i.e., density values were not improved. This was because Choiba presents an anatomical structure that blocks the chemical removal of lignin and hemicellulose and therefore limits wood densification, as explained earlier. In addition, the results showed that the higher compression ratio in the densified wood in all three specimens is related to delignification, since lower compressibility values are associated with densified specimens that have not been previously delignified. This demonstrates that the role of the delignification process before the HIP process is of vital importance. In other words, in the present work, high wood density values were achieved by simultaneous compression of all faces of the specimens, while preserving a significant volume of the material. This is highly interesting as may suggest different uses or applications for the treated wood since various studies have pointed out that volume loss is one of the problems that emerge during wood compression (Sandberg et al. 2013). Therefore, the HIP process overcomes one of the major disadvantages of traditional densification methods, which is the significant loss of wood volume. Previous studies have reported a CR of approximately 80% in the radial direction of densified wood to obtain a partial increase in density (Song et al. 2018; Shi et al. 2020). In contrast, our study achieves the theoretical density of the cell wall, guaranteeing a greater useful volume of wood. In this study, Sande DDW and NW under the HIP process (C2) showed an average CR in the radial direction of the wood of approximately 29.2% and 24.4%, respectively. In the tangential direction of the wood, the average CR was approximately 50.2% and 37.7% for DDW and NW, respectively. Meanwhile, Sande DDW under the HIP process (C1) showed an average CR of approximately 18.5% and 40.2% in the radial and tangential directions, respectively. This shows that pretreatment with an alkaline solution influences the higher CR of densified wood (Shi et al. 2020). Process parameters, such as pressure and temperature, also played a role in increasing CR. Traditional methods control the CR during densification using metal buffers (Laine et al. 2016). In contrast, the HIP process does not control this aspect, and methods of controlling it have not yet been studied. Therefore, we consider that one of the reasons

for the greater volume preservation by the HIP process in densified wood is isostatic compression, as the cell wall is compressed at the same time in different directions.

*Table 3-1 Shrinkage coefficient, anisotropy natural wood, and a densified wood compression ratio.*

| **Specimen** | **Shrinkage coefficient (%)** | | | | **Anisotropy R/T** | **Compression ratio (CR)** | |
|---|---|---|---|---|---|---|---|
| | Radial | Tangential | Longitudinal | Volumetric | | DNW (%) | DDW (%) |
| **Sande** | 4.43 ± 0.009 | 6.47 ± 0.001 | 0.20 ± 0.001 | 11.10 ± 0.012 | 1.52 ± 0.39 | 53.5 ± 0.12 | 65.3 ± 0.04 |
| **Andiroba** | 3.74 ± 0.003 | 6.78 ± 0.007 | 0.18 ± 0.001 | 10.71 ± 0.007 | 1.83 ± 0.24 | 55.2 ± 0.04 | 56.1 ± 0.04 |
| **Choiba** | 5.30 ± 0.008 | 7.49 ± 0.008 | 0.18 ± 0.0004 | 12.97 ± 0.015 | 1.44 ± 0.24 | 20.0 ± 0.10 | 31.3 ± 0.02 |

It can be recognized that on the other hand the HIP also generated a distorted (deformed) cross section as illustrated in Figure 3.4h because the wood tended to be compressed following the weakest directions, which strongly depends on the ring orientations. This distortion can lead to an additional loss of material when further processing the wood to a regular shape. For instance, in this investigation it was found that the resulting CR of the HIP process was 65%, which is a gain of about 15% with respect to previous investigations. However, if further processing to a regular shape, an additional 10% of material would be lost, minimizing the gains of the HIP process. A possible solution to this may be testing differently oriented cross sections to minimize distortion, as well as using densified plies to engineer densified wood laminates. These approaches may maximize the material gains of the HIP densification method.

Another relevant aspect is the color change in some DW specimens and in some DDW specimens compared to the color of NW, an effect evidenced in Fig 3.4d. This change in wood coloration is due to two factors: exposure to chemical agents during the delignification process and thermal exposure during the densification process, and the reasons why this color change occurs have been extensively explained elsewhere (Lesar et al. 2013; Shi et al. 2018, 2020; Meng et al. 2020; Xiang et al. 2022). During chemical exposure, some functional groups are altered (removal of chromophores from lignin, breaking of chemical bonds, and removal of extractives) while during thermal exposure some water-soluble compounds are altered.

The volume of the specimens was measured before and immediately after the HIP process to determine the degree of compressive strain. Blomberg J, et al. reported that immediate shape recovery can reach values of 40% (Blomberg et al. 2005). In contrast, after the HIP process, no immediate compressive shape recovery effects were observed in this study. According to previous reports, dimensional stability benefits from the implementation of post-treatments such as thermal modification (Laine et al. 2016), and hydrothermal fixation treatment (Wang et al. 2021), among others. This investigation did not involve additional treatments to eliminate shape recovery. We inferred that the hot pressing and the gradual release of parameters such as pressure and temperature at the end of the HIP process are among the reasons that explained the adaptation of the densified wood to its new state (compressed). These results are similar to those obtained by Laine et al. (2016), who by applying a thermal modification treatment on densified wood for 6 h at 200 °C significantly eliminated shape recovery. To confirm this inference, in this study, the effects on immediate shape recovery were studied at a temperature of 100 °C for 6 h of HIP process. Furthermore, the wood was not forced into a shape completely foreign to its anatomical structure, as is the case with uniaxial pressing. To further verify the possibility of shape recovery, immersion shape recovery tests were performed on the Sande specimen, since it was the species that showed both a high degree of delignification and proper densification behavior. Fig. 3.5 shows the WA behavior of Sande at different conditions (NW, NW painted, DDW, and DDW

painted) following full immersion in water for 30 min. Evidently, WA was higher for NW than for the other conditions. Moreover, there was a higher WA for those specimens that were not painted compared to those that were painted. However, the DDW showed water absorption slightly over (6.6%) that of the painted NW (3.5%). The implication is that the two-step process for wood densification proposed here can fully vanish the wood porosity, preventing WA for 30 minutes in a manner equivalent to that expected from commercial wood varnishes. This is because, during the HIP process, there is a reduction in the number of cell lumen of the treated wood, as explained previously. The closure of fiber and vessel cells showed a significant effect on TS, since the moisture absorption method presented a difference of 144% between NW and DDW, the swelling value being higher in NW. For TS, the DI water immersion method showed the opposite effect, with lower TS in NW than in DDW. Compared to painted DDW, a lower swelling value was observed in painted DDW than in NW. We note that this improvement in the dimensional stability of densified wood is similar to that found in the previous study of Song et al. (2018), who determined that wood densified in a two-step process and with surface coating with paint could withstand humid environments without alterations to their dimensional stability. By comparison, wood treated with our two-step densification process resists water immersion, which enables the developed material to improve its strength even in geographical locations with high rainfall. This is because the process promotes the hygroscopic dimensional stability of the material after the reduction of the number of hydrophilic groups by the degradation of hemicellulose (Xiang et al. 2022). After the removal of hemicellulose and lignin during delignification, the ability of wood to adsorb water molecules is reduced (Kuai et al. 2022), and this is further enhanced by coating the closed pores. In fact, this effect could be strengthened by the degradation of hemicellulose by the high temperature during the densification process (Mangurai et al. 2022). We consider that the incorporation of heat during densification significantly decreased the sensitivity of wood to moisture. Although this is a positive effect, dimensional stability could be standardized by a detailed study of the thermal variable of the process without including an additional step. It has

been reported that the thermal phase provides better dimensional stability to the densified wood (Pelit et al. 2016), but it also has significant adverse effects on the physical and mechanical properties of the wood due to the degradation of its chemical components (Shao et al. 2020). Finally, it is important to mention that total immersion tests were also performed for 24 h, nevertheless, the results of these tests were not statistically conclusive and, so they were not included in the present work.

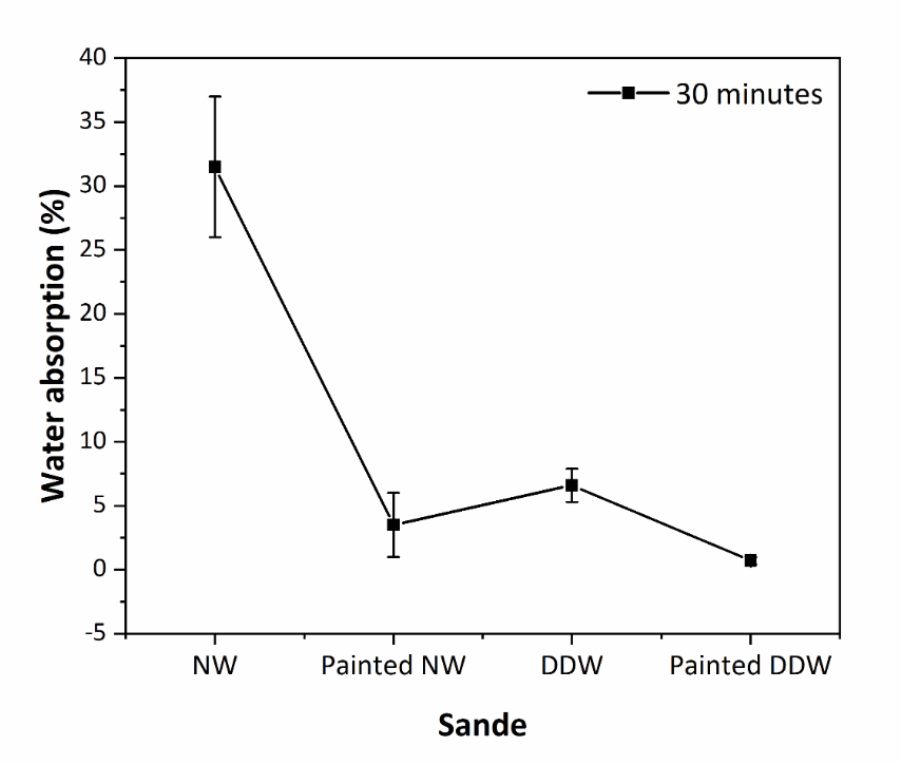


*Figure 3-5 Water absorption (WA) behavior of Sande at different conditions (NW, NW painted, DDW, and DDW painted) following full immersion in water for 30 min.*

### 3.4.4 Effect of HIP on mechanical properties

Figure 3.6 shows Sande mechanical properties following the two-step densification process. The perpendicular compressive strength of DDW was ~ 5.2 times greater than that of NW, while its tensile strength was shown not to be affected by the two-step densification process, as values

derived from mechanical tests yielded no significant statistical differences between DDW and NW. In addition, wood bending tests show that the strength and flexural modulus increased ~ 1.8 and ~ 1.5 times, respectively compared to that of NW. The lack of improvement in the tensile strength of densified wood could be explained by the fact that, by its nature, wood exhibits brittle behavior when subjected to tensile forces. Therefore, after densifying the wood and having partially removed the lignin, it is possible that the cellulose fibers could not improve this behavior; on the contrary, it seems that after the densification process, the fibers fractured a little earlier than those of the natural wood. This means that the densified wood did not increase in stiffness during tensile stresses, yet its stiffness did increase during compressive stresses. This explains the gain in both strength and stiffness of the wood during flexural tests, since, in general terms, the flexural strength of materials is governed by both compressive strength and tensile strength. This improvement in flexural strength could also indicate that the portion of neutral fiber during bending is no longer located right in the middle of the specimen, but is rather displaced a little higher, i.e., the area of the specimen subjected to compressive stress is much smaller compared to the area subjected to tensile stress. The results of the mechanical tests previously discussed are promising since they suggest potential uses or applications of the wood treated by the two-step densification process proposed in this work. For example, wood beams used in numerous structures are designed considering the main parameter the bending deformation. Therefore, the densified wood obtained here could be used to reinforce laminated timber beams. This reinforcement would consist of a densified wood plate located on the outermost part of the laminated beam, thus increasing the flexural strength of the element in question. Another important use could be derived from the exceptional gain in compressive strength.

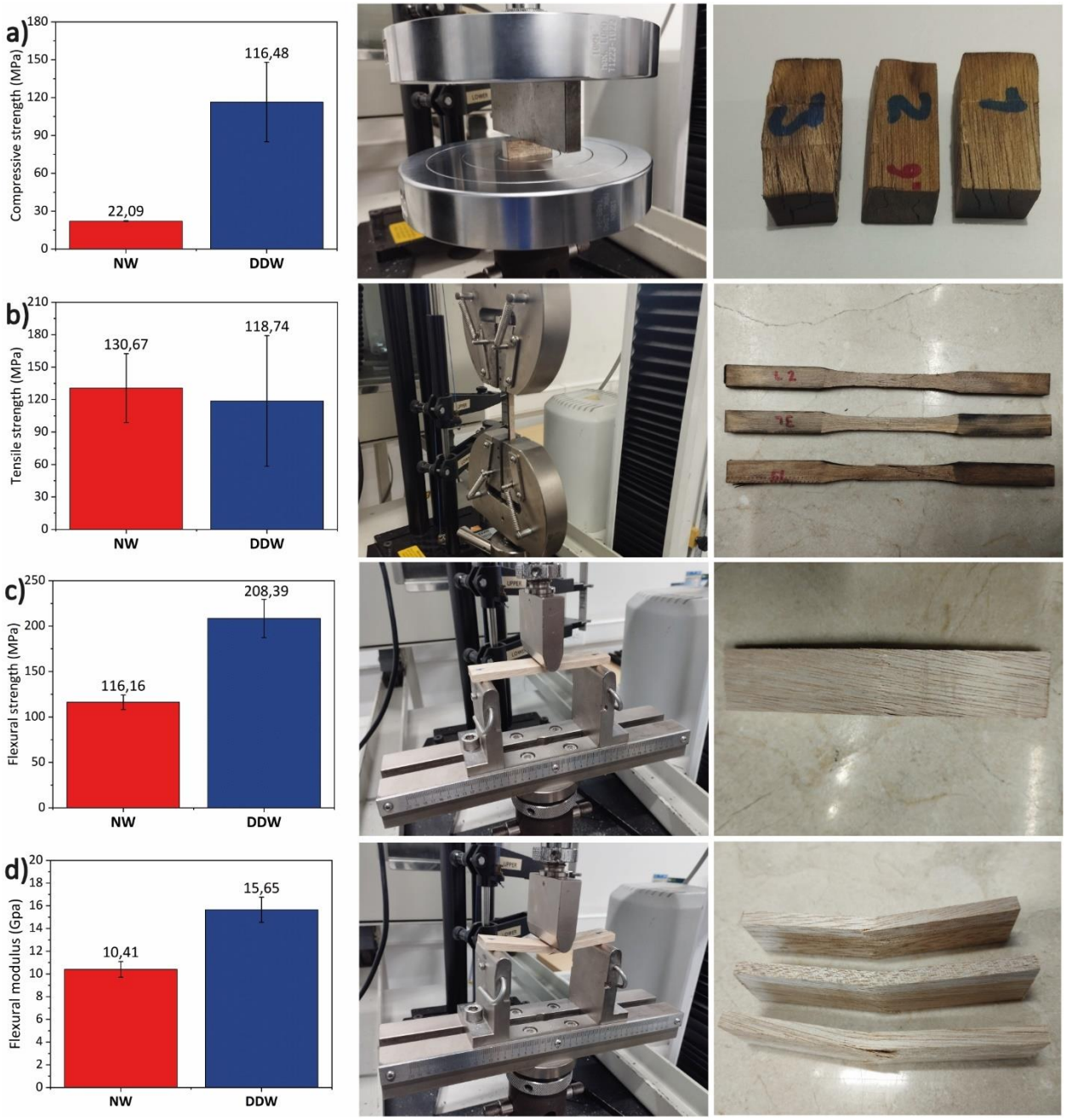


*Figure 3-6 Sande mechanical properties following the two-step densification process. (a) perpendicular-to-the-grain compressive strength, (b) tensile strength, (c) flexural strength, and (d) bending modulus.*

Normally, the mechanical connections between structural elements are the weakest and least rigid points. These results suggest that the replacement of steel elements (particularly plates) in timber

structures could be carried out using densified wood plates, as the embedding strength and fasteners' stiffness closely relates to the wood density (Xu et al. 2022). Another structural application could be manufacturing bearing plates, in which both perpendicular-to-the-grain compression strength and stiffness are essential.

## 3.5 Conclusions

In conclusion, in this work the potential of a two-step HIP wood densification method was investigated in three tropical hardwoods. The method has been shown to be very effective for all three investigated species, with one of them reaching full densification up to 1.47 g/cm$^3$, which is most complete densification reported for a hardwood species. Furthermore, the method has demonstrated clear advantages through its preservation of the virgin volume to a large extent, thanks to isostatic pressing. The obtained material also showed advantages in compared to previous densification methods regarding dimensional stability, avoidance of elastic shape recovery and exceedingly small water absorption. SEM analysis showed that specimens with a homogeneous anatomical structure, non-thick cell wall, and no marked defects in their anatomical structure are preferable for the efficient removal of basic chemical compounds from the wood. In addition, SEM also revealed that densified wood made from delignified wood had some lumens that were not completely closed, indicating that natural wood can be further compressed under this method. However, the density achieved in the Sande specimen significantly equals the cell wall density. A high degree of homogeneity is also presented in the densified wood. The material also showed enhanced mechanical properties, with an increase of about 5 times in compression perpendicular to grain, 2 times more flexural strength and 50% more flexural stiffness. Tensile strength was not appreciably increased, which may be attributable to the large brittleness of this property. The above results suggest that the use of HIP densification in wooden materials has great potential, overcoming several limitations of previous wood densification methods. New functionalities and advanced wood-based materials may be

investigated given the unique features achieved with these densification properties. The effectivity and relative physical and mechanical gains of the proposed method may be even greater for other lighter species, since all those investigated in this research were medium-density tropical hardwoods. Future research should focus on testing the method in softwoods. Furthermore, it should be investigated if the resulting shape can be controlled by considering ring orientation, because the material utilization would be enhanced by assuring that the resulting shape fits with the target geometry. In principle, this method should be capable of densifying any shape, not only rectangular cross sections, which is an important advantage that also should be assessed in future investigations.

# Chapter 4

# 4 Natural durability of densified *B. utile* exposed to field test using decomposing substrate at ground level.

This chapter corresponds to the evaluation of the resistance of the structural material obtained against the attack of biological degradation agents.

# Natural durability of densified *B. utile* exposed to field test using decomposing substrate at ground level.

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## 4.1 Abstract

This study investigated the natural decay process of HIP-densified Sande wood compared to non-densified Sande, Andiroba, and Choiba specimens. After delignification and densification via hot isostatic pressing (HIP), specimens were exposed to contrasting climatic conditions at two Colombian field sites for six months. Decay resistance was assessed using percentage weight loss (WL), SEM observations, and FTIR analysis. Our findings demonstrate the critical influence of modified anatomical structure and climatic factors (precipitation, humidity, and temperature) on the natural durability of HIP wood. Importantly, under milder climatic conditions, the HIP densification process significantly improves decay resistance. This suggests promising potential

for new HIP-processed wood materials, though further laboratory decay tests are needed to fully determine the ideal applications for this high-performance material.

**Keywords:** Durability, HIP densification, wood decay, tropical hardwoods.

## 4.2 Introduction

Natural durability is an important criterion of wood that relates to the performance and service life of the material, as of the products developed with that wood (Niamké et al. 2011; Plaschkies et al. 2014). Wood's durability is impacted by various environmental factors, both living and non-living. These include exposure to molds (Ligne et al. 2021), temperature, salt (Mi et al. 2020)), high humidity (Kim et al. 2020a), and water infiltration through rain (Saito 2017). Wood decomposition involves significant changes to its chemistry and composition, driven by those environmental factors and fungi (Manici et al. 2023). The specific type and quality of the wood heavily influence this process. Each wood species has unique properties that determine how quickly or slowly it breaks down (Polanco Tapia et al. 2014). Understanding wood's natural resistance to decay is crucial for its long-lasting performance. One important factor is density. Denser woods, like hardwoods, typically offer better resistance as their smaller vessel pores hinder fungal growth (Schilling et al. 2021). Beyond density, other inherent properties play a role. Hardwoods, for instance, tend to be more durable due to their unique anatomical structure, which often includes smaller vessel diameters (Dadzie and Amoah 2015). Fungi are the primary culprits behind wood decay, responsible for the most common type of wood damage (Kenneth E. Udele; Jeffrey J. Morrell; Arijit Sinha 2021; Embacher et al. 2023). These wood-rotting fungi break down the essential components of the wood cell wall, including cellulose, hemicelluloses, and lignin. Interestingly, the type and amount of lignin present in wood also significantly influence its natural durability (Dadzie and Amoah 2015). The combined influence of these factors, along with varying microorganism communities and environmental conditions, leads to diverse types of wood decay

(Martín and López 2023). This susceptibility ultimately shortens the lifespan and compromises the safety of wood products, particularly in construction applications. Thus, researchers often employ various technological processeses to enhance the natural durability of wood. One such process is wood densification, which aims to improve key properties like density, strength, and, of course, durability itself.

Studies have shown that additional treatments can improve the decay resistance of densified wood. These treatments include thermal post-treatment (Candelier et al. 2016; Pelit and Yalçın 2017), freezing and thermal treatments (De Avila Delucis et al. 2019), resin impregnation (Freitag et al. 2015), and a combination of different technological process such as ammonification, densification, and heat treatment (also known as the Lignamon process) (Baar et al. 2023). The goal of these treatments is to significantly increase the wood's resistance to degradation, especially fungal decay (Ringman et al. 2019). While densification alone might not be sufficient to enhance natural durability (Kutnar et al. 2011; Pelit and Yalçın 2017), the type of wood and the presence of natural compounds can also play a significant role in its overall resistance (Dadzie and Amoah 2015).

In previous chapters of this thesis, a two-step densification method using delignification and hot isostatic pressing (HIP) was proposed. This process increases wood density, improves mechanical performance, reduces shape recovery, and decreases hygroscopicity (Maturana et al. 2023). These enhanced characteristics position the resulting material as a high-performance option. To fully understand the potential of HIP wood as an engineered composite material, we must test its behavior under different conditions throughout its useful life. One crucial test is natural durability, which assesses the wood's resistance to biological decay (Deklerck et al. 2020). Researchers use various standardized tests to evaluate durability, including laboratory decay testing (Gao et al. 2016; Baar et al. 2023) and field performance tests (Ali et al. 2011). Laboratory tests concentrate on the specific fungi responsible for decomposition, while field tests assess the

overall extent of decay (Stirling et al. 2017). Field trials provide valuable insights into how wood degrades under real-world conditions (Tomak et al. 2022), as environmental factors directly influence decay (Martín and López 2023). These trials offer a vital understanding of the wood degradation process in practical applications (Mattos et al. 2014).

In this study, we evaluate the natural resistance of Sande (Brosimum utile) wood densified by the HIP process. Samples will undergo a 6-month field decomposition test in contact with soil using mini-blocks. Decay resistance across two different geographical locations will be assessed by weight loss, SEM, and FTIR analysis. This work will determine the behavior of HIP-densified wood against decay agents in natural outdoor conditions, informing its suitability for use in different climates.

## 4.3 Materials and methods

### 4.3.1 Materials

For this research, we used Sande (Brosimum utile), commercially sourced from the Chocó-Darien region. Samples were free of visible defects and fungal attack. We included two control species: Andiroba (Carapa guianensis), a medium-density tropical hardwood, and Choiba (Dipteryx oleifera), a high-density species. These control woods are widely used in the study region due to their desirable properties and provided a basis to evaluate the influence of anatomical structure on wood durability. To prepare the material, mini-blocks of 50 (R) × 50 (T) × 100 (L) $mm^3$ were cut from sawn wood stock. Prior to use, these samples were kiln-dried at 103°C for 24 hours until they reached a constant weight.

### 4.3.2 Decay resistance

The decay resistance of densified wood was evaluated following a modified EN113-2 standard (EN 113–2 2021). Decomposition tests were conducted at two geographically distinct sites in Colombia with contrasting climates: Site 1 (L1-Medellín): temperate-dry climate with a mean temperature of 21.0 °C and 1285.4 mm of precipitation during the study period (Figure 4-1a), and site 2 (L2-Quibdó): warm-pluvial climate with a mean temperature of 25.9 °C and 3835.6 mm of precipitation during the study period (Figure 4-1b). Climatic data for both locations were obtained from the Instituto de Hidrología, Meteorología y Estudios Ambientales de Colombia (IDEAM 2023). Both test sites employed a uniform decomposing substrate. It consisted of a 50% moisture content (MC) mixture of water, soil, and representative decomposing forest residues from each respective site. The mixture was sieved and homogenized. To facilitate the decomposition process, containers holding the substrate were bottom-perforated, allowing moisture exchange between the substrate and the surrounding soil. A physical barrier prevented direct exposure to rainfall. Prior to use, each bed was stabilized at room temperature for a week in an open-air environment. In parallel, wood specimens of three types - Sande, Andiroba, and Choiba - were conditioned in an oven at 20 °C ± 2 for one week. This ensured a constant weight through slow drying. The dimensions of the mini-blocks were 15 mm x 25 mm x 50 mm (R x T x L).

Experimental tests were carried out on densified Sande (Sande-D) using mini-blocks (15mm (R) x 15mm (T) x 50mm (L)). The smaller block dimensions were necessary due to the volume reduction caused by the densification process. Sande-D was produced using the densification process detailed in Chapter 3. Specimens were placed in contact with decomposition beds to evaluate the natural durability of these three tropical hardwood species.

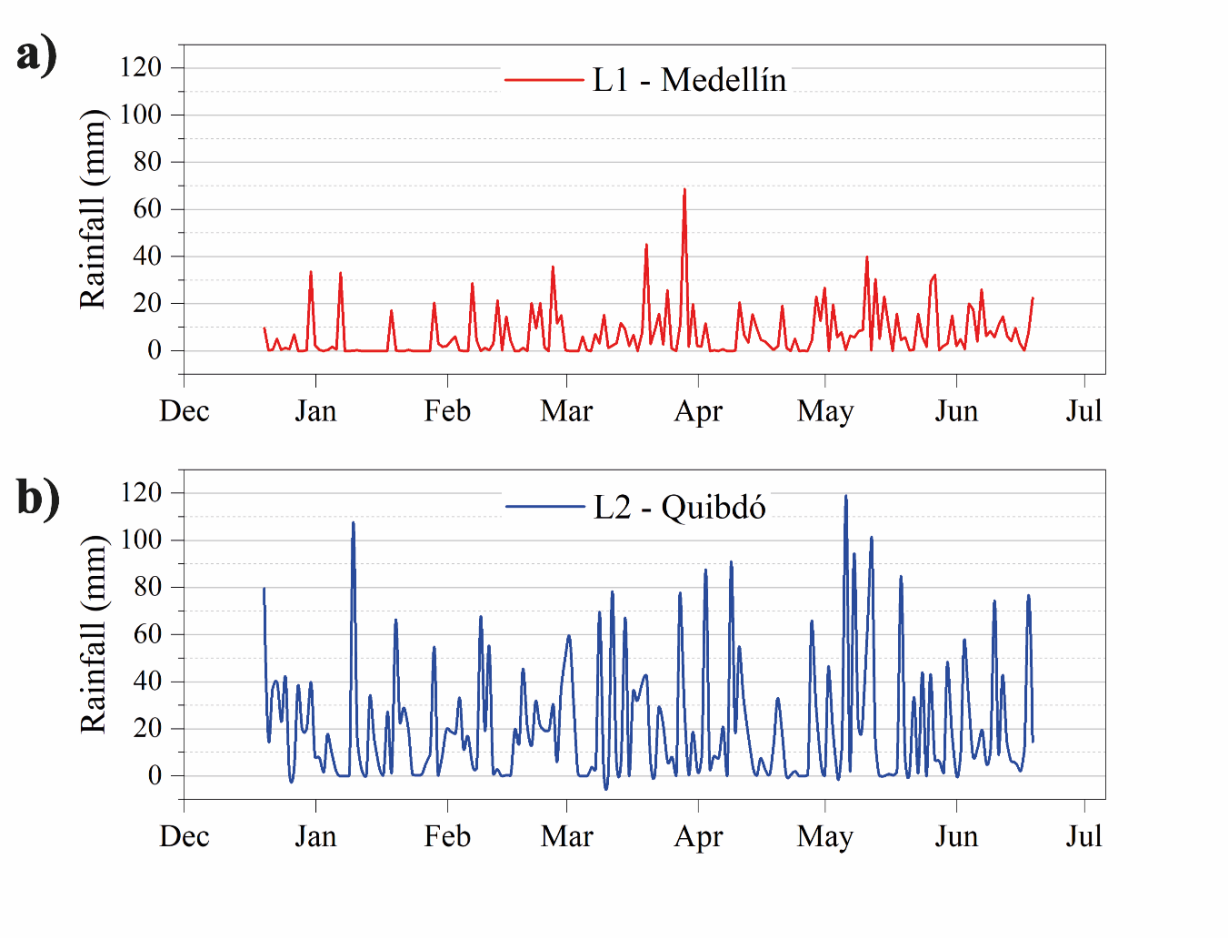


*Figure 4-1 Comparative illustration of precipitation recorded during the test period at exposure sites: (a) rainfall behavior at L1-Medellín; (b) rainfall behavior at L2-Quibdó.*

A total of 32 mini-blocks of natural wood were prepared for each wood species and 8 of Sande-D. These blocks were exposed to natural decay in the open air for 24 weeks in both designated geographical locations. Throughout the study period, the specimens were continuously monitored for any changes or variations. Following the exposure period, the fungal mycelium (the vegetative part of the fungus) was carefully removed from the wood surfaces using a brush. Subsequently, the specimens were oven-dried at a controlled temperature of 103°C ± 2°C for 24 hours to achieve a constant weight. To assess natural durability, the percent weight loss (WL) was measured. This value was calculated using the following formula:

$$\text{WL}\ (\%) = \frac{w_1 - w_2}{w_1}$$

Where $w_1$ represents the dry weight of the conditioned samples before degradation, $w_2$ represents the weight of the dry sample after the decomposition test. The average values of weight loss were then calculated as the average of *n* experimental values for each condition and specimen. Durability class (DC) was subsequently determined based on the obtained weight loss percentages and the classification criteria outlined in EN 350 (EN 350 2017) standard.

### 4.3.3 Measurements and characterization

Attenuated total internal reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was used for sample characterization (Spectrum Two, PerkinElmer, MA, USA). The analysis was conducted with a scan range of 4000-450 $cm^{-1}$, a resolution of 4.0 $cm^{-1}$, and an average of 24 scans per specimen. The NW and densified wood were prepared as thin sections, with thicknesses lower than 1 mm, using a precision knife. One measurement was performed per specimen. Spectra were recorded in transmittance mode versus wavenumber to investigate the effects of the decay process on the specimens' chemical composition.

A scanning electron microscope (SEM, JEOL JSM-6490LV) was used to examine the morphology and microstructure of a densified wood specimen's cross-section. Operating at accelerating voltages of 15 and 20 kV, with a beam current of 85 amperes, the SEM provided detailed images. The cryofracture technique was employed to prepare the densified specimens, ensuring the preservation of their microstructure. ImageJ software (Schneider et al. 2012) was used to analyze and quantify observed features. Finally, the spectrum was imported into Origin software for further analysis.

Fungal colonization of wood specimens was assessed by collecting decomposing samples from both exposure sites, L1-Medellín and L2-Quibdó, for subsequent analysis at the Grupo

Interdisciplinario de Estudios Moleculares (GIEM) laboratory at the University of Antioquia (Medellín, Colombia). Taxonomic keys were employed to identify the fungal species present during the testing period. At L1-Medellín, the dominant fungal inhabitants were identified as *Trichoderma spp*. and *Aspergillus niger*. In contrast, the analysis of samples from L2-Quibdó revealed the presence of *Trichoderma spp*. alongside an unidentified fungal species.

## 4.4 Results and discussion

### 4.4.1 Percent weight loss in different regions and rainfall intensity

Field tests conducted in Medellín and Quibdó, despite their contrasting climatic conditions and rainfall patterns, provided consistent estimates of the natural durability of Sande, Andiroba, and Choiba hardwoods. These findings align with established research indicating the reliability of field tests for assessing wood's natural durability (Ali et al. 2011). The percentage of weight loss serves as a widely accepted indicator of this durability (Jurgensen et al. 2006; Lipeh et al. 2021). Figure 4.2 presents a detailed breakdown of the weight loss experienced by the hardwood mini-blocks during 24 weeks of exposure to field conditions. Notably, similar values of percentage weight loss were observed across L1-Medellín and L2-Quibdó for Sande, Andiroba, and Choiba hardwoods, irrespective of the differences in rainfall intensity (Figure 4-1).

A key principle is that the higher the percentage weight loss (%WL), the lower the wood's natural durability (Dadzie and Amoah 2015). Sande-NW exhibited a notably higher WL (about 11%) (Figure 4-2a). Andiroba-NW specimens demonstrated approximately 5% WL at both L1-Medellín and L2-Quibdó, while Choibá-NW showed a similar WL of just 3% across the exposure sites. Based on these WL values, Sande-NW is classified as moderately durable (DC 3), Andiroba-NW as durable (DC 2), and Choiba-NW as very durable (DC 1).

These results in natural wood underscore the influence of wood species, anatomical factors (wood quality), geographic regions, and the wood's growing conditions (Bahman Ghiassi and Paulo B. Lourenço 2019). A crucial factor is that fast-growing wood tends to decay more rapidly than slow-growing wood (Venugopal et al. 2016). This is relevant as hardwoods generally exhibit greater density due to their slower growth. Wood density has been linked to durability and decay resistance (Schilling et al. 2021). Choibá, with its high density and slower growth compared to Sande and Andiroba (as described in Chapter 2, Table 2-1), demonstrated a lower decay rate. The anatomical structure analysis of the studied specimens, presented in Chapter 2, highlights the anatomical differences that could contribute to the enhanced natural durability observed in Choibá.

Under high rainfall intensity at L2-Quibdó, Sande-D exhibited significantly higher percentage weight loss values compared to Sande-D at L1-Medellín and the control specimens at both sites. Notably, this behavior wasn't observed in natural Sande-NW at L2-Quibdó. This difference likely stems from the partial lignin removal (47.4%) in Sande-D (Chapter 2, Figure 2-2 b, c). Lignin contributes to wood's hydrophobicity, and its absence makes the material more susceptible to water absorption (Ma et al. 2022). Consequently, under Quibdó's frequent rainfall (Figure 4-2), the delignified wood's water adsorption likely increased, accelerating decay – a common phenomenon in wood materials exposed to such climates (Saito 2017).

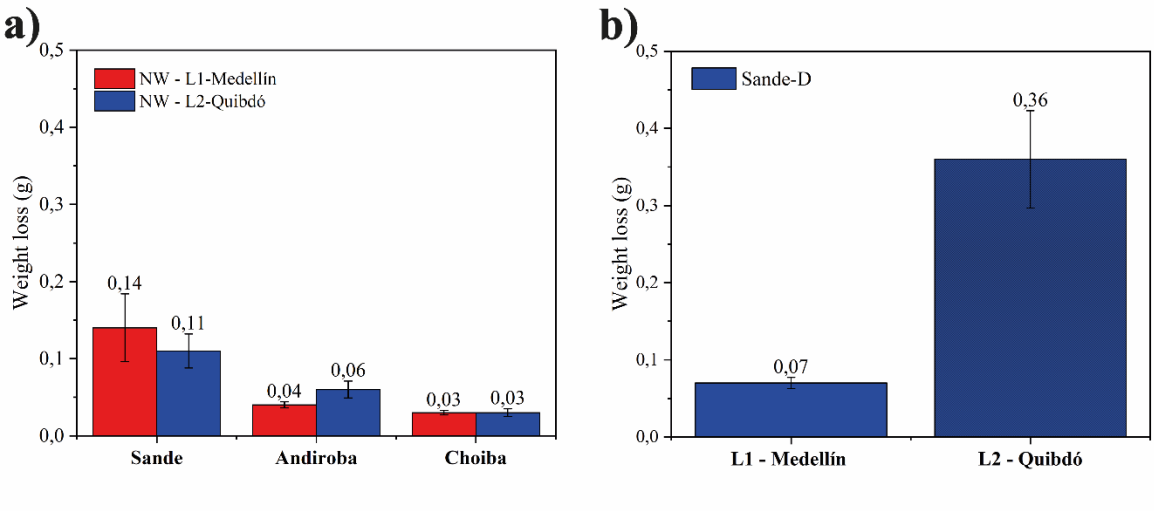


*Figure 4-2 Weight loss of the mini-blocks after 24 weeks of natural durability test: (a) weight loss of the natural wood specimens at site L1-Medellín and L2-Quibdó; (b) weight loss of Sande-D at site L1-Medellín and L2-Quibdó.*

L1-Medellín experienced an average of 7 rainy days per month, significantly less than L2-Quibdó's average of 20 days. This difference in moisture input led to variations in the physical appearance of the wood after 12 weeks of exposure. As rainfall duration is a crucial factor in wood decay (Brischke et al. 2006), the higher moisture levels at L2-Quibdó likely promoted greater colonization of the specimens. In Figure 4-3, the Sande-NW surface exhibits the most notable changes after 24 weeks, while control specimens of Andiroba-NW and Choibá-NW show less surface alteration. Sande-NW displays severe discoloration and loss of gloss, indicative of degradation. Sande-D at L2-Quibdó also demonstrates progressive deterioration (Figure 4-3l), while Sande-D at L1-Medellín appears unchanged (Figure 4-3k), aligning with their respective %WL values. Notably, in the initial weeks of exposure, mold growth was observed on Sande-NW at the L2-Quibdó site, consistent with the promotion of mold in environments with high humidity and temperature (Martín and López 2023). Andiroba and Choibá specimens at L2-Quibdó did not display this mold colonization. This difference likely arises from variations in their anatomical structures influencing mold susceptibility. Specifically, Choibá's thick fiber walls and narrow

lumens (Chapter 2, Figure 2-3) increase its density and impede moisture penetration. Consequently, the wetting of Choibá's anatomical structure is reduced, potentially hindering mold establishment and slowing degradation processes compared to Sande.

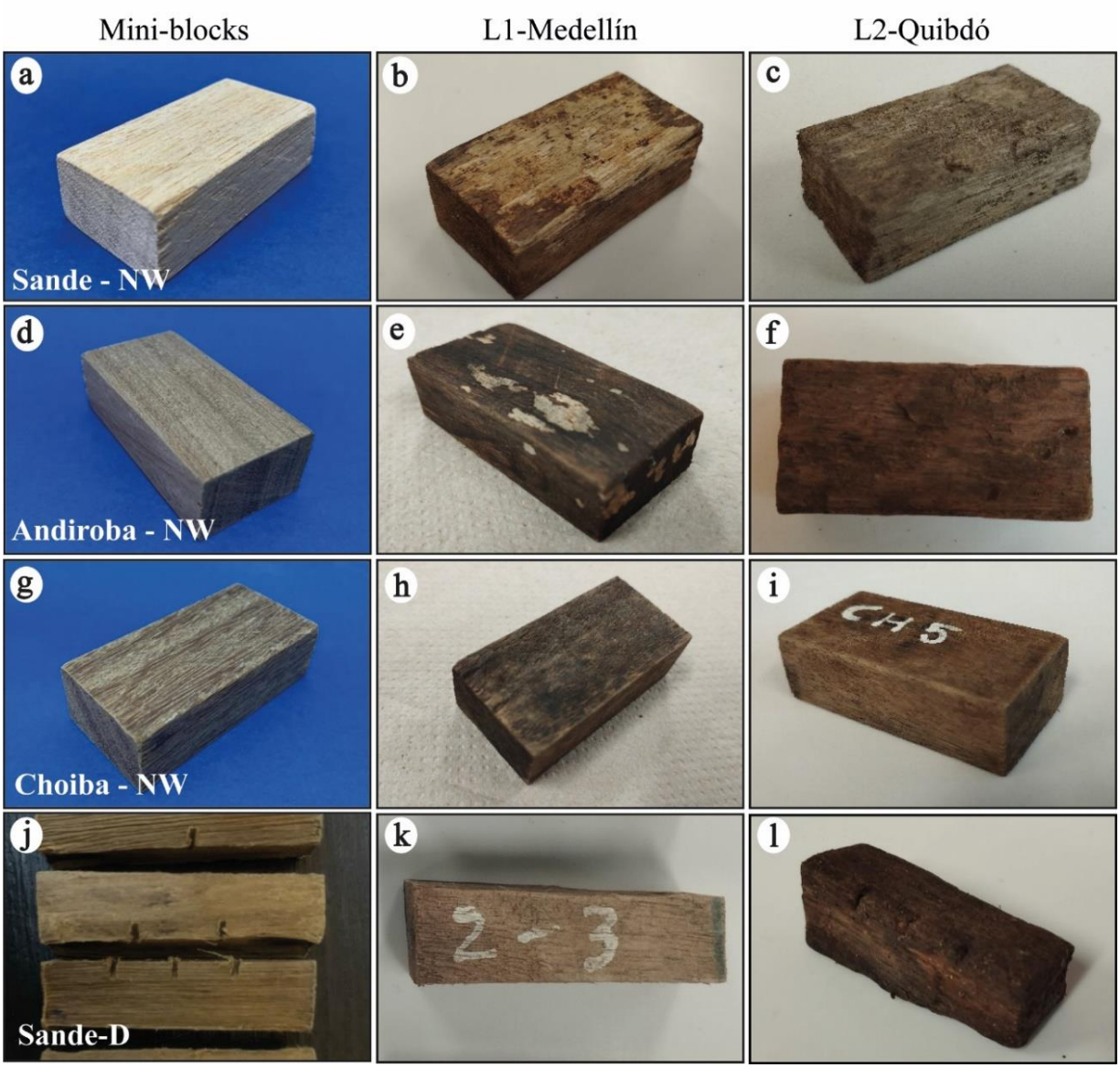


*Figure 4-3 Comparison of the effects of the degradation process in the mini-blocks after 24 weeks of exposure: (a, b, and c) Sande-NW; (d, e, and f) Andiroba-NW; (g, h, and i) Choibá-NW; (j, k, and l) Sande-D.*

Temperature plays a crucial role in wood decay processes, influencing dynamic physicochemical phenomena like adsorption, diffusion, capillary condensation, and active moisture transport during wetting and drying cycles (Brischke and Alfredsen 2020). The mean daily temperatures at L1-Medellín ranged from 15.6 to 30.9 °C, and from 21.9 to 34.3 °C at L2-Quibdó (IDEAM 2023). The average temperatures were 21.04 and 25.86 °C for L1-Medellin and L2-Quibdó, respectively (IDEAM 2023). Additionally, L2-Quibdó exhibited a higher average daily relative humidity (87.1%) compared to L1-Medellín (78.9%) (IDEAM 2023). This higher equilibrium moisture content in Sande-D specimens at L2-Quibdó likely contributes to increased moisture retention, potentially favoring the growth of decay fungi (Ali et al. 2021).

### 4.4.2 Effect of the decay on the wood

The densified Sande-D specimens exhibited contrasting decay rates across the two exposure sites. At L1-Medellín, Sande-D achieved a WL of 7.3%, significantly lower than the WL of natural Sande-NW, indicating improved durability (durable-DC 2). This suggests that the two-step modification process successfully reduced degradation susceptibility in Sande. This improvement likely stems from the HIP process significantly reducing porosity, thus limiting water absorption (Maturana et al. 2023). This modified behavior may mimic denser anatomical structures like those found in Choibá, where narrow lumens hinder water penetration and enhance decay resistance. Conversely, Sande-D at L2-Quibdó experienced severe degradation with a WL of 36.3% (not durable-DC 5). This highlights the powerful influence of L2-Quibdó's climate and fungal environment on the material's breakdown, overcoming the initial protective effects of the modification process. Initially, Sande-D did show delayed decay compared to natural Sande-NW at L1-Medellín, likely due to the reduced water absorption stemming from its hygroscopic dimensional stability (Maturana et al. 2023). However, under L2-Quibdó's high rainfall, the Sande-D's hygroscopicity continuously increased, leading to cell wall swelling (Baar et al. 2023).

Additionally, fungi alter wood composition and elevate its hygroscopicity through respiration and moisture transport (Thybring 2017). This colonization, amplified by a multitude of fungal individuals, likely accelerated the decay rate (Banik et al. 2024). This highlights the critical impact of local environmental conditions, especially moisture content, on a wood product's vulnerability to biological attacks (Repič et al. 2022; Martín and López 2023). Decay fungi characteristically decrease the weight of wood by development through the vascular tissues and degrading cell wall components partially or completely (Li et al. 2022). The contrasting degradation of Sande-D demonstrates that density alone may not determine natural durability, as suggested by certain studies (Brischke and Alfredsen 2023).

Figure 4-4 presents FTIR spectra (4000-500 $cm^{-1}$ range, with a focus on 1800-800 $cm^{-1}$) revealing the effects of natural degradation on the structural compounds of the studied woods. Peak assignments are based on existing literature (Mattos et al. 2014). The broad peak around 3350 $cm^{-1}$ corresponds to -OH stretching vibrations (primarily from cellulose), while 2890 $cm^{-1}$ is attributed to HN vibrations. Control specimens exhibited distinct behaviors. For Choibá, peaks at 3350 and 2890 $cm^{-1}$ intensified at both sites, consistent with natural decomposition. Andiroba showed a similar peak increase for 3350 $cm^{-1}$ at L2-Quibdó, but not L1-Medellín. Its HN peak intensity decreased only at L2-Quibdó. Conversely, Sande demonstrated a decrease in the 3350 and 2890 $cm^{-1}$ peaks at both sites, likely due to a reduction in intermolecular water and hydroxyl groups of cellulose and hemicellulose resulting from decomposition in both environments. Interestingly, Sande-D displayed an increase in the 3350 and 2890 $cm^{-1}$ peaks (Figure 4-4b). This heightened hydrophilicity within the modified wood increases its susceptibility to swelling and biodegradation (Chang et al. 2024). These findings suggest the degradation of cellulose components during the decomposition process (Can et al. 2023).

Analysis of post-test Sande-D from L1-Medellín revealed a significant change at the 1735 $cm^{-1}$ peak, indicating alterations to the C=O stretching of xylan. Moreover, Sande-D from both sites

exhibited an increase in the 1592 and 1505 $cm^{-1}$ peaks, associated with C=C stretching in lignin's aromatic ring and the benzene ring stretch, respectively. The most pronounced increase occurred at 1505 $cm^{-1}$. These spectral changes likely reflect fungal modification of lignin structure rather than complete degradation (Wang et al. 2014). The decomposition process within the HIP-modified wood clearly altered multiple cell wall components. This is demonstrated by variations in peaks representing cellulose and hemicellulose functional groups (1367, 1319, 1235, 1161, and 896 $cm^{-1}$, with 1367 $cm^{-1}$ corresponding to cellulose C1). Additionally, changes in representative lignin peaks were also observed. This ability to degrade wood to its initial constituents is unique to wood decay fungi (Li et al. 2022). Furthermore, under the given test conditions, isolating the effects to a specific decay mechanism is not feasible.

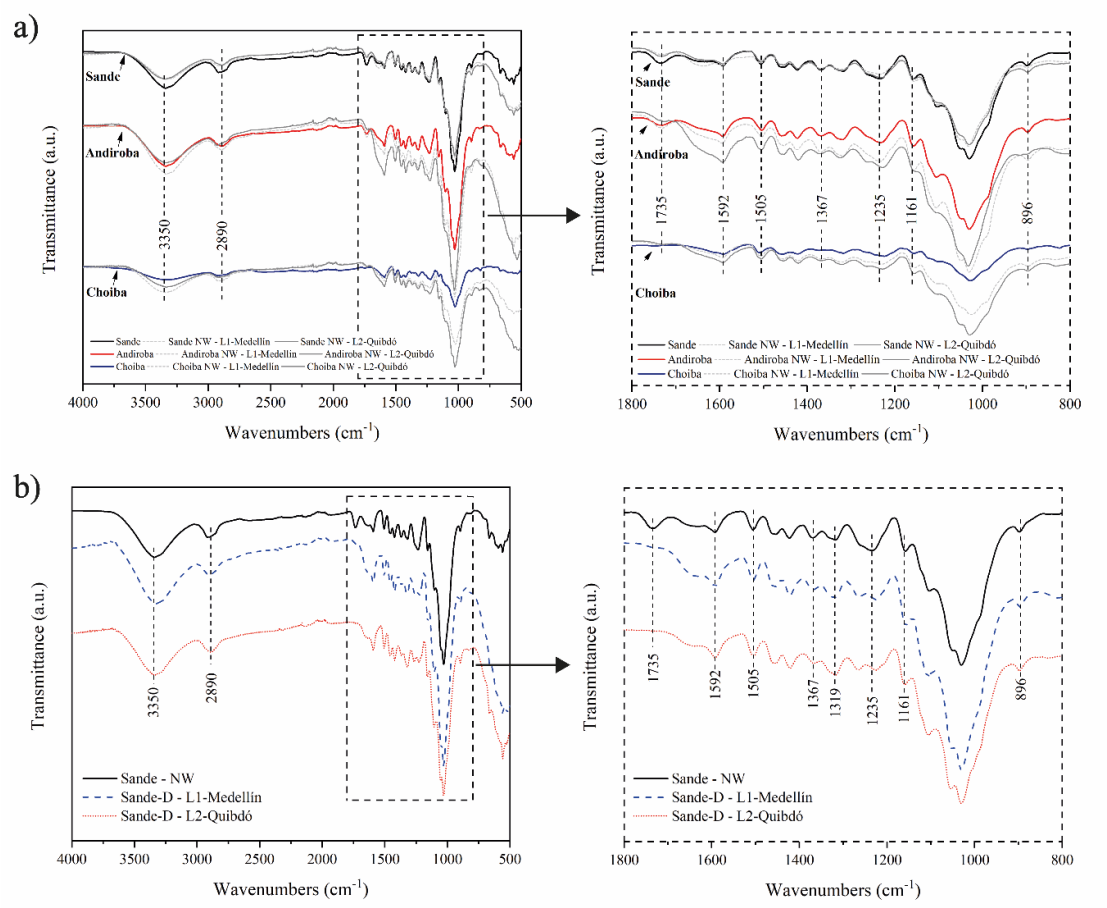


*Figure 4-4 FTIR spectra of wood subjected to natural durability test: (a) natural wood specimens; (b) Sande-D specimen.*

SEM analysis of degraded Sande-D cell walls (Figure 4-5) highlights the impact of the HIP process on wood performance. Initially collapsed pores (Figure 4-5a) exhibited a reversal of volume reduction due to material wetting from precipitation and ambient humidity (Figure 4.5 b, c). This, combined with the weakening and irregular shaping of the microstructure (Figure 4.5c), suggests the degradation of lignin, hemicelluloses, and cellulose (Kim et al. 2015), likely caused by multiple biodegrader species.

Cell wall damage associated with biodegraders, particularly in tracheids adjacent to vessel lumens, was evident in control specimens at both sites (Figure 4-5b). This observation implies that vessel lumens acted as dispersal channels for these organisms. The severity of cell wall

damage was greater in L2-Quibdó specimens. While the high temperatures of the densification process could contribute to the thermal degradation of hemicelluloses and lignin (Kutnar et al. 2011), it's worth noting that the factors influencing wood's natural durability are complex. Durability is affected by density, anatomical features, the type and amount of extractives, and the specific characteristics of lignin (Dadzie and Amoah 2015; Gao et al. 2018).

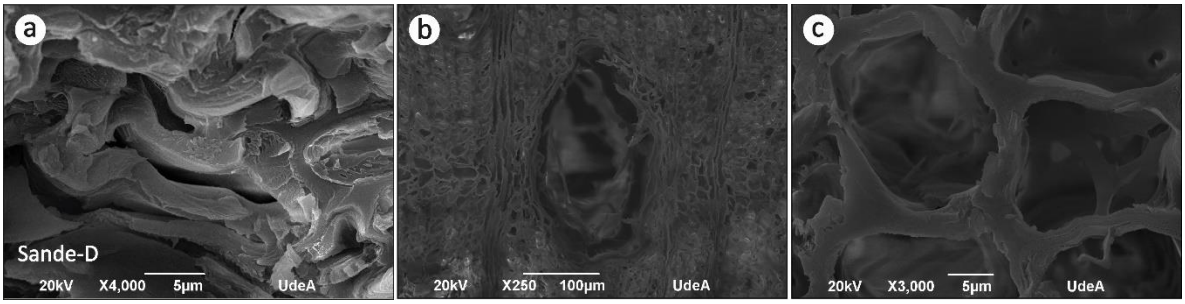


*Figure 4-5 SEM images showing cross-sections of Sande-D wood. (a) Anatomical structure densified in the HIP process. (b) Recovery of the volume of the vessel lumens of the anatomical structure. (c) Microstructure weakens and volume recovery of fiber lumens.*

While our study provides novel insights into the effects of HIP densification on natural durability, certain limitations should be acknowledged. A crucial one is the limited number of species densified using HIP technology thus far. Furthermore, to fully understand the interplay of factors influencing the HIP material, additional studies from various perspectives are required. For instance, the role of non-structural chemical compounds like extractives, known to influence durability (Lipeh et al. 2021) and linked to phenolic composition (Lajnef et al. 2018), warrants further investigation. Analyzing the mineral content after the delignification process used within the HIP method would also be valuable. Despite these limitations, our results hold significant implications for the use of HIP-densified wood, demonstrating its potential for increased natural durability under less severe climatic conditions.

## 4.5 Conclusions

Our findings indicate that the HIP densification process enhances wood's natural durability, especially in milder climatic conditions. This improvement stems from the modified anatomical characteristics and physical properties of the HIP wood, offering increased resistance to decay factors and potentially extending its service life. While less pronounced in the challenging warm pluvial climate, the positive effects of HIP densification remain significant.

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# Chapter 5

# 5 Final conclusions

In this chapter, I synthesize the findings from Chapters 2, 3, and 4, demonstrating how they collectively address the central objective of this dissertation. I present key conclusions, discuss their broader implications, and propose future research directions to further advance wood densification technologies.

## 5.1 Global remarks

This research focuses on developing a high-performance structural material from low-density tropical hardwoods. By addressing the limitations of less utilized wood varieties, we aim to reduce reliance on overexploited timber species. Our strategy involves a two-stage mechanical densification method called hot isostatic pressing (HIP), which significantly enhances wood's physical, chemical, and mechanical properties. Our research demonstrates the potential of strategically combining chemical and mechanical techniques to optimize the densification of tropical hardwoods. Specifically, alkaline delignification as a pre-treatment shows promise for medium-density species like B. utile, facilitating subsequent densification. The two-step HIP densification approach achieved unprecedented density levels while maintaining the original sample volume and improving key properties. While delignification proved somewhat non-uniform, these findings suggest that a tailored pre-treatment, followed by HIP, offers a promising path for creating high-performance materials derived from underutilized tropical wood resources.

The first objective of the thesis is dealt with in Chapter 2, where a delignification process, based on the identification of its main ultrastructural components, was defined as a pre-treatment for its subsequent densification. This treatment was based on the improvement of the chemical conditions of the cell wall by modifying (partial elimination) the content of cell wall constituents such as lignin and hemicellulose. In summary, the analysis of delignified specimens confirmed that alkaline chemical treatment is a process with non-uniform effects on the removal of lignin and hemicellulose in the anatomical structure of the wood. However, the results obtained suggest that medium-density tropical hardwoods such as *B. utile* can be easily delignified using the treatment studied.

Chapter 3 focuses on the second objective of this work and the first points of the last objective. To achieve this, the results of the previous objective were used as a first step. In summary, a very effective equiaxial pressure process has been demonstrated to achieve the most complete

densification ever recorded for a frond species. Clear advantages were demonstrated in terms of largely maintaining the original volume of the samples, a high degree of homogeneity in the densified wood, and improved physical and mechanical properties. Water absorption capacity is reduced. Limitations such as shape recovery and dimensional stability are also eliminated.

The last objective is addressed in Chapter 4, where the natural durability of densified Sande wood against natural decay agents is evaluated. In summary, a higher decay resistance of densified sand under mild climatic conditions (temperate - dry) has been demonstrated, but the results require further experimentation.

## 5.2 Future work

This doctoral thesis successfully introduces a new mechanical densification method that significantly reduces wood porosity and approaches cell wall density. This achievement opens up promising avenues for further research and refinement. Here are potential future work directions to consider:

- **Overall process model**: Conduct comparative studies across diverse timber species, including fast-growing varieties widely used in the timber industry. Analyze how anatomical variations influence optimal process parameters for different wood types. It is also important to determine the glass transition temperature of the studied woods and the influence it may have on the HIP densification process. This will enable the development of standardized guidelines for the densification method, increasing its versatility and broadening its potential applications.

- **Implementation of the developed material in the industry:** Investigate the feasibility of scaling up the isostatic densification process to produce materials with commercially viable dimensions. Explore the potential of densified wood for diverse structural applications, including its use as a sustainable alternative to steel connectors in modern timber construction.

- **Shape study**: Explore the possibility of manipulating the final shape of densified wood by strategically aligning the wood during the densification process. This could involve considering the natural orientation of the tree's growth rings. A successful outcome would significantly improve material utilization by allowing for precise control over the final geometry, minimizing waste and maximizing the efficiency of the process.

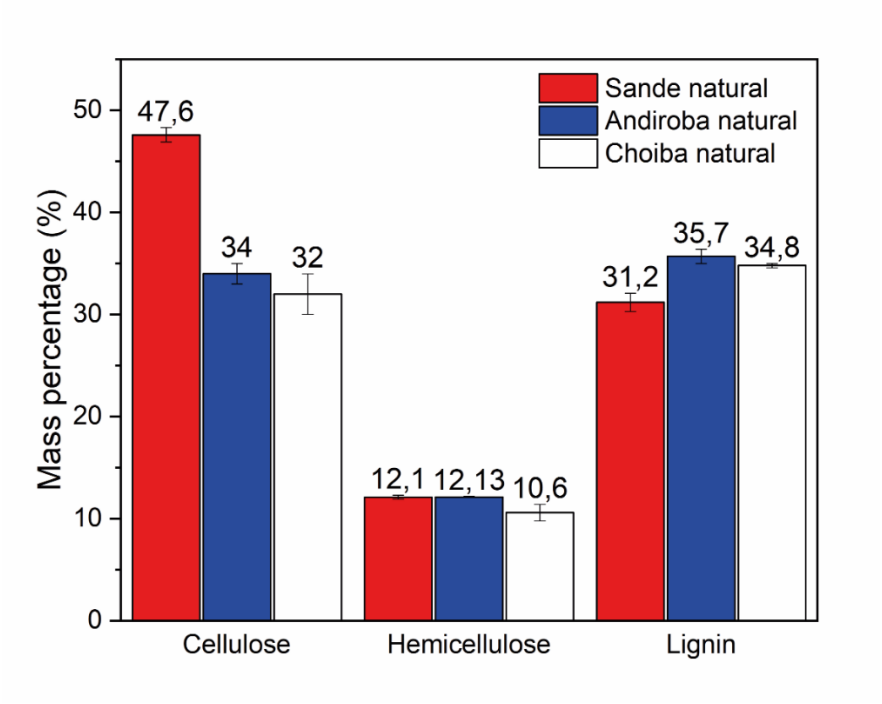
- **Achieving Superior Dimensional Stability**: Investigate the role of temperature and time to further optimize dimensional stability in densified wood. This research has demonstrated the potential of high-temperature treatments during isostatic pressing. Future studies should explore variations in both temperature and treatment duration to determine how these parameters influence the degree of dimensional stability achieved.

- **Improved natural durability**: Investigate the effects of pressure, temperature, and treatment duration on the natural durability of densified wood. While this study demonstrated improved durability under specific conditions, refining process parameters could further enhance resistance to decay in diverse environments. It would also be worthwhile to consider combining densification with the incorporation of resins or preservatives to broaden the material's resistance to a wider range of biological degradation factors.

- **Economic feasibility**: Conduct a comprehensive technical-economic analysis of the HIP process to determine its commercial viability. This analysis should factor in costs associated with raw materials, process efficiency, and the potential market value of the resulting products.

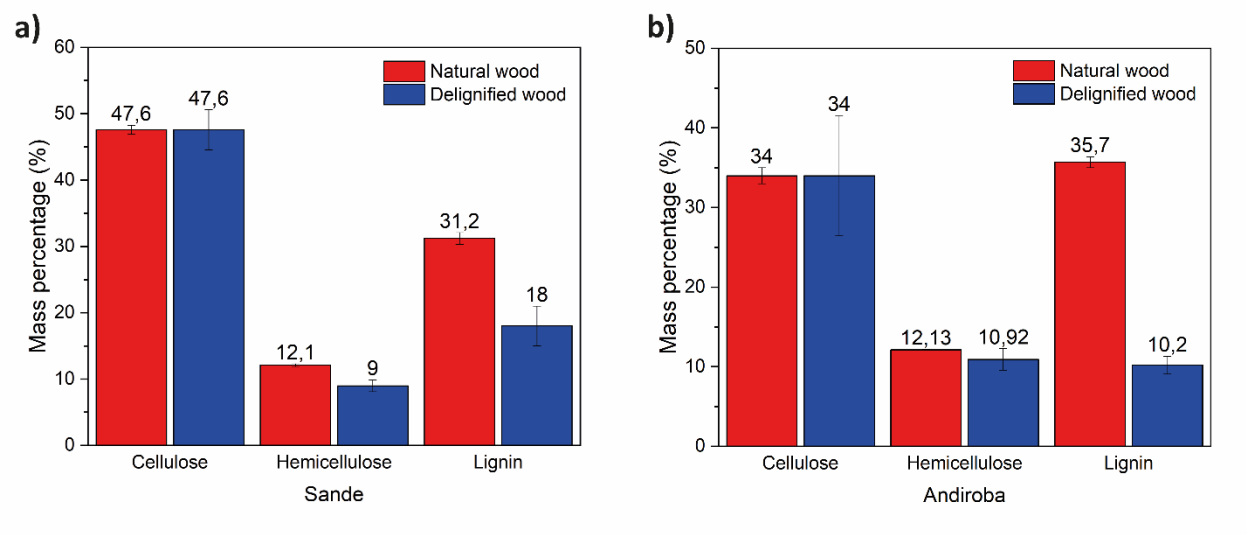
# 6 Annexes

## 6.1 Annex 1



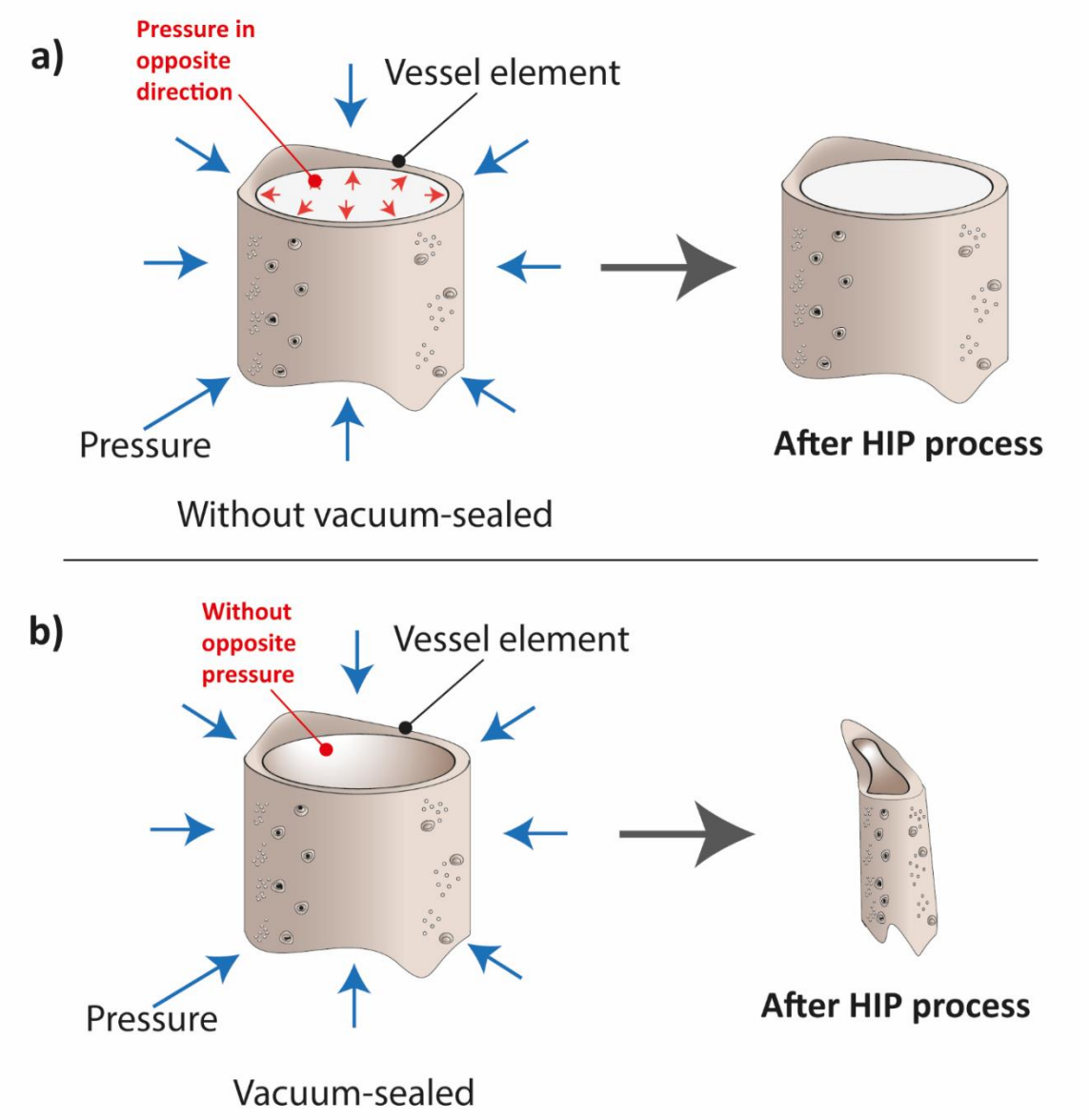

***Annex 1*** *Figure S1. Relative cellulose, hemicellulose, and lignin content in the natural wood of the specimens studied.*

## 6.2 Annex 2



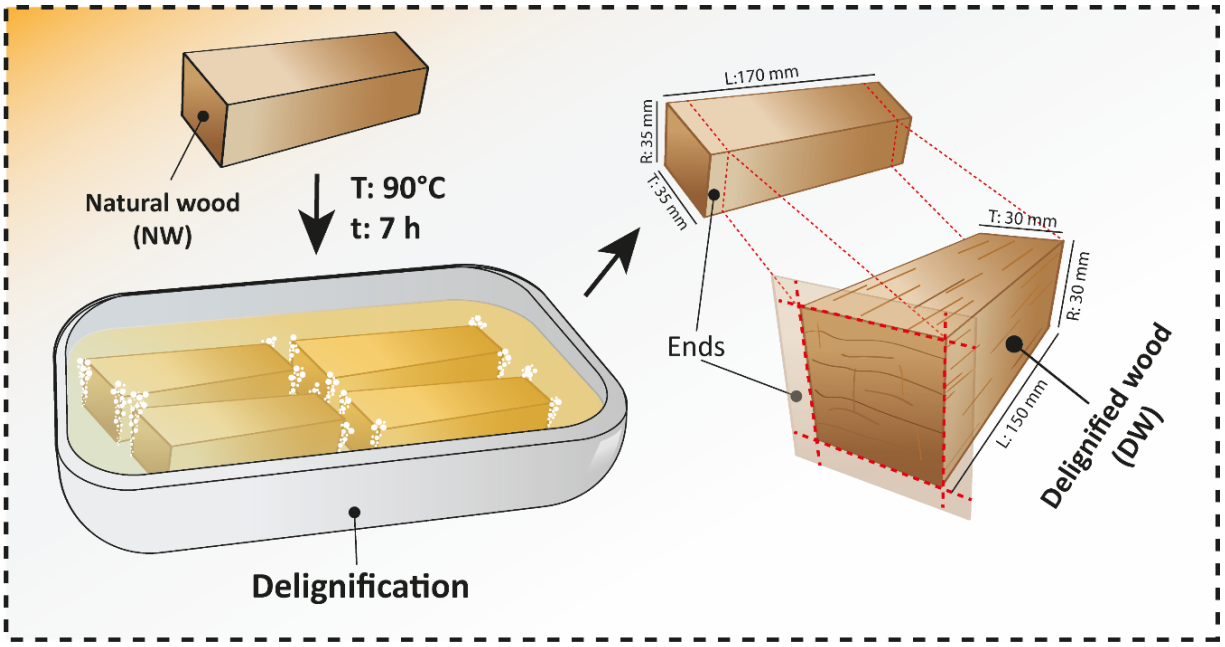

***Annex 2*** *Figure S2. Comparison of relative cellulose, hemicelluloses, and lignin content in delignified wood. a) Delignified Sande. b) Delignified Andiroba.*

## 6.3 Annex 3




***Annex 3*** *Figure S3. Graphical illustration of the anatomical effect of the HIP densification process. (a) Nullification of the densification pressure due to the presence of fluids inside the cell lumens that provide an opposing pressure to the process. (b) Reduction of the cell lumen generated by the densification pressure in the absence of an opposing pressure from inside the cells*

## 6.4 Annex 4




***Annex 4*** *Figure S4. Graphical illustration of delignified wood preparation.*