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Termite Resistance, Chemical and Mechanical Characterization of *Paulownia tomentosa* Wood before and after Heat Treatment

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Abstract: The introduction of new species in forest management must be undertaken with a degree of care, to help prevent the spread of invasive species. However, new species with higher profitability are needed to increase forest products value and the resilience of rural populations. *Paulownia tomentosa* has an extremely fast growth. The objective and novelty of this work was to study the potential use of young Paulownia trees grown in Portugal by using heat treatment to improve its properties, thereby allowing higher value applications of the wood. The average chemical composition of untreated and heat-treated wood was determined. The extractive content was determined by successive Soxhlet extraction with dichloromethane (DCM), ethanol and water as solvents. The composition of lipophilic extracts was performed by injection in GC-MS with mass detection. Insoluble and soluble lignin, holocellulose and α-cellulose were also determined. Physical (density and water absorption and dimensional stability) and mechanical properties (bending strength and bending stiffness) and termite resistance was also determined. Results showed that extractive content increased in all solvents, lignin and α-cellulose also increased and hemicelluloses decreased. Compounds derived from the thermal degradation of lignin were found in heat-treated wood extractions. Dimensional stability improved but there was a decrease in mechanical properties. Resistance against termites was better for untreated wood than for heat-treated wood, possibly due to the thermal degradation of some toxic extractives.

Keywords: chemical composition; heat treatment; mechanical properties; *Paulownia tomentosa*; termites

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1. Introduction

In the last few years there has been an increased scarcity of high-quality wood, particularly due to environmental concerns. Additionally, due to less availability, there are high

environmental impacts resulting from long-distance transportation. The use of alternative domestic woods is seen as a means of overcoming some of these environmental concerns by forestry associations in many countries. In Portugal, the main commercial wood species are eucalypt (*Eucalyptus globulus*) and maritime pine (*Pinus pinaster*). Eucalypt is mostly used for pulp and paper [1] while pine is used in the sawmill industry (43%), to produce pellets (25%), particleboards (16%) and pulp and paper (13%), respectively [2]. In the last few years, Portuguese forests have experienced several catastrophic wildfires, destroying plantations that will take more than 50 years to recover. Therefore, new species with shorter rotation periods and less susceptibility to fire are now being considered as a way to prevent the destruction of years of labor and nature biodiversity, whilst increasing the resilience of rural populations and forest profitability. *Paulownia tomentosa* is a species that has been known to grow very fast in several parts of the world. Paulownia wood can be cut after 15 years, producing wood with dimensions that could only be achieved in 45 years with traditional species such as pine [3]. Even with shorter rotation periods such as 6–7 years, it is possible to produce a cubic meter of wood from one tree, albeit of an inferior quality [3]. These authors stated that Paulownias can grow up to 3 m a year and reach 10 to 20 m height in ideal conditions, and that within 10 years old these trees can achieve 30–40 cm diameter at breast height (approximately 1.30 m height). Furthermore, Paulownias show a high rate of carbon absorption and very good fire resistance resulting from its honeycombed cellular structure and relatively low lignin content [4], which makes it a very sustainable tree [5]. One of the main problems of Paulownia wood is its low density which has been reported to be around 0.35 g/cm^3 [1], making this wood unsuitable for structural purposes but very interesting for insulation materials or for example for sculptures due to its easiness to shape [6,7]. Additionally, to its low weight, the thermal conductivity of air-dried Paulownia (with a density of 0.317 g/cm^3) has been reported to be around 0.104 W/(mK), 0.105 W/(mK) and 0.155 W/(mK) in the tangential, radial and longitudinal directions, respectively [3], which could be improved after heat treatment, reaching values within the range of standard thermal insulation materials [8]. The thermal conductivity of Paulownia is slightly lower than that of *Populus tremula* (density 0.382 g/cm^3) with 0.115 W/(mK), 0.151 W/(mK) and 0.181 W/(mK) for tangential, radial and longitudinal directions [9] and substantially lower than spruce (density 0.430 g/cm^3 at 12% R.H.) that has around 0.268 W/(mK) in longitudinal direction [10]. Other studies have revealed this wood to be durable against several xylophages due to its high tannin content [6]. As referred, low densities and therefore low mass, together with adequate thermal conductivity and reasonable natural durability characteristics makes Paulownia wood very interesting to be used in buildings as insulation material where mechanical properties do not present a substantial problem. Further noteworthy uses of the wood could be as interior or exterior cladding.

There is, however, a problem with wood dimensional stability that can affect the service life for products of this material due to crack formation by moisture-induced stress [11]. Heat treatment is a well-known procedure of wood modification to increase dimensional stability and durability, which has been widely described before [12–15]. The applicability of heat treatment has been demonstrated by the wide range of timber species that have been considered to date [16,17], including Paulownia species [18].

Generally, heat treatment has been reported as a method to decrease equilibrium moisture content (EMC) and increase dimensional stability by decreasing shrinking and swelling in wet and dry cyclic monitoring. The increased stability depends on treatment time and temperature (according to the mass loss) and on the species used [19–23]. The improvement of dimensional stability has been stated to be due to a wide range of factors, from the reduction of various accessible hydroxyl groups, mainly by the degradation of hemicelluloses [24,25], to the degradation of the amorphous parts of cellulose [26–30] and to condensation reactions in lignin with some degradation products [28,30]. This set of factors causes wood to have a lower affinity with water. No factor alone could explain the increase in dimensional stability. For example, Rautkari et al. [31] studied the role

of the accessibility of hydroxyl groups in controlling EMC, though no good correlation between them could be found. Therefore, they concluded that there should be an additional mechanism.

Along with dimensional stability, durability is also known to increase due to heat treatment, mainly durability against fungi [32]. Most studies show, however, that a high temperature is needed to obtain improvements in resistance to degradation by fungi [33–35]. From all fungi, white rot has been reported to be the less affected by heat treatment has shown by heat-treated radiata pine wood, where no significant improvement was seen against *Trametes versicolor* [36]. A recent study showed that the degradation of *Postia placenta* in thermally modified wood was initially inhibited, causing a lag in the degradation ratio in untreated wood. However, when degradation began, structural integrity and genetic expression showed similar patterns in both materials although the degradation rate was lower for modified wood [37].

In relation to termites, the application of heat treatment has been shown to provide low or no additional protection. Scots pine (*Pinus sylvestris*) treated at six different temperatures: 140, 160, 180, 200, 230 and 260 °C showed no improvements in the resistance against termites [38]. The same has been reported for other woods species as spruce and ash [39]. Nevertheless, some results showed a higher mortality rate for heat-treated pine and eucalypt [40].

The mechanical properties, such as static bending resistance and dynamic bending resistance are the most affected by heat treatments [21,41,42], nevertheless compressive strength and tension strength perpendicular to the grain also decrease [43]. The modulus of elasticity decreases, but only for more severe treatments [21,44]. It has been reported that the fact that bending strength decreases more than the modulus of elasticity is due to elasticity increases resulting from an increase of crystallinity. Consequently, the effect of the increase in crystallinity is noted in the beginning of treatment but with the prolongation of the treatment, the effect of thermal degradation becomes the dominant process, leading to the decrease of the modulus of elasticity [45].

Chemical composition changes with heat treatment and these play an important role on the modification of wood properties. Hemicelluloses are known to be the first compounds affected by heat, probably due to their amorphous nature, low molecular weight and branched structure [30,46,47]. Since hemicelluloses have been reported to be closely linked to mechanical properties, a high degradation on these compounds will significantly impact reductions of mechanical properties [48]. Even though cellulose is more resistant than hemicelluloses, there is a degradation of amorphous cellulose and consequently an increase in its crystallinity, which leads to greater inaccessibility of hydroxyl groups to water molecules [26,28]. On the other hand, crystallinity and the orientation of cellulose fibers have been reported to increase the stiffness of the secondary cell walls [48,49]. Even though lignin is affected by heat treatment, its relative percentage increases with treatment [50,51], mainly due to the degradation of the hemicelluloses and due to the breakdown products of hemicelluloses contributing to char formation when determining lignin by acid digestion techniques as stated before [15]. Chemical redistribution and lignification of the cell walls is known to increase rigidity [48], the relative percentage of lignin increases and the newly-formed condensation reaction having an increased impact on wood mechanical properties after heat treatment.

One of the most successful heat treatment processes is the ThermoWood® process [52] that began in Finland but is now used in several countries such as Sweden, Turkey, Japan and Portugal. Currently, the commercial production in Portugal mainly comprises pine and ash woods. This work intends to determine the potential of young Paulownia trees wood to be used as heat-treated wood in order to constitute a good alternative material for interior or exterior facades and contribute to building insulation.

2. Materials and Methods

2.1. Material

Young Paulownia wood samples (maximum 3 years old trees, without clear distinction between heartwood and sapwood) from a plantation in the Viseu region, Portugal were used for the tests. Central boards of approximately 150 mm width were cut from three trees. Half of the boards were then heat treated in an industrial facility in Sertã, Portugal at 212 °C in accordance with the ThermoWood® process using Thermo D treatment parameters. Untreated samples were obtained from the remaining half.

2.2. Chemical Composition and Lipophilic Extractives

Samples from the central boards were cut into small pieces, milled in a Retsch SMI mill (Haan, Germany), followed by sifting in a Retsch AS200 (Haan, Germany) sifter during 20 min at 0.83 Hz.

Chemical composition was determined by extracting approximately 10 g of milled sample (40–60 mesh fraction) in a Soxhlet apparatus and using solvents of increasing polarity: dichloromethane (6 h), ethanol (16 h) and hot water (16 h). The extractive content was determined in relation to the dry mass.

The determination of lignin content was made by the Klason method, in a sample free of extractives. This method consists in two hydrolysis processes, the first with sulfuric acid at 72% for 1 h and the second with sulfuric acid at 3% for 4 h in reflux. Since this procedure is quite time consuming, the second hydrolysis was replaced by an autoclave hydrolysis at 120 °C for 1 h. The lignin percentage was corrected to include the extractive content. Soluble lignin was determined by measuring the absorption at 205 nm of the solution obtained in Klason filtrate in accordance with Tappi UM 250 [53].

The acid chlorite method was used to solubilize lignin, obtaining holocellulose as an insoluble residue. This process can go up to 8 h to remove most of the lignin. A solution of sodium chlorite was prepared by dissolving 8.5 g in distilled water and 250 mL (solution A), whilst 250 mL of a solution B was prepared by dissolving 13.5 g of NaOH in 50 mL of distilled water, adding 37.5 mL of acetic acid and completing with water until 250 mL. Approximately 2 g of extracted wood was placed in a 1 L flask which 160 mL of distilled water, 20 mL of solution A and 20 mL of solution B in a water bath at 70 °C. At the end of every hour, a further 20 mL of each solution was added. The procedure was repeated until the whole sample became white. The samples were then filtered into previously dry and weighed N°2 crucibles and washed abundantly with cold water, ending with 15 mL of acetone. The crucibles were dried in an oven at 60 °C for 24 h and 1 h at 100 °C. The holocellulose (HC) content was determined in relation to initial dry wood.

To determine α-cellulose, 0.5 g of dry holocellulose were weighed and placed in a 100 mL beaker with 2.5 mL of 17.5% NaOH and covered with a watch glass. Then, the glasses were placed in the thermal bath at a temperature of 20 °C. The samples were removed from the bath after 30 min and 15 min later 8.25 mL of water at 20 °C were added, placing it in the thermal bath for another hour. Afterwards the samples were removed from the bath and the solutions were filtered in pre-weighed crucibles, initially washing with 25 mL of 8.3% NaOH and finally with distilled water. During filtration, the suction was stopped whenever the cellulose was covered with water, to allow stirring with a glass rod, before the suction being resumed. This was repeated at least twice. After this, 3.75 mL of 10% acetic acid was added to the crucible without turning on the suction for 3 min. Finally, the material was washed with an excess of water. The crucibles were dried at 60 °C overnight followed by 105 °C for 1 h, allowed to cool down and weighed. The cellulose content was determined in relation to initial dry mass.

Hemicellulose content was determined by difference between holocellulose and α-cellulose.

In order to determine lipophilic extractives 3 mg of the dichloromethane extract were derivatized with 30 µL of pyridine and 30 µL of N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) (Macherey Nagel, Dueren, Germany), in accordance to Esteves et al. [50]. The vials

(1 mL) were closed and introduced in an oven at 60 °C where they remained for 20 min. Afterwards the vials were cooled down, samples were injected in a gas chromatograph (HP 6890 Series GC, Agilent, Santa Clara, CA, USA) equipped with an Agilent DB-5 ms column and a mass detector (5973 N Agilent Series, Santa Clara, CA, USA). 1 µL was injected in splitless mode. GC-MS oven temperature started at 100 °C for 5 min, followed by an increase of 5 °C for min until 310 °C, maintaining this maximum temperature for 15 min. Extractive compounds were identified by comparing their EI mass spectra with NIST17 library.

2.3. Termite Resistance

The resistance of the untreated and heat-treated Paulownia wood samples (10 replicates; 50 × 25 × 15 mm) against the subterranean termite *Reticulitermes grassei* (Blattodea: Isoptera: Rhinotermitidae) was determined according to EN 117 [54]. Untreated sapwood samples of maritime pine (10 replicates) were used as virulence controls. The termites were collected in a forest of maritime pine in Sesimbra region, Portugal and kept in the laboratory for less than two weeks before used for the tests.

Glass containers were filled with a layer of about 6 cm loose fill and humidified sand (4 parts of Fontainebleau sand® to 1 of distilled water) and to each container, 250 workers were added as well as 1–3 soldiers and 3–5 nymphs. After installation of the termites, the test specimens were placed inside the containers. All test containers were kept in a conditioned chamber at 24 ± 2 °C and relative humidity of 80% ± 5% for 8 weeks or until all termites were visibly dead.

Termite resistance was determined by registering the survival rate (SR) (percentage of living termites at the end of the test) and visual examination and grading of the cleaned test specimens using the standard rating system (0 = no attack, 1 = attempted attack, 2 = slight attack, 3 = average attack and 4 = strong attack). The test is considered valid if all virulence control test specimens reach a final level of attack of "4" and have an average survival rate above 50%.

Additionally, the wood mass loss (%) was also calculated as follows:

$$ML\ (\%) = \frac{(m_{01} - m_{02})}{m_{01}} \times 100 \quad (1)$$

where ML is the mass loss after termite exposure, m_{01} is the dry mass of heat-treated or untreated wood samples before termite exposure and m_{02} is the dry mass of heat-treated or untreated wood samples after termite exposure. The wood dry mass was determined by drying the wood samples at 103 °C. The initial and final moisture contents were also determined according to EN13183-1 [55]. The initial moisture content was obtained from extra sets of 4 replicates and was 11.64 ± 0.08 for maritime pine sapwood, 9.97 ± 1.06 for Paulownia sapwood and 5.23 ± 0.39 for heat-treated Paulownia.

2.4. Physical and Mechanical Properties

Air-dry density was determined for untreated and heat–treated wood conditioned at 20 °C and 65% relative humidity by weighing cubic 20 mm samples, cut from the already described boards with faces oriented in the three directions and measuring the wood dimensions. An average of 10 replicates was used.

Bending strength and stiffness were determined on untreated and heat-treated wooden test specimens, by a three-point bending test in a Servosis ME-405/5 universal test machine (Servosis S.L., Madrid, Spain) with 360 × 20 × 20 mm in transverse, radial and tangential directions, respectively. Samples were conditioned at 20 °C and 65% relative humidity prior mechanical testing. The samples were placed with the radial face oriented upwards and maintained on two supports distanced 340 mm from each other. In this case, 10 replicates were made for each assay.

The modulus of elasticity (MOE) was calculated according to the Formula (2):

$$\mathrm{MOE}\left(\mathrm{N/mm^2}\right) = \frac{\Delta \mathrm{F} \times \mathrm{L}^3}{4 \times \Delta \mathrm{x} \times \mathrm{b} \times \mathrm{h}^3} \quad (2)$$

where $\Delta F/\Delta x$ corresponds to the slope of the elastic zone in N/mm, L is the length of the span between the two axes in mm (340 mm), h is the height and b the width of the sample, both expressed in mm. The tests to determine bending strength were performed on the same machine used to determine the modulus of elasticity. The average speed of the assay was calculated so that rupture happens approximately 2 min after the start of the assay. Bending strength was calculated according to EN 310 [56] using the Formula (3):

$$\text{Bending Strength}\left(\mathrm{N/mm^2}\right) = \frac{3 \times \mathrm{F} \times \mathrm{L}}{2 \times \mathrm{b} \times \mathrm{h}^2} \quad (3)$$

where F is the force at the breaking point in N and the other variables are the same as before. For each sample, 10 replicates were made.

Water absorption, shrinking and swelling were determined in treated and untreated wood cubic samples with approximately 20 mm edge, with faces oriented in three directions from the central boards described before, using three cycles of 0% (Oven at 100 °C) and 100% (Water at 20 °C). The process started in the oven where the samples were kept for 24 h. After that samples were allowed to cool down, weighed and wood dimensions in the radial, tangential and longitudinal directions were evaluated with a digital caliper ($L1_{0\%}$). Then, samples were placed in the water bath for 24 h, removed and cleaned with a paper towel. Mass and dimensions were determined again.

The swelling of the samples was determined in relation to the dimensions of initial dry wood. The dimensional stability increase with heat treatment was determined by the Anti-Swelling Efficiency (ASE) that gives the difference between the swelling coefficient of treated and untreated samples between 0% and 100% environments.

$$\mathrm{ASE}_{100\ (\%)} = \left(\frac{S_{nt} - S_t}{S_{nt}}\right) \times 100 \quad (4)$$

where S_{nt} and S_t represent the swelling between 0% relative humidity and 100% relative humidity for non-treated (*nt*) and treated (*t*) samples. ASE determinations were made in radial, tangential and longitudinal directions and total ASE corresponding to the volume change.

3. Results and Discussion

3.1. Chemical Composition

The knowledge of wood chemical composition before and after heat treatment can give a good perspective of the changes occurring in wood during the treatment and provide some insight on the reasons for changes in the wood properties. Untreated Paulownia wood, especially from young trees, is highly influenced by the plantation sites. Young Paulownia (up to 3 years), grown in Portugal, showed that cellulose represents around 40% of the total composition, followed by hemicelluloses with 36% and 24% for lignin, respectively (Table 1). The most representative extractives were ethanol (3.6%), followed by dichloromethane (1.9%) and water (1.8%) (Table 1). Nevertheless, *Paulownia tomentosa* from Shaanxi Province in China (4 years old) has a similar chemical composition with 42% cellulose, 20% hemicellulose and 21% lignin [57]. The main difference is the amount of hemicelluloses that here was determined by difference from holocellulose content and was significantly higher than the presented study. Paulownia wood (unknown age) from Turkey presented a lignin content of 22% with α-cellulose representing 48% which is also not much different than the obtained here [58]. These authors, however reported a significantly higher amount for water extractives (around 10%), but the age of the trees was not specified. In accordance to Gong and Bujanovic [59] 14–18 years-old Paulownia trees

has approximately 24% lignin and 8.8% acetone/water extractives, which were similar to the results obtained here for younger aged wood. Very different results were presented by Mecca et al. [60], where a lignin percentage of 37.6% for Paulownia wood (age not mentioned) and 54.5% holocellulose was reported. It is possible that the sample used could be of a much older tree, since it is expected that lignin might increase with wood age, due to lignification of the cell wall.

As a result of heat treatment, hemicellulose relative percentage decreased to around 22% while all the other compounds showed an increase. For example, α-cellulose increased from 40% to 49%, nonetheless there might be some degradation of amorphous cellulose leading to a percentage increase in α-cellulose that mostly represents crystalline cellulose. As expected, there was an increase in lignin content from 24% to 30% and also an increase in all the extractable amounts in dichloromethane, ethanol and water (Table 1). These results are in accordance with previous studies where hemicellulose has been recognized as the most affected structural compound [24,30,47,50]. Lignin increased with heat treatment which has already been mentioned by several authors [24,28,50,61–63] which has been attributed to the higher lignin resistance to heat degradation and also to condensation reactions between lignin and some of the degradation products that are resistant to sulfuric acid in the Klason method and therefore accounted as lignin.

Table 1. Chemical composition of untreated and heat-treated Paulownia wood.

Sample	Extractives (%)			Lignin (%)			α-Cellulose (%)	Hemic (%)
	Dic	Ethanol	Water	Total	Insoluble	Sol.		
Paulownia	1.92	3.60	1.84	7.36	23.48	0.23	40.17	36.34
HT Paulownia	2.82	9.74	2.31	14.87	29.46	0.14	49.77	21.76

α-Cellulose content also increased with the heat treatment. Previous studies have shown that the increase or decrease in cellulose is highly dependent on the treatment itself but also on the analysis method. Cellulose crystallinity is known to increase due to the degradation of amorphous cellulose as reported by Bhuiyan and Hirai [28]. Therefore, at least for treatments under less harsh conditions, α-cellulose percentage is likely to increase due to the decrease of hemicelluloses. Similar results were reported by Boonstra and Tjeerdsma [29] with heat-treated Norway spruce, Scots pine and radiata pine. Likewise, Sikora et al. [64] also reported an increase in cellulose content of heat-treated spruce determined by the Seifert method.

Table 2 presents the lipophilic extractives of untreated and heat-treated Paulownia wood. Only about 70% of the extracts could be identified. Untreated Paulownia dichloromethane extractives are mainly constituted by fatty acids such as palmitic, octadecadienoic, octadecenoic, stearic and arachidic acids, terpenic structures such as serruginol (meroterpene), dehydroabietic acid (resin acid) or β-sitosterol (phytosterol), a lignan (sesamin), some alkanes such as heptacosane and pentacosane, some phenolics such as vanillin, vanillic acid, vanillyl alcohol or 4-hydroxy-3-methoxyphenylglycol.

It is interesting to note that whilst the level of sesamin increased in heat treatments in this study, there was no indication of the presence of episesamin as noted when heating Paulownia in vacuum heat treatment to a temperature of 210 °C [65]

As expected during heat treatment, some of the initial compounds tend to disappear whilst new ones are identified. From the initial extractives the highest decrease was observed for β-sitosterol and palmitic acid. With the prolongation of the treatment, some of the original compounds were not detected, whilst some new compounds appeared or increased in the relative amount detected such as vanillin, syringaldehyde, vanillic acid, syringic acid, coniferaldehyde and sinapaldehyde. All these compounds have been associated with lignin degradation before, although they can also result from the degradation of other phenolic compounds [24,50].

Table 2. Lipophilic extractives (Dichloromethane) of untreated and heat-treated wood.

Name	Untreated	Heat-Treated
Glycerol, 3TMS derivative	6.63%	1.31%
Vanillin, TMS derivative	1.22%	2.18%
Tyrosol, 2TMS derivative	0.52%	-
Piperonylic acid	6.63%	2.40%
3,4-Dihydroxybenzaldehyde, 2TMS derivative	-	0.44%
4-Hydroxybenzoic acid, 2TMS derivative	-	0.44%
2,6-Dimethoxyhydroquinone, 2O-TMS derivative	-	1.53%
Syringaldehyde, TMS derivative	-	4.58%
Veratric acid, TMS derivative	-	0.22%
Vanillyl alcohol, 2TMS derivative	1.40%	
Vanillic Acid, 2TMS derivative	2.09%	5.23%
4-Hydroxy-3-methoxyphenylglycol, 3TMS derivative	0.70%	-
Myristic acid, TMS derivative	0.87%	-
(3-Hydroxy-4-methoxyphenyl)ethylene glycol 3TMS deivative	1.75%	-
Azelaic acid, 2TMS derivative	-	2.61%
Coniferyl aldehyde, TMS derivative	-	3.92%
Syringic acid, 2TMS derivative	-	2.83%
trans-Coniferryl alchool, 2O-TMS derivative	-	0.44%
Sinapaldehyde, TMS derivative	-	9.59%
Palmitic Acid, TMS derivative	15.53%	2.40%
trans-Sinapyl alcohol, 2O-TMS derivative	-	0.22%
Lapachol, TMS derivative	-	10.02%
9,12-Octadecadienoic acid (Z,Z)-, TMS derivative	5.41%	3.05%
11-Octadecenoic acid, (Z)-, TMS derivative	5.24%	1.96%
Stearic acid, TMS derivative	5.76%	0.65%
Dehydroabietic acid, TMS derivative	2.79%	4.58%
Ferruginol, TMS derivative	0.87%	-
Pentacosane	1.22%	-
Arachidic acid, TMS derivative	1.57%	-
Heptacosane	1.05%	-
(+)-Sesamin	16.58%	36.60%
β-Sitosterol, TMS derivative	22.16%	2.83%

3.2. Termite Resistance

The results obtained on the resistance to subterranean termites of untreated and heat-treated Paulownia wood are summarized in Table 3.

Table 3. Average results of survival, mass loss, final moisture content and grade of attack after exposure to *R. grassei* (n = 10).

Wood	Final Moisture Content (%)	Survival (%)	Average Mass Loss (%)	Average Grade of Attack
P. tomentosa	44.12 ± 18.91	17.48 ± 25.28	3.35 ± 3.81	2.10 ±1.73
P. tomentosa heat-treated	49.35 ± 18.94	52.28 ± 30.84	9.11 ± 4.72	3.83 ± 0.41
Maritime pine control	51.72 ± 11.41	66.44 ±7.58	7.09 ± 0.96	4

Results show a high variability of Paulownia durability, especially concerning the termite survival rate which is 17.5% on average, lower than the corresponding standard deviation. The termites were not able to survive on six of the 10 replicates tested. Nevertheless, when they survived, the level of attack was high. The age of the sampled trees probably explains the high variability. It was not possible to separate heartwood and sapwood, thus the test specimens with no survival are most likely to be those where heartwood had already formed.

Heat treatment did not increase Paulownia wood durability against termites, in accordance to results previously reported by several authors. For instance, vacuum heat-treated maritime pine treated at six different temperatures from 140 °C to 260 °C did not

show an increased durability [38] similarly to Korean pine (*Pinus koraiensis*), and lodgepole pine (*Pinus contorta*) heat-treated at temperatures from 170 °C to 230 °C and time from 90 min to 270 min [66]. It seems that heat treatment decreased wood durability, which could be seen by the increased termite survival rate from 17.5% to 49.4% and by the average grade of attack from 2.1 on average to 3.8. These results can be due to the degradation of some toxic compounds present in untreated Paulownia wood. Similar results were reported before where untreated tropical species exhibited higher durability than heat-treated wood with very low attack level and 100% mortality by termites [39]. Some authors tried to overcome this higher susceptibility of heat-treated wood to termites by combining heat treatment with borax impregnation dissolved in aqueous solution of polyglycerol methacrylate, thereby obtaining good results [67].

3.3. Physical and Mechanical Properties

Untreated Paulownia wood already has low mechanical properties, with its bending strength (63 MPa) being almost half that of maritime pine wood (*Pinus pinaster*) (108 MPa) [68]; similarly MOE is 6676 MPa which is also almost half of untreated maritime pine (10,900 MPa) [68]. Nevertheless, when comparing with other Paulownia woods from different plantation sites, the observed mechanical properties are not that low. For instance, 6 years-old Paulownia from Turkey [3] had a MOE of 4280 MPa and a bending strength of 44 MPa, lower than the 6676 MPa and 63 MPa obtained here. Wood grown in South Korea (age not mentioned) presented 42 MPa bending strength and 3600 MPa for MOE. The main reasons for these different results might be that wood in Portugal has grown slowly and wood density is 443 kg/m^3 which is higher than the density presented for wood grown in Turkey in the study by Akyildiz and Son [3], 317 kg/m^3 or for wood grown in Korea, 270 kg/m^3 Hidayat et al. [69] or 260 kg/m^3 Kim et al. [70].

Heat treatment is known to affect some mechanical properties of wood. One of the main reasons might be the decrease in wood density during the treatment. Density was fond to decrease from 443 to 399 kg/m^3, roughly corresponding to a 10% decrease. Similar decreases on density after different heat treatment methods and for different species has been reported before (Table 4). For instance, for spruce and beech wood treated by the French Retification method, a density decreases from 623 kg/m^3 and 447 kg/m^3 to 617 kg/m^3 and 381 kg/m^3, respectively, was found [71,72], whilst for the Plato® process, decreases in density for Scots pine and Norway spruce of 10% and 8.5%, respectively, have been reported [73].

Table 4. Physical and mechanical properties of untreated and heat-treated Paulownia wood EN310.

Sample	Density (kg/m^3)		MOE (MPa)		Bending Strength (MPa)	
	Average	STD	Average	STD	Average	STD
Untreated Paulownia	443	14	6676	1185	63	10
Heat-Treated Paulownia	399	9	5761	791	32	2

The density decrease cannot be separated from the significant decrease on hemicellulose content as observed herein (Table 1). As suggested by Kvietková et al. [74], the density decrease is mostly due to the degradation of hemicelluloses and to the evaporation of extractives. These authors also stated that density decreased with both increasing temperature treatment and treatment times as reported before [75].

Bending strength and stiffness (MOE) are two of the most important mechanical properties for structural applications. Untreated Paulownia wood has already low bending strength and stiffness, and as such is not suitable for structural applications. Nevertheless, with heat treatment these mechanical properties are even weaker. The highest decrease is observed for bending strength that decreases from 63 MPa to 32 MPa which corresponds to almost 50% reduction. In relation to MOE the decrease is lower, from 6676 MPa to 5761 MPa. Hemicelluloses have been reported to be the most important structural compound in most

of the mechanical properties since it is responsible for the flexibility of wood. Good relationships between hemicellulose content and bending strength have been reported before [76]. Therefore, the high decrease in hemicellulose content (Table 1) might be one of the main reasons for the decrease in bending strength and stiffness. In addition, the increase observed in the relative content of lignin might be responsible for the increased wood rigidity.

Dimensional stability is one of the most important wood properties, since changes in wood dimensions between dry and wet states occurring below the fiber saturation point, lead to the formation of cracks and therefore to some mechanical degradation [11]. Figure 1 presents the dimension variations for untreated and heat-treated wood on radial, tangential and longitudinal directions along the three cycles, after water (100%) and oven (0%). As expected in the end of the first cycle, after water soaking, all the dimensions increased. Results show that dimensional variations are higher for the tangential direction, followed by radial and longitudinal directions. The dimensional changes are lower for heat-treated wood in all directions after the first cycle. After the first step in water the dimensions of the samples do not return to their initial size as can be seen by the swelling between initial dry wood and oven step in the second or third cycles. Nevertheless, there seems to be no further swelling between the second and third cycles after the oven. In relation to the water soaking step, there is no considerable differences between the three cycles although there are slightly higher swellings after the third cycle.

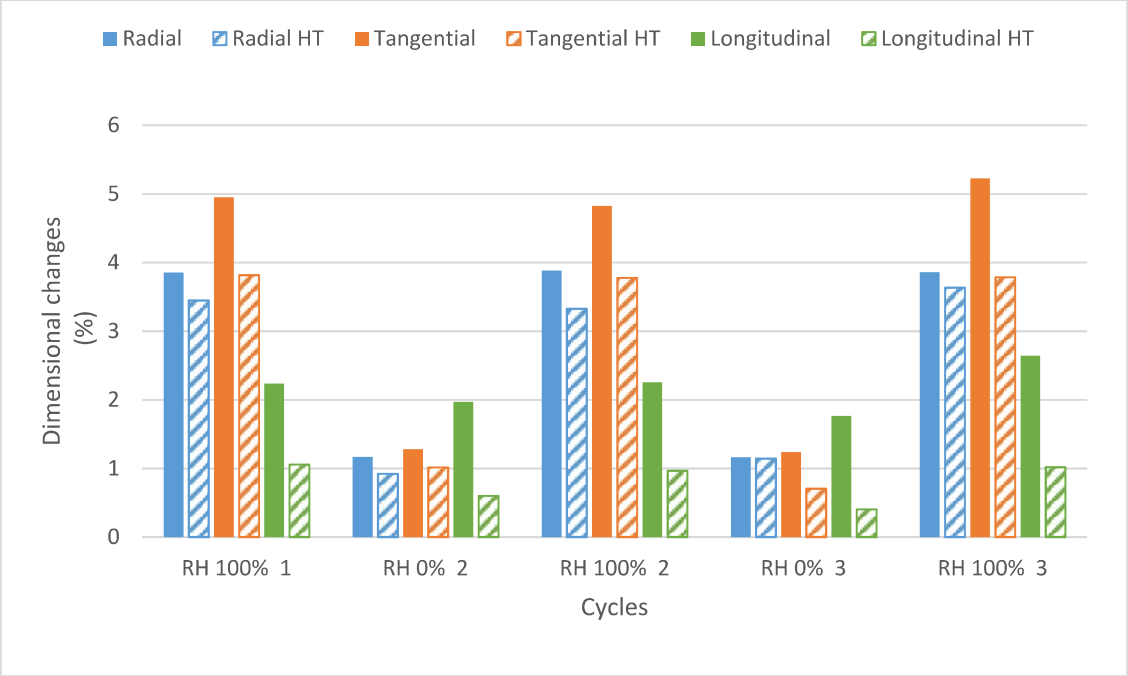

Figure 1. Dimensional changes in radial, tangential and longitudinal directions for untreated and heat-treated wood along the three cycles.

The ASE determined here was between 100% (water) and 0% (oven) in radial, tangential and longitudinal directions. Longitudinal ASE (around 35%) is higher than tangential (around 25%) and radial ASE (around 10%) but it is based on smaller dimensional changes (Figures 1 and 2). Tangential ASE is substantially higher than radial ASE, which means that the improvements are higher on the tangential direction. These better results in tangential direction decrease wood anisotropy since the differences between radial and tangential swelling are attenuate as can be seen in Figure 1. After three cycles only radial ASE decreased slightly, while tangential ASE even increases a little due to the higher swelling of untreated wood in tangential direction. Volumetric ASE is influenced by the changes in all directions. There is an increase followed by a decrease between the second and third cycles.

One of the main advantages of heat treatment is the improvement of wood dimensional stability that has been reported before to achieve more than 50% in some cases. For instance, Esteves et al. [21] studied the dimensional stability changes in heat-treated *Pinus pinaster* and *Eucalyptus globulus* wood exposed in 35%, 65% and 85% relative humidity and concluded that the best ASEs were obtained at 35% relative humidity with around 57% for pine wood and 90% for eucalypt wood treated at 190–210 °C in the tangential direction. These authors stated that the increase in ASE was higher for 35% air relative humidity, and lower for 65% and 85% relative humidity. The maximum values for radial ASE85 were 27–38% for pine wood and 54–62% for eucalypt wood. Therefore, $ASE_{100\%}$ determined here was expected to be lower. Nevertheless, the dimensional stability of Paulownia wood did not seem to improve significantly, since there was only a 25% increase in tangential direction and 10% increase in radial direction which would not justify the use of heat treatment with the consequential decrease in mechanical properties and with the associated treatment cost. Additionally, durability against termites seems to reduce with the treatment. A higher treatment temperature or time would probably increase dimensional stability but would certainly also increase the mechanical degradation of wood.

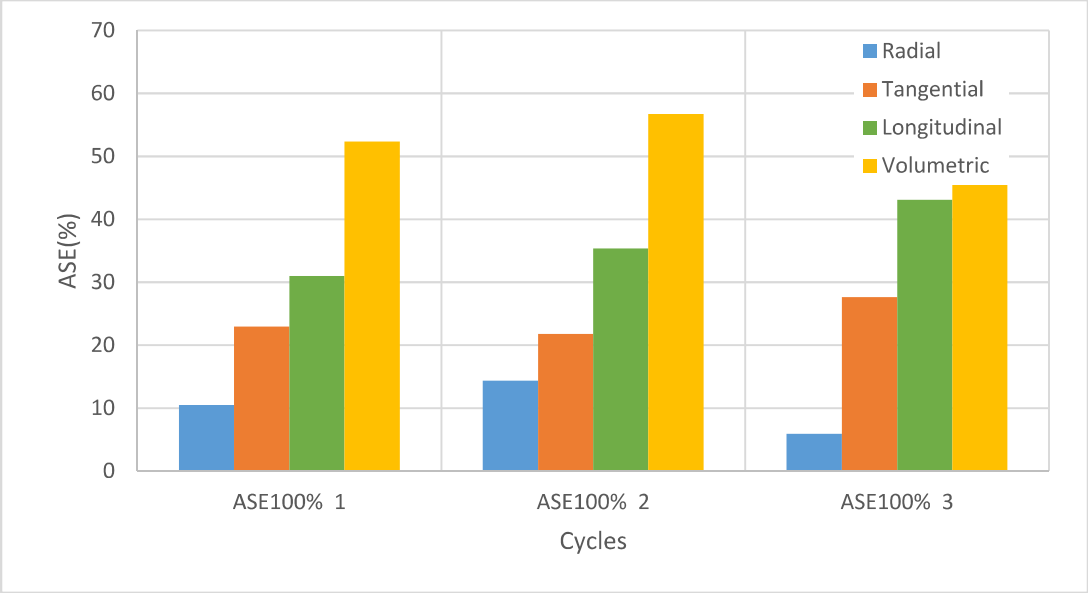

Figure 2. Anti-Swelling efficiency of thermally modified Paulownia.

Figure 3 presents the water absorption after the water soaking step for untreated and heat-treated wood over three successive cycles. Water absorption was higher for untreated wood along the three cycles and results suggest that there are no major differences between any of the cycles. However there seems to be a slight increase in water absorption of heat-treated wood after the third cycle. Similar results were presented earlier for untreated and heat-treated jack pine (*Pinus banksiana* Lamb.) and aspen (*Populus tremuloides* Michx.) wood, treated at 210 °C and 200 °C for 40 min, respectively [77]. These authors obtained a 20% and 12% water absorption for untreated and heat-treated jack pine and 30% and 26% for untreated and heat-treated aspen after water soaking for 24 h. Paulownia wood absorbed much more water than jack pine or aspen, for untreated (around 50%) or heat-treated (around 40–45%) but much less than untreated and heat-treated sugi (*Cryptomeria japonica)* (180 °C, 2 h) with an absorption of around 90% for untreated and slightly lower for heat-treated wood after 24 h immersion [78].

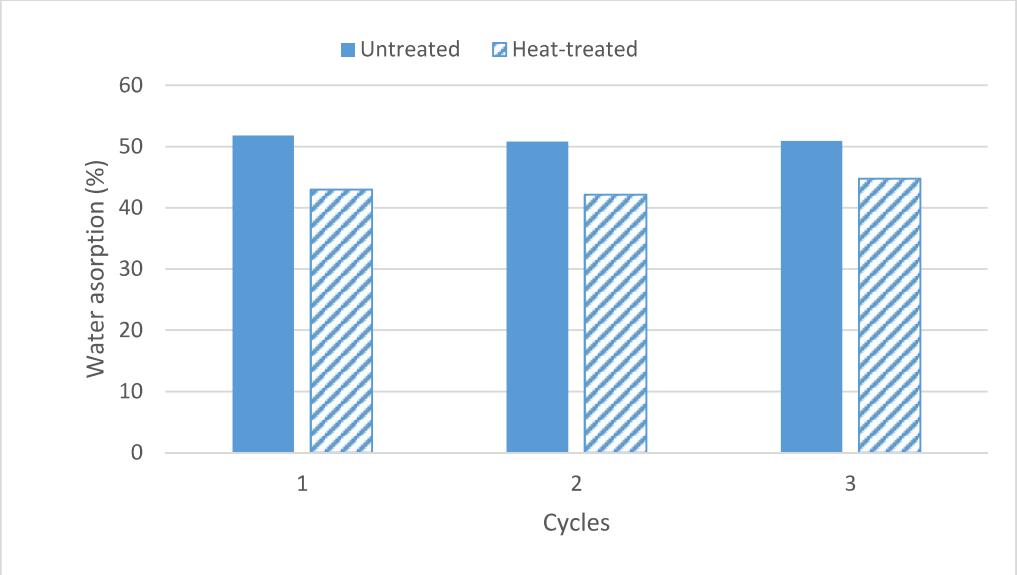

Figure 3. Water absorption of untreated and heat-treated wood.

4. Conclusions

This work intended to determine the potential of wood from young Paulownia trees to be processed using heat treatment methods to constitute a good alternative material for interior or exterior facades and contribute to building insulation. Hemicellulose relative percentage decreased as a result of the heat treatment, while all the other compounds showed an increase, such as α-cellulose, lignin and an increase in all the extractable amounts in dichloromethane, ethanol and water. Some of the original compounds were not detected in heat-treated wood, whilst some new compounds appeared or increased in the relative amount such as vanillin, syringaldehyde, vanillic acid, syringic acid, coniferaldehyde and sinapaldehyde which have previously been associated with lignin degradation. The density decreased, similar to bending strength and stiffness. The radial ASE was around 10%, tangential around 23% and longitudinal around 30%. After three cycles there was no significant decrease on dimensional stability and there was even a slight tangential ASE increase. Water absorption decreased with heat treatment and there were no major differences between any of the cycles except for a slight increase in water absorption of heat-treated wood after the third cycle. Additionally, durability against termites seems to reduce with the treatment, which can be due to the degradation of some toxic natural extractives. This is important and should be taken into account when using heat-treated wood for insulation. A higher treatment temperature or time would probably increase dimensional stability but would certainly also increase the mechanical degradation of wood. Further work must be carried out in order to study the different envisaged applications for this wood.

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References

1. Amaral, J. A fileira do eucalipto: Alguns aspetos macroeconómicos e macro-setoriais. In *Cultivar. Cadernos de Análise e Prospetiva*, 1st ed.; Sampaio, A., Dimas, B., Diniz, E., Morais, A., Moura, A., Garção, B., Sequeira, H., Loureiro, H., Esteves, P., Rego, P., et al., Eds.; Gabinete de Planeamento, Políticas e Administração Geral: Lisboa, Portugal, 2018; Volume 14, pp. 55–60.
2. Gonçalves, J.; Teixeira, P.; Carneiro, S. *Valorizar o pinheiro-Bravo: A Perspetiva de Mercado*, 1st ed.; Centro Pinus-Associação para a Valorização da Floresta de Pinho: Viana do Castelo, Portugal, 2020; 40p, ISBN 978-972-98308-8-4.
3. Akyildiz, M.H.; Kol, H.S. Some Technological Properties and Uses of Paulownia (*Paulownia tomentosa* Steud.) Wood. *J. Environ. Biol.* **2010**, *31*, 351–355.
4. Li, P.; Oda, J. Flame Retardancy of Paulownia Wood and Its Mechanism. *J. Mater. Sci.* **2007**, *42*, 8544–8550. [CrossRef]
5. El-Showk, S.; El-Showk, N. *The Paulownia Tree. An Alternative for Sustainable Forestry*; Crop Development: Rabat, Morocco, 2003; pp. 1–8.
6. Icka, P.; Damo, R.; Icka, E. Paulownia tomentosa, a Fast Growing Timber. *Ann. Valahia Univ. Targoviste Agric.* **2016**, *10*, 14–19. [CrossRef]
7. Yadav, N.K.; Vaidya, B.N.; Henderson, K.; Lee, J.F.; Stewart, W.M.; Dhekney, S.A.; Joshee, N. A Review of Paulownia Biotechnology: A Short Rotation, Fast Growing Multipurpose Bioenergy Tree. *Am. J. Plant Sci.* **2013**, *4*, 2070. [CrossRef]
8. Pásztory, Z.; Horváth, N.; Börcsök, Z. Effect of Heat treatment Duration on the Thermal Conductivity of Spruce and Poplar Wood. *Eur. J. Wood Wood Prod.* **2017**, *75*, 843–845. [CrossRef]
9. Örs, Y.; Şenel, A. Thermal Conductivity Coefficients of Wood and Wood-Based Materials. *Turk. J. Agric. For.* **1999**, *23*, 239–246.
10. Krišťák, Ľ.; Igaz, R.; Ružiak, I. Applying the EDPS Method to the Research into Thermophysical Properties of Solid Wood of Coniferous Trees. *Adv. Mater. Sci. Eng.* **2019**, *2019*, 1–9. [CrossRef]
11. Sandberg, D.; Söderström, O. Crack Formation Due to Weathering of Radial and Tangential Sections of Pine and Spruce. *Wood Mater. Sci. Eng.* **2006**, *1*, 12–20. [CrossRef]
12. Esteves, B.; Pereira, H. Wood Modification by heat treatment: A Review. *BioResources* **2009**, *4*, 370–404. [CrossRef]
13. Hill, C.A. *Wood Modification: Chemical, Thermal and Other Processes*; John Wiley & Sons: Hoboken, NJ, USA, 2006; Volume 5, ISBN 0-470-02173-X.
14. Sandberg, D.; Kutnar, A.; Mantanis, G. Wood Modification Technologies-a Review. *iFor. Biogeosci. For.* **2017**, *10*, 895. [CrossRef]
15. Hill, C.; Altgen, M.; Rautkari, L. Thermal Modification of Wood—A Review: Chemical Changes and Hygroscopicity. *J. Mater. Sci.* **2021**, *56*, 6581–6614. [CrossRef]
16. Jones, D.; Ormondroyd, G.O.; Curling, S.F.; Popescu, C.-M.; Popescu, M.-C. Chemical compositions of natural fibres. In *Advanced High Strength Natural Fibre Composites in Construction*; Elsevier: Amsterdam, The Netherlands, 2017; pp. 23–58.
17. Sandberg, D.; Kutnar, A.; Karlsson, O.; Jones, D. *Wood Modification Technologies: Principles, Sustainability, and the Need for Innovation*; CRC Press: Boca Raton, FL, USA, 2021.
18. Kaygin, B.; Gunduz, G.; Aydemir, D. Some Physical Properties of Heat-Treated Paulownia (*Paulownia elongata*) Wood. *Dry. Technol.* **2009**, *27*, 89–93. [CrossRef]
19. Tuong, V.M.; Li, J. Effect of Heat treatment on the Change in Color. *BioResources* **2010**, *5*, 1257–1267.
20. Srinivas, K.; Pandey, K.K. Effect of Heat treatment on Color Changes, Dimensional Stability, and Mechanical Properties of Wood. *J. Wood Chem. Technol.* **2012**, *32*, 304–316. [CrossRef]
21. Esteves, B.; Marques, A.V.; Domingos, I.; Pereira, H. Influence of Steam Heating on the Properties of Pine (*Pinus pinaster*) and Eucalypt (*Eucalyptus globulus*) Wood. *Wood Sci. Technol.* **2006**, *41*, 193–207. [CrossRef]
22. Guller, B. Effects of Heat treatment on Density, Dimensional Stability and Color of *Pinus nigra* Wood. *Afr. J. Biotechnol.* **2014**, *11*, 2204–2209.
23. Dirol, D.; Guyonnet, R. The Improvment of Wood Durability by Retification Process. In Proceedings of the the International Research Group on Wood Preservation; Section 4, Report Prepared for the 24 Annual Meeting. IRGWP: Stockholm, Sweden, 1993; pp. 1–11.
24. Esteves, B.; Graça, J.; Pereira, H. Extractive Composition and Summative Chemical Analysis of Thermally Treated Eucalypt Wood. *Holzforschung* **2008**, *62*, 344–351. [CrossRef]
25. Weiland, J.-J.; Guyonnet, R. Study of Chemical Modifications and Fungi Degradation of Thermally Modified Wood Using DRIFT Spectroscopy. *Holz als Roh und Werkstoff* **2003**, *61*, 216–220. [CrossRef]
26. Wikberg, H.; Maunu, S.L. Characterisation of Thermally Modified Hard-and Softwoods by 13C CPMAS NMR. *Carbohydr. Polym.* **2004**, *58*, 461–466. [CrossRef]
27. Bhuiyan, T.R.; Hirai, N. Study of Crystalline Behavior of Heat-Treated Wood Cellulose during Treatments in Water. *J. Wood Sci.* **2005**, *51*, 42–47. [CrossRef]
28. Boonstra, M.J.; Tjeerdsma, B. Chemical Analysis of Heat-treated Softwoods. *Holz Roh Werkst.* **2006**, *64*, 204–211. [CrossRef]

29. Herrera, R.; Erdocia, X.; Llano-Ponte, R.; Labidi, J. Characterization of Hydrothermally Treated Wood in Relation to Changes on Its Chemical Composition and Physical Properties. *J. Anal. Appl. Pyrolysis* **2014**, *107*, 256–266. [CrossRef]
30. Tjeerdsma, B.F.; Boonstra, M.; Pizzi, A.; Tekely, P.; Militz, H. Characterisation of Thermally Modified Wood: Molecular Reasons for Wood Performance Improvement. *Holz als Roh und Werkstoff* **1998**, *56*, 149–153. [CrossRef]
31. Rautkari, L.; Hill, C.A.; Curling, S.; Jalaludin, Z.; Ormondroyd, G. What Is the Role of the Accessibility of Wood Hydroxyl Groups in Controlling Moisture Content? *J. Mater. Sci.* **2013**, *48*, 6352–6356. [CrossRef]
32. Herrera, R.; Erdocia, X.; Labidi, J.; Llano-Ponte, R. Chemical Analysis of Industrial-Scale Hydrothermal Wood Degraded by Wood-Rotting Basidiomycetes and Its Action Mechanisms. *Polym. Degrad. Stab.* **2015**, *117*, 37–45. [CrossRef]
33. Candelier, K.; Thevenon, M.-F.; Petrissans, A.; Dumarcay, S.; Gerardin, P.; Petrissans, M. Control of Wood Thermal Treatment and Its Effects on Decay Resistance: A Review. *Annal. For. Sci.* **2016**, *73*, 571–583. [CrossRef]
34. Dubey, M.K.; Pang, S.; Walker, J. Changes in Chemistry, Color, Dimensional Stability and Fungal Resistance of *Pinus radiata* D. Don Wood with Oil Heat treatment. *Holzforschung* **2012**, *66*, 49–57. [CrossRef]
35. Ayata, U.; Akcay, C.; Esteves, B. Determination of Decay Resistance against *Pleurotus ostreatus* and *Coniophora puteana* Fungus of Heat-Treated Scotch Pine, Oak and Beech Wood Species. *Maderas Ciencia y Tecnología* **2017**, *19*, 309–316. [CrossRef]
36. Boonstra, M.; Van Acker, J.; Kegel, E.; Stevens, M. Optimisation of a Two-Stage Heat treatment Process: Durability Aspects. *Wood Sci. Technol.* **2007**, *41*, 31–57. [CrossRef]
37. Ringman, R.; Pilgaard, A.; Kölle, M.; Brischke, C.; Richter, K. Effects of Thermal Modification on *Postia placenta* Wood Degradation Dynamics: Measurements of Mass Loss, Structural Integrity and Gene Expression. *Wood Sci. Technol.* **2016**, *50*, 385–397. [CrossRef]
38. Surini, T.; Charrier, F.; Malvestio, J.; Charrier, B.; Moubarik, A.; Castéra, P.; Grelier, S. Physical Properties and Termite Durability of Maritime Pine *Pinus pinaster* Ait., Heat-Treated under Vacuum Pressure. *Wood Sci. Technol.* **2012**, *46*, 487–501. [CrossRef]
39. Sivrikaya, H.; Can, A.; de Troya, T.; Conde, M. Comparative Biological Resistance of Differently Thermal Modified Wood Species against Decay Fungi, *Reticulitermes grassei* and *Hylotrupes bajulus*. *Maderas Ciencia y Tecnología* **2015**, *17*, 559–570. [CrossRef]
40. Esteves, B. Technological Improvement of Portuguese Woods by Heat Modification. Ph.D. Thesis, School of Agronomy, Lisbon University, Lisbon, Portugal, 2006.
41. Yildiz, S. Physical, Mechanical, Technological and Chemical Properties of Beech and Spruce Wood Treated by Heating. Ph.D. Thesis, Karadeniz Technical University, Trabzon, Turkey, 2002.
42. Kim, G.-H.; Yun, K.-E.; Kim, J.-J. Effect of Heat treatment on the Decay Resistance and the Bending Properties of Radiata Pine Sapwood. *Material und Organismen* **1998**, *32*, 101–108.
43. Korkut, S.; Akgül, M.; Dündar, T. The Effects of Heat treatment on Some Technological Properties of Scots Pine (*Pinus sylvestris* L.) Wood. *Bioresour. Technol.* **2008**, *99*, 1861–1868. [CrossRef] [PubMed]
44. Shi, J.L.; Kocaefe, D.; Zhang, J. Mechanical Behaviour of Quebec Wood Species Heat-Treated Using ThermoWood Process. *Holz als Roh und Werkstoff* **2007**, *65*, 255–259. [CrossRef]
45. Kubojima, Y.; Okano, T.; Ohta, M. Bending Strength and Toughness of Heat-Treated Wood. *J. Wood Sci.* **2000**, *46*, 8–15. [CrossRef]
46. Nuopponen, M.; Vuorinen, T.; Jämsä, S.; Viitaniemi, P. Thermal Modifications in Softwood Studied by FT-IR and UV Resonance Raman Spectroscopies. *J. Wood Chem. Technol.* **2005**, *24*, 13–26. [CrossRef]
47. Sivonen, H.; Maunu, S.L.; Sundholm, F.; Jämsä, S.; Viitaniemi, P. Magnetic Resonance Studies of Thermally Modified Wood. *Holzforschung* **2002**, *56*, 648–654. [CrossRef]
48. Berglund, J.; Mikkelsen, D.; Flanagan, B.M.; Dhital, S.; Gaunitz, S.; Henriksson, G.; Lindström, M.E.; Yakubov, G.E.; Gidley, M.J.; Vilaplana, F. Wood Hemicelluloses Exert Distinct Biomechanical Contributions to Cellulose Fibrillar Networks. *Nat. Commun.* **2020**, *11*, 1–16. [CrossRef]
49. Burgert, I.; Keplinger, T. Plant Micro-and Nanomechanics: Experimental Techniques for Plant Cell-Wall Analysis. *J. Exp. Botan.* **2013**, *64*, 4635–4649. [CrossRef]
50. Esteves, B.; Videira, R.; Pereira, H. Chemistry and Ecotoxicity of Heat-Treated Pine Wood Extractives. *Wood Sci. Technol.* **2010**, *45*, 661–676. [CrossRef]
51. Windeisen, E.; Strobel, C.; Wegener, G. Chemical Changes during the Production of Thermo-Treated Beech Wood. *Wood Sci. Technol.* **2007**, *41*, 523–536. [CrossRef]
52. Jones, D.; Sandberg, D.; Giacomo, G. *Wood Modification in Europe: A State-of-the-Art about Processes, Products, Applications*; Firenze University Press: Firenze, Italy, 2019.
53. TAPPI. TAPPI. TAPPI UM 250. In *Acid-Soluble Lignin in Wood and Pulp*; TAPPI Press: Atlanta, GA, USA, 2000.
54. CEN. *EN 117 Wood Preservatives—Determination of Toxic Values against Reticulitermes Species (European Termites) (Laboratory Method)*; CEN: Brussels, Belgium, 2012.
55. CEN. *EN 13183-1 Moisture Content of a Piece of Sawn Timber—Part 1: Determination by Oven Dry Method*; CEN: Brussels, Belgium, 2002.
56. CEN. *EN 310 Wood-Based Panels: Determination of Modulus of Elasticity in Bending and of Bending Strength*; CEN: Brussels, Belgium, 1993.
57. Ye, X.; Zhang, Z.; Chen, Y.; Cheng, J.; Tang, Z.; Hu, Y. Physico-Chemical Pretreatment Technologies of Bioconversion Efficiency of *Paulownia Tomentosa* (Thunb.). *Steud. Ind. Crops Prod.* **2016**, *87*, 280–286. [CrossRef]
58. Kalaycioglu, H.; Deniz, I.; Hiziroglu, S. Some of the Properties of Particleboard Made from Paulownia. *J. Wood Sci.* **2005**, *51*, 410–414. [CrossRef]
59. Gong, C.; Bujanovic, B.M. Impact of Hot-Water Extraction on Acetone-Water Oxygen Delignification of *Paulownia* Spp. and Lignin Recovery. *Energies* **2014**, *7*, 857–873. [CrossRef]

60. Mecca, M.; D'Auria, M.; Todaro, L. Effect of Heat treatment on Wood Chemical Composition, Extraction Yield and Quality of the Extractives of Some Wood Species by the Use of Molybdenum Catalysts. *Wood Sci. Technol.* **2019**, *53*, 119–133. [CrossRef]
61. Ding, T.; Gu, L.; Liu, X. Influence of Steam Pressure on Chemical Changes of Heat-Treated Mongolian Pine Wood. *BioResources* **2011**, *6*, 1880–1889.
62. Brosse, N.; El Hage, R.; Chaouch, M.; Pétrissans, M.; Dumarçay, S.; Gérardin, P. Investigation of the Chemical Modifications of Beech Wood Lignin during Heat treatment. *Polym. Degrad. Stab.* **2010**, *95*, 1721–1726. [CrossRef]
63. Mohareb, A.; Sirmah, P.; Pétrissans, M.; Gérardin, P. Effect of Heat treatment Intensity on Wood Chemical Composition and Decay Durability of *Pinus patula*. *Eur. J. Wood Wood Prod.* **2012**, *70*, 519–524. [CrossRef]
64. Sikora, A.; Kačík, F.; Gaff, M.; Vondrová, V.; Bubeníková, T.; Kubovskỳ, I. Impact of Thermal Modification on Color and Chemical Changes of Spruce and Oak Wood. *J. Wood Sci.* **2018**, *64*, 406–416. [CrossRef]
65. D'Auria, M.; Mecca, M.; Todaro, L. High Temperature Treatment Allows the Detection of Episesamin in Paulownia Wood Extractives. *Nat. Prod. Res.* **2020**, *34*, 1326–1330. [CrossRef]
66. Ra, J.-B.; Kim, K.-B.; Leem, K.-H. Effect of Heat treatment Conditions on Color Change and Termite Resistance of Heat-Treated Wood. *J. Korean Wood Sci. Technol.* **2012**, *40*, 370–377. [CrossRef]
67. Salman, S.; Thévenon, M.F.; Pétrissans, A.; Dumarçay, S.; Candelier, K.; Gérardin, P. Improvement of the Durability of Heat-Treated Wood against Termites. *Maderas Ciencia y Tecnología* **2017**, *19*, 317–328. [CrossRef]
68. Esteves, B.; Nunes, L.; Domingos, I.; Pereira, H. Comparison between Heat-treated Sapwood and Heartwood from *Pinus pinaster*. *Eur. J. Wood Wood Prod.* **2014**, *72*, 53–60. [CrossRef]
69. Hidayat, W.; Qi, Y.; Jang, J.-H.; Febrianto, F.; Kim, N.H. Effect of Mechanical Restraint on the Properties of Heat-Treated *Pinus koraiensis* and *Paulownia tomentosa* Woods. *BioResources* **2017**, *12*, 7539–7551.
70. Kim, Y.K.; Kwon, G.J.; Kim, A.R.; Lee, H.S.; Purusatama, B.; Lee, S.H.; Kang, C.W.; Kim, N.H. Effects of Heat treatment on the Characteristics of Royal Paulownia (*Paulownia tomentosa* (Thunb.) Steud.) Wood Grown in Korea. *J. Korean Wood Sci. Technol.* **2018**, *46*, 511–526.
71. Yildiz, S.; Gezer, E.D.; Yildiz, U.C. Mechanical and Chemical Behavior of Spruce Wood Modified by Heat. *Build. Environ.* **2006**, *41*, 1762–1766. [CrossRef]
72. Yildiz, U.C.; Yildiz, S.; Gezer, E.D. Mechanical and Chemical Behavior of Beech Wood Modified by Heat. *Wood Fiber Sci.* **2005**, *37*, 456–461.
73. Boonstra, M.J.; Van Acker, J.; Tjeerdsma, B.F.; Kegel, E.V. Strength Properties of Thermally Modified Softwoods and Its Relation to Polymeric Structural Wood Constituents. *Ann. For. Sci.* **2007**, *64*, 679–690. [CrossRef]
74. Kvietková, M.; Gašparík, M.; Gaff, M. Effect of Thermal Treatment on Surface Quality of Beech Wood after Plane Milling. *BioResources* **2015**, *10*, 4226–4238. [CrossRef]
75. Korkut, D.S.; Guller, B. The Effects of Heat treatment on Physical Properties and Surface Roughness of Red-Bud Maple (*Acer trautvetteri* Medw.) Wood. *Bioresour. Technol.* **2008**, *99*, 2846–2851. [CrossRef]
76. Winandy, J.E.; Lebow, P.K. Modeling Strength Loss in Wood by Chemical Composition. Part I. An Individual Component Model for Southern Pine. *Wood Fiber Sci.* **2001**, *33*, 239–254.
77. Kocaefe, D.; Shi, J.L.; Yang, D.-Q.; Bouazara, M. Mechanical Properties, Dimensional Stability, and Mold Resistance of Heat-Treated Jack Pine and Aspen. *For. Prod. J.* **2008**, *58*, 88.
78. Kartal, S.N.; Hwang, W.-J.; Imamura, Y. Water Absorption of Boron-Treated and Heat-Modified Wood. *J. Wood Sci.* **2007**, *53*, 454–457. [CrossRef]