

Article

The Impact of Thermal Treatment on Structural Changes of Teak and Iroko Wood Lignins

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Abstract: Thermal modification is an environmentally friendly method to improve dimensional stability, durability, and aesthetic properties of wood. Changes in lignin as one of the main wood components markedly influence wood product properties and recycling possibilities of thermowood at the end of its life cycle. Teak and iroko wood samples were thermally treated at the temperatures of 160 °C, 180 °C and 210 °C following the Thermowood process. Dioxane lignin was isolated from treated and untreated wood and analysed by nitrobenzene oxidation (NBO), size exclusion chromatography (SEC) and Fourier transform infrared spectroscopy (FTIR). The yields of both acid-insoluble and dioxane lignins increased with an increasing treatment temperature. Dioxane lignins are GS-types containing more guaiacyl units compared to syringyl ones with S/G ratios of 0.91 and 0.84, respectively. In the process of thermal modification, several degradation and condensation reactions were observed. The cleavage of methoxyl groups and side chains, oxidation reactions, cleavage of the β -O-4 ether linkage and cross-linking radicals arising at higher temperatures were all confirmed. However, during the thermal treatment, teak lignin changed in a different way than iroko lignin, e.g., the molecular weight of iroko lignin decreased at all applied temperatures while it increased at 180 °C and 210 °C in teak lignin, and the change in S/G ratio and the cleavage of alkyl-aryl bonds are different in both wood species.

Keywords: wood; teak; iroko; thermal treatment; lignin

1. Introduction

Wood is a natural, renewable, mostly inexpensive and easily accessible material. Modification is applied to overcome weak points of the wood material that are mainly related to moisture sensitiveness, hardness, low dimensional stability, low resistance to wear, UV irradiation, to bio-deterioration against fungi, termites, and marine borers [1]. Wood thermal treatment is an economical and environment friendly pretreatment. It can be performed in range of 160 to 260 °C in different environments, e.g., air, vacuum, nitrogen and oil. Its main objective is to improve dimensional stability and durability, but sometimes thermal treatment is used to change the aesthetic properties of wood. The wood colour becomes darker depending on the treatment temperature, time, and environment [2–4].

Tropical woods generally have a great resistance to biological agents and mechanical wear, and a good dimensional stability and interesting wood figure. Many species of exotic wood are used for exterior constructions, decking, claddings, garden furniture or special plywood [5,6]. Teak is one of the most valuable woods, but its use is limited by scarcity and high cost. It is currently used in the construction of boats, flooring, decorative objects and veneer. Because of its colour and durability, iroko is suggested as a substitute for teak. Its durability makes it suitable for boat building, piles, other marine work, and railroad crossties. Other uses include joinery, furniture, and cabinetwork [7–9].

Extractives in tropical wood allow for exceptional resistance against damage caused by insects and fungi. However, their impact on the weathering process retardation is lower. This process begins with the photodegradation of lignin by adsorption of photons from sunlight with chromophores of lignin macromolecules-conjugated carbonyls, etc. [10]. The authors of the reference paper investigated colour and chemical changes during the natural and artificial weathering of seven tropical wood samples and found a particularly significant decrease of lignin, a decrease of conjugated and unconjugated carbonyl groups, and a decrease of cellulose crystallinity [10]. High-value wood surfaces for exclusive wood-based floorings, furniture and interior outfitting of residences, luxury yachts, aircrafts, and railway vehicles are preferentially made of dark coloured tropical wood species [11]. The thermal modification of tropical wood species can be used to colour homogenization for decorative purposes. Despite the good physical and mechanical properties of the teak wood, it presents important colour changes when exposed to UV radiation. In the case of teak wood, thermal treatment can be an alternative to improve the durability of sapwood, modify the colour of sapwood to match with that of heartwood, providing a more stable wood colour when exposed to UV radiation, thus adding more value to the final product and increasing its competitiveness on the market [12].

Heat modification is expected to improve the physical properties of young (15-years old) teak wood. The results showed that the density of the teak wood slightly decreased after heat treatment. However, its dimensional stability improved substantially, under its reduced water absorption. Furthermore, the surface of the young teak became darker, with a more even brown colour [13]. The lightness of teak wood was the most affected colour attribute during the thermal treatment [14]. The thermowood process of iroko wood caused its density decrease, colour darkening, and a considerable improvement of dimensional stability [15]. Similar changes were observed during thermal treatment of iroko and padauk wood [16].

Lignin is one of the most abundant organic materials. Its environmentally friendly characteristics and physical and chemical properties enable valuable utilisation [17]. Its changes during thermal treatment influence several wood properties, mainly colour, however, exposure to daylight often causes brightening or greying. It was found that the discoloration of dark wood is not only caused by UV-induced bond cleavage and oxidation of the lignin macromolecule causing the formation of coloured low-molecular fragments, but also by changes in extractives. During thermal treatment, some α -O-4 and β -O-4 linkages may be cleaved with the formation of free phenolic units that could be involved in condensation reactions. Simultaneous degradation and condensation reactions lead to the less decrease of molecular weight than expected from the extent of cleaved ether structures [11,18–20].

Available information on the thermal treatment of exotic wood species includes mainly changes in extractives, mechanical properties, colour and wood dimensional stability. However, data on their lignin changes are rare, although they are important to improve protection against weathering and wider recycling of thermowood at the end of its life cycle. The aim of this work was therefore to investigate structural changes of lignins of selected tropical wood species during the treatment by the Thermowood process.

2. Materials and Methods

2.1. Wood Thermal Modification

Teak (*Tectona grandis* L.f) (density—711 kg·m⁻³) and iroko (*Milicia excelsa* (Welw.) C.C. Berg) (density—615 kg·m⁻³) were harvested in Myanmar and Gabon, respectively [14,16]. Wood samples with the dimensions 20 × 20 × 300 mm (T × R × L) were modified at the temperatures of 160 °C, 180 °C and 210 °C in an open system thermal modification chamber (Type S400/03, LAC Ltd., Rajhrad, Czech Republic) following the ThermoWood process [21]. Untreated (reference, denoted as 20 °C) and thermally modified samples were ground to sawdust and extracted in the Soxhlet apparatus with a mixture of ethanol and toluene according to the ASTM D1107-96 standard [22]. Acid-insoluble lignin (Klason lignin) was determined according to Sluiter et al. [23].

2.2. Lignin Isolation

The lignin isolation from the wood samples was performed using mild acidolysis and dioxane as a solvent by modified method [24]. Extracted wood flour with size ≤ 0.355 mm (10 g) was placed in a 500 mL three-necked flask fitted with a dropping funnel, a nitrogen bubbler and a reflux condenser. An amount of 100 mL of dioxane/water (9:1, *v/v*) with 1.82 g HCl (equivalent to 0.2 M) was slowly added. The mixture under nitrogen atmosphere was refluxed at 80 °C for 5 h. Then, the mixture was cooled to room temperature, filtered, neutralized by addition of ammonium acetate, and concentrated in vacuum at the temperature of 40 °C. Lignin was precipitated by slowly dropping of dioxane solution into the cold water.

2.3. Nitrobenzene Oxidation

Alkaline nitrobenzene oxidation (NBO) was carried out in a stainless-steel bomb by modified method of Āurkoviĉ et al. [25]. An amount of 50 mg of dioxane lignin was reacted with 5 mL of 2 M NaOH and 0.4 mL of nitrobenzene at the temperature of 180 °C for 2 h. The stainless-steel bomb was then cooled down immediately with cold water. The excess of nitrobenzene was extracted with CH₂Cl₂ two times, and the organic phase was removed. The aqueous phase acidified by 2 M HCl to pH around 2.5 was extracted with CH₂Cl₂ thrice. Then the organic phase was collected and dried with anhydrous Na₂SO₄, gently evaporated in nitrogen stream, and dissolved in methanol/water (1/1). NBO products were analysed by high performance liquid chromatography (HPLC) in an Agilent 1200 apparatus equipped with diode array detector at 240 nm, Kinetex column 2.6 μ m C18 (100 \times 4.6 mm), mobile phase water/methanol/propionic acid (88/4/8/0.1), flow rate 1 mL·min⁻¹, temperature 35 °C. The quantification was performed with the external calibration using standards obtained from Sigma-Aldrich (St. Louis, MO, USA).

2.4. Size Exclusion Chromatography (SEC)

The molecular weight distribution (MWD) of lignin was evaluated by a modified method [25]. The lignin samples were dissolved in *N,N*-dimethylformamide (DMF, 2 mg·mL⁻¹), filtered through a 0.45 μ m filter and placed in a 2 mL autosampler vial prior to SEC analysis. The separation was performed on an Agilent 1200 HPLC system equipped two PolarGel-M columns (7.5 mm \times 300 mm) and a diode array detector, using dimethylformamide + 2% trifluoroacetic acid + 0.1% LiBr as the mobile phase (1.0 mL·min⁻¹) at 35 °C. A calibration curve was constructed with polystyrene standards from 500 to 98,900 g·mol⁻¹. The data were collected using ChemStation for LC 3D systems (version Rev. B.04.03 [21]) software and calculated with the Clarity GPC module (version 7.4.01.088).

2.5. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra were recorded on a Nicolet iS10 spectrometer equipped with Smart iTR ATR accessory using diamond crystal. Four measurements for each sample were performed. Each spectrum was obtained by 32 scans in the range from 4000 cm⁻¹ to 800 cm⁻¹ with a resolution of 4 cm⁻¹. Measured spectra were baseline corrected and analysed in absorbance mode by OMNIC 8.0 software.

2.6. Statistical Analysis

The data were subjected to an analysis of variance (ANOVA), and the significant differences between the means were determined using Duncan's multiple range test with a *p*-value of 0.05.

3. Results and Discussion

The advantage of using dioxane lignin for structural studies are minimal structural changes of lignin during its preparation and good extraction yields [26,27].

3.1. Klason and Dioxane Lignin Yields

Lignin content in teak wood ranges from 30 to 43% [28–31]. Unmodified (reference) wood in this work has lignin content within this range (35.42%), as reported previously [32]. The apparent insoluble lignin content increased during thermal modification, when compared to the reference sample and the sample treated at the temperature of 210 °C by 14% and 27% for teak and iroko, respectively. Duncan's multiple range test shows that Klason lignin yields change significantly for both wood species (for iroko KL from the temperature of 180 °C). This is mainly due to hemicellulose degradation, which leads to condensation products as acid-insoluble residues [33]. The amount of lignin that can be extracted with dioxane depends to a large extent on the degree of its condensation [34]. The results of dioxane lignin yields (Table 1) show that the yield of lignin from wood increased 2.1-fold and 1.7-fold for teak and iroko, respectively, and these changes are significant. Similarly, the slight increase of dioxane lignin yields was observed at heat sterilization of pine wood in the temperatures up to 120 °C [25]. On the other hand, yields of dioxane lignin in spruce heated wood increased up to temperatures of approx. 210 °C, and with an increased temperature (up to 270 °C), it rapidly decreased [34].

Table 1. Klason and dioxane lignin yields from untreated and thermally treated tropical wood species (mean \pm SD, % odw).

Wood	20 °C	160 °C	180 °C	210 °C
Teak—KL	35.42 \pm 0.04	39.30 \pm 0.15	39.52 \pm 0.04	40.52 \pm 0.06
Iroko—KL	29.03 \pm 0.25	29.00 \pm 0.11	29.90 \pm 0.18	36.92 \pm 0.19
Teak—DL	8.64 \pm 0.11	11.38 \pm 0.14	15.32 \pm 0.23	18.32 \pm 0.25
Iroko—DL	4.13 \pm 0.05	4.52 \pm 0.06	4.72 \pm 0.11	7.20 \pm 0.10

3.2. Nitrobenzene Oxidation Products Analysis

Teak has a GS-lignin, with a monomeric composition determined by Py-GC/MS(FID) of H:G:S 1:34:24 (sapwood) and 1:29:23 (heartwood) and S/G ratios of 0.71 and 0.81, respectively [28,35]. Similar values—50.6% guaiacyl units, 46.0% syringyl units, 3.4% *p*-hydroxyphenyl units, with S/G ratio 0.91—were found by nitrobenzene oxidation (Table 2). On the other hand, Faix et al. (1987) [36] found up to 70% of guaiacyl structural units in teak lignin. The ratio of syringyl units to guaiacyl (S/G) decreases with an increasing temperature, the yield of NBO products significantly increases except at the highest temperature. The results indicate the predominance of degradation reactions at lower temperatures and condensation reactions at the temperature of 210 °C.

Table 2. Nitrobenzene oxidation products of teak dioxane lignins (mean \pm SD, %).

Wood	20 °C	160 °C	180 °C	210 °C
<i>p</i> -Hydroxybenzoic acid	0.09 \pm 0.03	0.12 \pm 0.00	0.11 \pm 0.01	0.11 \pm 0.00
<i>p</i> -Hydroxybenzaldehyde	0.81 \pm 0.22	1.10 \pm 0.02	1.24 \pm 0.03	0.98 \pm 0.02
Vanillic acid	0.21 \pm 0.03	0.27 \pm 0.04	0.51 \pm 0.16	0.20 \pm 0.01
Vanilline	13.13 \pm 1.20	18.30 \pm 0.72	22.66 \pm 0.54	23.93 \pm 0.30
Syringic acid	3.10 \pm 0.45	2.45 \pm 0.16	3.74 \pm 0.15	3.20 \pm 0.04
Syringaldehyde	9.02 \pm 0.61	13.31 \pm 0.30	15.14 \pm 0.15	11.92 \pm 0.15
Total yield on DL	26.36 \pm 2.46	35.55 \pm 1.41	43.40 \pm 0.41	40.34 \pm 0.22
S/G ratio	0.91 \pm 0.00	0.85 \pm 0.01	0.81 \pm 0.01	0.63 \pm 0.01

Like teak lignin, iroko has a GS-lignin, containing more guaiacyl units compared to syringyl ones with an S/G ratio of 0.84 (Table 3). Some authors reported higher values of the S/G ratio for iroko lignin, 0.92 (by Py-GC-MS) and 1.005 (by FTIR) respectively [37,38]. Differences may be caused by other methods of the isolation of lignin as well as different methods of analysis. The yield of NBO products gradually increased up to 180 °C, then decreased, however, the changes are mostly insignificant. The increase in NBO products may suggest that iroko lignin treated at lower temperatures

may be structurally modified to an easily degradable form. A similar trend was observed in the S/G ratio, indicating preferential contribution of G-type lignin to the condensation reaction as reported by Kim et al. (2014) [39].

Table 3. Nitrobenzene oxidation products of iroko dioxane lignins (mean \pm SD, %).

Wood	20 °C	160 °C	180 °C	210 °C
<i>p</i> -Hydroxybenzoic acid	0.16 \pm 0.00	0.19 \pm 0.01	0.19 \pm 0.02	0.16 \pm 0.00
<i>p</i> -Hydroxybenzaldehyde	1.42 \pm 0.03	1.60 \pm 0.03	1.74 \pm 0.06	1.46 \pm 0.03
Vanillic acid	0.23 \pm 0.02	0.35 \pm 0.04	0.52 \pm 0.08	0.30 \pm 0.04
Vanilline	20.69 \pm 0.68	20.55 \pm 0.37	20.77 \pm 0.68	19.03 \pm 0.95
Syringic acid	1.56 \pm 0.06	2.45 \pm 0.11	2.89 \pm 0.11	1.22 \pm 0.06
Syringaldehyde	15.95 \pm 0.16	18.04 \pm 0.31	19.14 \pm 0.93	16.50 \pm 0.53
Total yield on DL	40.01 \pm 0.78	43.18 \pm 0.44	45.25 \pm 1.74	38.67 \pm 1.81
S/G ratio	0.84 \pm 0.02	0.98 \pm 0.04	1.03 \pm 0.04	0.92 \pm 0.01

3.3. Molecular Weight Determination

Lignin isolated from the untreated teak wood has a molecular weight of about 7100 g·mol⁻¹; in the available literature, no adequate data were found for comparison. In the thermal treatment of teak wood, its molecular weight (MW) and polydispersity (PD) decreased at a temperature of 160 °C (Table 4). Elution profiles confirmed a cleavage of the intermediate molecular portions of the lignin macromolecule (Figure 1). At higher temperatures (180 °C and 210 °C), both degradation and condensation reactions occur simultaneously, resulting in increased polydispersity and expanded peaks in the chromatogram (Figure 1). Changes in MW and PD are significant, except the difference in PD between temperatures 180 °C and 210 °C. Condensation reactions are predominant at 210 °C, leading to a lignin molecular weight increase and to a decrease in the yield of NBO products. The reduction in M_n and M_w indicates that the lignin molecules were fragmented into smaller units. Oxidized lignin can undergo re-polymerization as can be observed in our GPC data and as reported by other authors [40,41]. Simultaneous degradation and condensation reactions were also confirmed by the heating of MWL lignin isolated from poplar wood [39]. The lignin thermal degradation leads to the arising of phenoxy radicals through a hydrogen atom abstraction process. They could undergo coupling reactions with the corresponding C5-centered mesomeric radical derivatives to generate new 4-O-5 and 5-5' linkages, respectively [42,43].

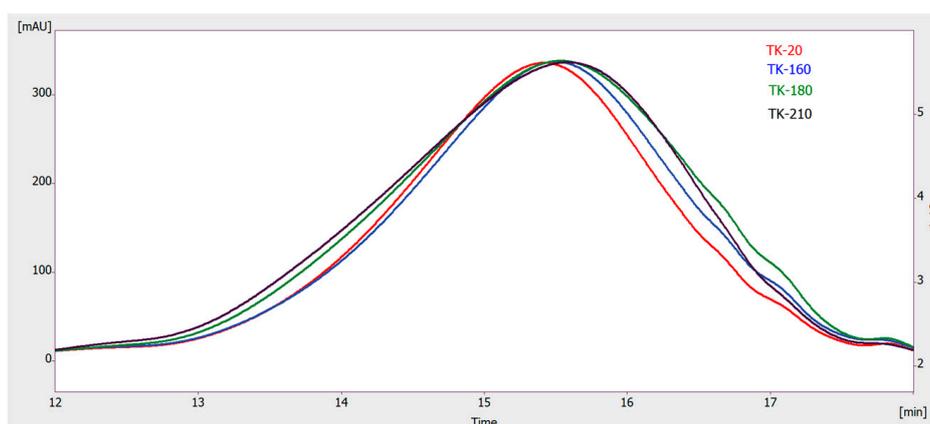


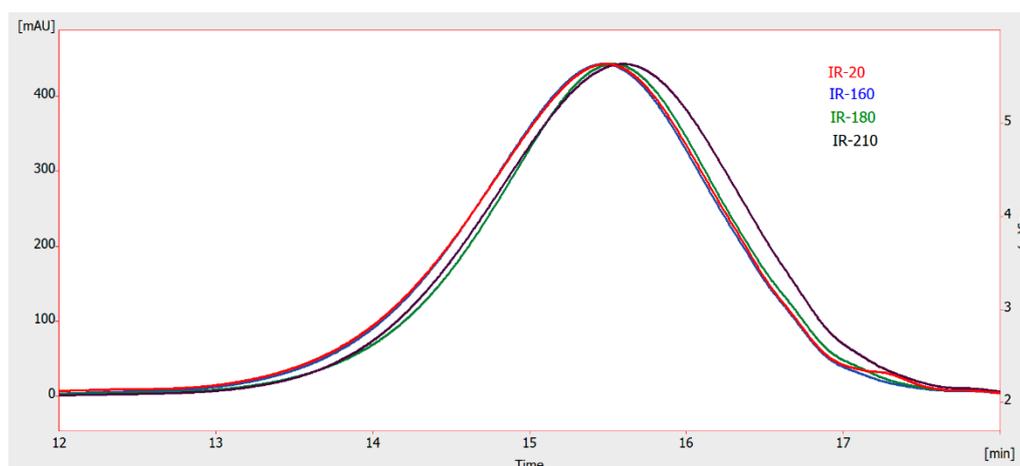
Figure 1. Chromatograms of lignins isolated from untreated and thermally modified teak wood.

Table 4. Results of macromolecular characteristics of lignins from teak wood. Data represent mean \pm SD.

T (°C)	M_w (g·mol ⁻¹)	M_n (g·mol ⁻¹)	M_z (g·mol ⁻¹)	PD
20	7145 \pm 76	1929 \pm 24	44,401 \pm 2435	3.70 \pm 0.07
160	6076 \pm 159	1740 \pm 37	28,668 \pm 2240	3.49 \pm 0.15
180	6632 \pm 259	1691 \pm 23	34,131 \pm 2232	3.92 \pm 0.15
210	7531 \pm 230	1874 \pm 35	35,901 \pm 1618	4.02 \pm 0.14

Note: M_w = weight average molecular weight (MW), M_n = number average MW, M_z = z average MW, PD (polydispersity) = M_w/M_n .

Lignin isolated from iroko wood has a different molecular weight (about 38% lower) and polydispersity (about 44% lower) when compared to teak lignin. These values ($M_w = 4500$ g·mol⁻¹, $M_n = 2100$ g·mol⁻¹, PD = 2.1) are lower than those published by Zikeli et al. (2019) [37]—($M_w = 13,900$ g·mol⁻¹, $M_n = 2300$ g·mol⁻¹, PD = 5.7). The differences may be due to different growth locality, lignin isolation procedure, and the chromatographic method itself. During the thermal treatment, iroko lignin changes in a different way than teak lignin. At 160 °C, low molecular weight lignin fragments are degraded (Figure 2), resulting in a slight increase in molecular weight and a negligible decrease in polydispersity. Degradation reactions are predominant at 180 °C and the molecular weight decreases by almost 10% when compared to the original sample. Changes in MW are significant, some changes in PD are significant, while others are not. The temperature of 210 °C causes both condensation and degradation reactions (which prevail) and the molecular weight decreases (Figure 2, Table 5). A similar trend was observed at the thermal modification of oak wood [44].

**Figure 2.** Chromatograms of lignins isolated from untreated and thermally modified iroko wood.**Table 5.** Results of macromolecular characteristics of lignins from iroko wood. Data represent mean \pm SD.

T (°C)	M_w (g·mol ⁻¹)	M_n (g·mol ⁻¹)	M_z (g·mol ⁻¹)	PD
20	4463 \pm 37	2136 \pm 31	9994 \pm 239	2.09 \pm 0.02
160	4576 \pm 38	2207 \pm 37	11,029 \pm 575	2.07 \pm 0.04
180	4034 \pm 49	1998 \pm 31	9133 \pm 456	2.02 \pm 0.03
210	3359 \pm 23	1835 \pm 31	8320 \pm 80	2.10 \pm 0.03

Note: See Table 4 for symbols.

3.4. FTIR Spectra Analysis

The most frequent changes in lignin structure are determined in the FTIR spectra around the bands: 1720, 1600, 1500, 1460, 1420, 1370, 1326, 1266, 1220 and 1120 cm⁻¹ [45,46]. A wide band in the range of 3300–3500 cm⁻¹ and bands of about 2940 cm⁻¹ and 2850 cm⁻¹ can also be used to detect

changes in lignin. The changes in both wood species, teak and iroko, are similar, thus their FTIR spectra will be evaluated together.

Broad bandwidth low absorbance around 3400 cm^{-1} (OH stretching vibration in primary or secondary alcohols, as well as in phenolic groups in lignin) [4,47] predominantly decreases with an increasing temperature. The reduction of hydroxyl groups is accompanied by condensation of lignin and oxidation to C=O groups [48,49] and was observed in thermally treated teak wood [50]. Bands near of 2937 and 2840 cm^{-1} (arising from C–H stretching vibrations in methyl, methylene and methoxyl groups and tertiary CH groups) [51–53] show only insignificant changes (especially in teak wood). The band found in the carbonyl region between 1700 – 1730 cm^{-1} (C=O stretching in unconjugated functional groups of aldehydes, ketones, esters and carboxylic acids) [51,52,54]. Our results showed an increase in the absorbance at 1715 cm^{-1} (teak) and 1712 cm^{-1} (iroko) (Figures 3 and 4). The increase may be confirmation of the more pronounced cleavage of the β -alkyl-aryl ether bonds and the subsequent formation of new C=O groups in the lignin structure. This results in an increase in the amount of acetyl and carboxyl groups from the lignin [52,55]. The mentioned changes are due to splitting of aliphatic side chains in lignin accompanied by cleavage of β -O-4 bonds during its heat treatment [56,57]. Similarly, the cleavage of the β -O-4 linkages and the splitting of the aliphatic methoxyl chains from the aromatic ring in lignin were observed at steam-heat treated teak wood [58].

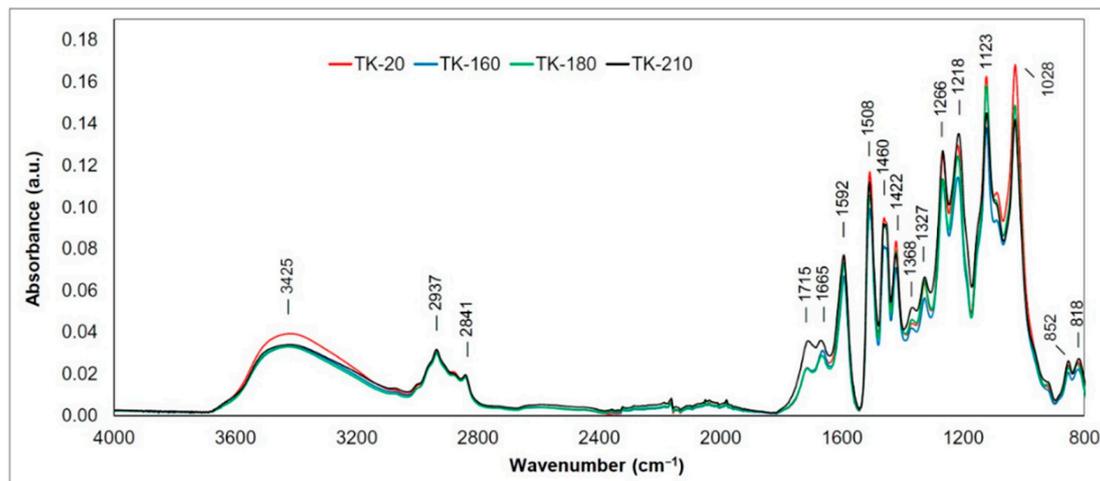


Figure 3. Fourier transform infrared (FTIR) spectra of the untreated and thermally modified teak wood lignin.

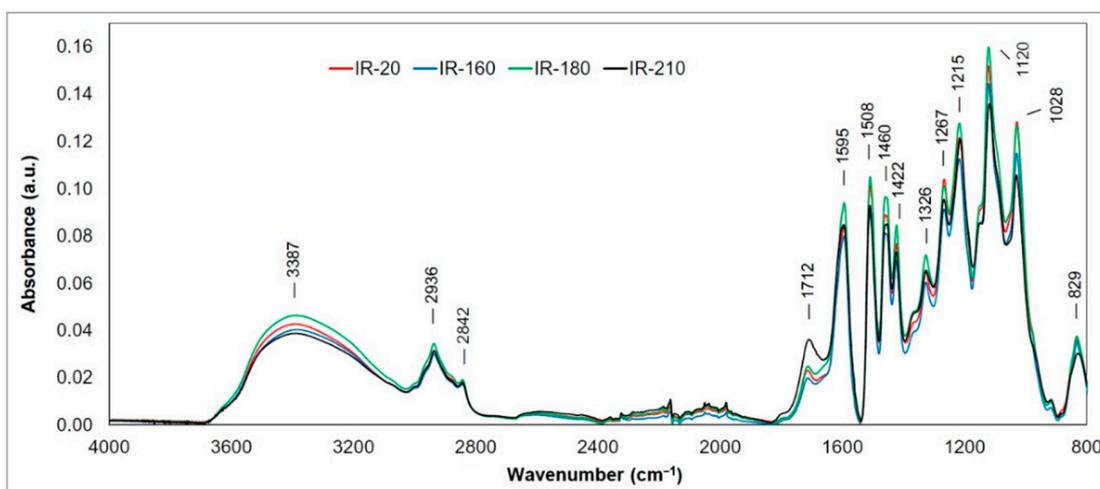


Figure 4. FTIR spectra of the untreated and thermally modified iroko wood lignin.

An increase in the band at 1665 cm^{-1} (C=O stretching in various conjugated groups in lignin) [59,60] was observed at teak wood at $210\text{ }^{\circ}\text{C}$ (this band did not appear at any temperature value for the iroko wood). This trend may be an indicator of the cleavage of α -alkyl-aryl ether linkages [25]. The peaks near 1600 cm^{-1} and 1500 cm^{-1} (C=C aromatic skeletal vibrations) [61,62] show only small changes with increasing temperature (a more pronounced decline is noticeable in the iroko wood). This trend suggests the relative thermal stability of the lignin aromatic structures [63].

At bands of 1460 cm^{-1} and 1422 cm^{-1} (asymmetric C–H deformations in lignin and carbohydrates) [51,64], a slight decrease with increase of used treatment temperature was noted. Thus, the decrease of absorbance in iroko was more pronounced than in teak (this may be due to a more notable cleavage of methoxyl groups in the iroko). According to Cheng et al. [65], the decrease absorbance may be due to a decrease in the methoxyl groups in lignin. The peak absorbance around 1327 cm^{-1} (C–O vibration in syringyl derivatives-condensed structures in lignin) [38,62] increased permanently, except for the iroko at the highest temperature, where a decreased absorbance was observed. This suggests the condensation reactions in lignin structure (more pronounced in teak than iroko wood) as observed by Li et al. (2015) [58] for teak wood. A similar trend was also found for the band absorbances around 1265 cm^{-1} and 1220 cm^{-1} (C–O stretching of guaiacyl units) [63,66]. Considering the absorbance values at $1265\text{--}1267\text{ cm}^{-1}$, it can be assumed that the proportion of guaiacyl units in the teak wood lignin is higher than in iroko. In contrast, the NBO results show a higher S/G ratio in teak lignin compared to iroko lignin. This difference may be because NBO provides the results only for non-condensed lignin substructure, while FTIR and SEC analyses show the properties of the whole dioxane lignin. Larger amounts of guaiacyl units in teak lignin according to the FTIR method indicate their greater condensation, resulting in lower yields of NBO products and higher S/G ratio relative to iroko lignin.

The band at 1120 cm^{-1} (C–H vibration in lignin) is typical of syringyl units [67,68]. This band markedly decreased with an increasing temperature in both wood species. Compared to the band near 1220 cm^{-1} , there is a notable decrease in absorbance, which may be due to higher thermal stability of guaiacyl structures against syringyl ones, as reported by Ragauskas et al. [69].

4. Conclusions

During the thermal treatment of teak and iroko wood, the apparent insoluble lignin content increased, when compared to the reference sample and the sample treated at the temperature of $210\text{ }^{\circ}\text{C}$ by 14% and 27%, respectively. The yields of dioxane lignin from wood increased 2.1-fold for teak and 1.7-fold for iroko. Both teak and iroko lignins are GS-types containing more guaiacyl units compared to syringyl ones with S/G ratios of 0.91 and 0.84, respectively. In the process of thermal modification, several degradation and condensation reactions were observed. The cleavage of methoxyl groups and side chains, oxidation reactions, cleavage of the β -O-4 ether linkage and cross-linking radicals arising at higher temperatures as reported by other authors at various conditions of lignin treatment were all confirmed. However, during the thermal treatment, teak lignin changes in a different way than iroko lignin, e.g., the molecular weight of iroko lignin decreased at all applied temperatures while it increased at $180\text{ }^{\circ}\text{C}$ and $210\text{ }^{\circ}\text{C}$ in teak lignin, and the change in S/G ratio and the cleavage of alkyl-aryl bonds are different in both wood species. This can lead to various alterations of the physical and mechanical properties in the process of thermal modification and in the recycling of treated wood.

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References

1. Sandberg, D.; Kutnar, A.; Mantanis, G. Wood modification technologies—A review. *iFor. Biogeosci. For.* **2017**, *10*, 895–908. [CrossRef]
2. Papadopoulou, A.N. Advances in Wood Composites. *Polymers* **2020**, *12*, 48. [CrossRef]
3. Sikora, A.; Kačík, F.; Gaff, M.; Vondrová, V.; Bubeníková, T.; Kubovský, I. Impact of thermal modification on color and chemical changes of spruce and oak wood. *J. Wood Sci.* **2018**, *64*, 406–416. [CrossRef]
4. Taghiyari, H.R.; Hosseini, G.; Tarmian, A.; Papadopoulou, A.N. Fluid Flow in Nanosilver-Impregnated Heat-Treated Beech Wood in Different Mediums. *Appl. Sci.* **2020**, *10*, 1919. [CrossRef]
5. Reinprecht, L.; Kmet'ová, L.; Iždinský, J. Fungal decay and bending properties of beech plywood overlaid with tropical veneers. *J. Trop. For. Sci.* **2012**, *24*, 490–497.
6. Darmawan, W.; Herliyana, E.N.; Gayatri, A.; Lumongga, D.; Hasanusi, A.; Gerardin, P. Microbial growths and checking on acrylic painted tropical woods and their static bending after three years of natural weathering. *J. Mater. Res. Technol.* **2019**, *8*, 3495–3503. [CrossRef]
7. Laskowska, A.; Kozakiewicz, P.; Zbieć, M. Determination of the colour parameters of iroko wood subjected to artificial UV light irradiation. *Ann. WULS SGGW For. Wood Technol.* **2018**, *102*, 133–138.
8. Richter, H.G.; Dallwitz, M.J. 2000 Onwards. Commercial Timbers: Descriptions, Illustrations, Identification, and Information Retrieval. Available online: <http://delta-intkey.com> (accessed on 9 April 2019).
9. Wagenführ, R. *Holzatlas (The Atlas of Wood)*, 6th ed.; Fachbuchverlag Leipzig im Carl Hanser Verlag: München, Germany, 2007; p. 816. ISBN 978-3-446-40649-0.
10. Reinprecht, L.; Mamoňová, M.; Pánek, M.; Kačík, F. The impact of natural and artificial weathering on the visual, colour and structural changes of seven tropical woods. *Eur. J. Wood Prod.* **2018**, *76*, 175–190. [CrossRef]
11. Passauer, L.; Prieto, J.; Müller, M.; Rössler, M.; Schubert, J.; Beyer, M. Novel color stabilization concepts for decorative surfaces of native dark wood and thermally modified timber. *Prog. Org. Coat.* **2015**, *89*, 314–322. [CrossRef]
12. Garcia, R.A.; Lopes, J.O.; Nascimento, A.M.; Latorraca, J.V.F. Color stability of weathered heat-treated teak wood. *Maderas Cienc. Tecnol.* **2014**, *16*, 453–462. [CrossRef]
13. Priadi, T.; Suharjo, A.A.C.; Karlinasari, L. Dimensional stability and colour change of heat-treated young teak wood. *Int. Wood Prod. J.* **2019**, *10*, 119–125. [CrossRef]
14. Gašparík, M.; Gaff, M.; Kačík, F.; Sikora, A. Color and chemical changes in teak (*Tectona grandis* L. f.) and meranti (*Shorea* spp.) wood after thermal treatment. *BioResources* **2019**, *14*, 2667–2683. [CrossRef]
15. Icel, B.; Beram, A. Effects of industrial heat treatment on some physical and mechanical properties of iroko wood. *Drvna Ind.* **2017**, *68*, 229–239. [CrossRef]
16. Kroupa, M.; Gaff, M.; Karlsson, O.; Myronycheva, O.; Sandberg, D. Effects of thermal modification on bending properties and chemical structure of Iroko and Padauk. In Proceedings of the 9th European Conference on Wood Modification, Burgers' Zoo Arnhem, The Netherlands, 17–18 September 2018; Jos, C., Thomas, H., Bôke, T., Holger, M., Brigitte, J., Jos, G., Eds.; Wageningen: SHR Wageningen, The Netherlands, 2018; pp. 155–161, ISBN 978-90-829466-1-1.
17. Chi, Z.; Hao, L.; Dong, H.; Yu, H.; Liu, H.; Wang, Z.; Yu, H. The innovative application of organosolv lignin for nanomaterial modification to boost its heavy metal detoxification performance in the aquatic environment. *Chem. Eng. J.* **2020**, *382*, 122789. [CrossRef]
18. Morales, A.; Labidi, J.; Gullón, P. Assessment of green approaches for the synthesis of physically crosslinked lignin hydrogels. *J. Ind. Eng. Chem.* **2020**, *81*, 475–487. [CrossRef]
19. 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 Werkst.* **1998**, *56*, 149–153. [CrossRef]
20. Lourenço, A.; Araújo, S.; Gominho, J.; Pereira, H.; Evtuguin, D. Structural changes in lignin of thermally treated eucalyptus wood. *J. Wood Chem. Technol.* **2020**, *40*, 258–268. [CrossRef]
21. Ditommaso, G.; Gaff, M.; Kačík, F.; Sikora, A.; Sethy, A.; Corleto, R.; Razaeei, F.; Kaplan, L.; Kubš, J.; Das, S.; et al. Interaction of technical and technological factors on qualitative and energy/ecological/economic indicators in the production and processing of thermally modified merbau wood. *J. Clean. Prod.* **2020**, *252*, 119793. [CrossRef]

22. ASTM. *ASTM D1107-96: Standard Test Method for Ethanol-Toluene Solubility of Wood*; American Society for Testing and Materials: Philadelphia, PA, USA, 2013.
23. Sluiter, A.; Hames, B.; Ruiz, R.; Scarlata, C.; Sluiter, J.; Templeton, D.; Crocker, D. *Determination of Structural Carbohydrates and Lignin in Biomass*; Laboratory analytical procedure (LAP); National Renewable Energy Laboratory: Golden, CO, USA, 2012; NREL/TP-510-42618.
24. Kačík, F.; Luptáková, J.; Šmíra, P.; Nasswetrová, A.; Kačíková, D.; Vacek, V. Chemical alterations of pine wood lignin during heat sterilization. *BioResources* **2016**, *11*, 3442–3452. [[CrossRef](#)]
25. Ďurkovič, J.; Kačík, F.; Mamoňová, M.; Kardošová, M.; Longauer, R.; Krajňáková, J. The effects of propagation techniques on cell wall chemistry and wood anatomy in micropropagated and grafted plants of the Dutch elm hybrid 'Dodoens'. *J. Am. Soc. Hortic. Sci.* **2015**, *140*, 3–11. [[CrossRef](#)]
26. Evtuguin, D.V.; Neto, C.P.; Silva, A.M.S.; Domingues, P.M.; Amado, F.M.L.; Robert, D.; Faix, O. Comprehensive study on the chemical structure of dioxane lignin from plantation *Eucalyptus globulus* wood. *J. Agric. Food Chem.* **2001**, *49*, 4252–4261. [[CrossRef](#)] [[PubMed](#)]
27. Aguayo, M.G.; Ruiz, J.; Norambuena, M.; Mendonça, R.T. Structural features of dioxane lignin from *Eucalyptus globulus* and their relationship with the pulp yield of contrasting genotypes. *Maderas Cienc. Tecnol.* **2015**, *17*, 625–636. [[CrossRef](#)]
28. Lourenço, A.; Pereira, H. Compositional Variability of Lignin in Biomass. *Intech Open* **2018**, *2*, 64–98. [[CrossRef](#)]
29. Miranda, I.; Sousa, V.; Pereira, H. Wood properties of teak (*Tectona grandis*) from a mature unmanaged stand in East Timor. *J. Wood Sci.* **2011**, *57*, 171–178. [[CrossRef](#)]
30. Lukmandaru, G. Chemical characteristics of teak wood attacked by *Neotermes tectonae*. *BioResources* **2015**, *10*, 2094–2102. [[CrossRef](#)]
31. Windeisen, E.; Klassen, A.; Wegener, G. On the chemical characterization of plantation teakwood from Panama. *Holz als Roh-und Werkst.* **2003**, *61*, 416–418. [[CrossRef](#)]
32. Gaff, M.; Kačík, F.; Gašparík, M.; Todaro, L.; Jones, D.; Corleto, R.; Makovická Osvaldová, L.; Čekovská, H. The effect of synthetic and natural fire-retardants on burning and chemical characteristics of thermally modified teak (*Tectona grandis* L. f.) wood. *Constr. Build. Mater.* **2019**, 551–558. [[CrossRef](#)]
33. Esteves, B.; Pereira, H. Wood modification by heat treatment: A review. *BioResources* **2009**, *4*, 370–404. [[CrossRef](#)]
34. Bubeníková, T.; Luptáková, J.; Kačíková, D.; Kačík, F. Characterization of macromolecular traits of lignin from heat treated spruce wood by size exclusion chromatography. *Acta Fac. Xylologiae* **2018**, *60*, 33–42. [[CrossRef](#)]
35. Lourenço, A.; Neiva, D.; Gominho, J.; Marques, A.V.; Pereira, H. Characterization of lignin in heartwood, sapwood and bark from *Tectona grandis* using Py-GC-MS/FID. *Wood Sci. Technol.* **2015**, *49*, 159–175. [[CrossRef](#)]
36. Faix, O.; Meier, D.; Grobe, I. Studies on isolated lignins and lignins in woody materials by pyrolysis-gas chromatography-mass spectrometry and off-line pyrolysis-gas chromatography with flame ionization detection. *J. Anal. Appl. Pyrolysis* **1987**, *11*, 403–416. [[CrossRef](#)]
37. Zikeli, F.; Vinciguerra, V.; D'Annibale, A.; Capitani, D.; Romagnoli, M.; Mugnozza, G.S. Preparation of Lignin Nanoparticles from Wood Waste for Wood Surface Treatment. *Nanomaterials* **2019**, *9*, 281. [[CrossRef](#)] [[PubMed](#)]
38. Mvondo, R.R.N.; Meukam, P.; Jeong, J.; Meneses, D.D.S.; Nkeng, E.G. Influence of water content on the mechanical and chemical properties of tropical wood species. *Results Phys.* **2017**, *7*, 2096–2103. [[CrossRef](#)]
39. Kim, J.Y.; Hwang, H.; Oh, S.; Kim, Y.S.; Kim, U.J.; Choi, J.W. Investigation of structural modification and thermal characteristics of lignin after heat treatment. *Int. J. Biol. Macromol.* **2014**, *66*, 57–65. [[CrossRef](#)] [[PubMed](#)]
40. Das, L.; Xu, S.; Shi, J. Catalytic Oxidation and Depolymerization of Lignin in Aqueous Ionic Liquid. *Front. Energy Res.* **2017**, *5*, 21. [[CrossRef](#)]
41. Davaritouchaee, M.; Hiscox, C.W.; Terrell, E.; Mancini, J.R.; Chen, S. Mechanistic studies of milled and Kraft lignin oxidation by radical species. *Green Chem.* **2020**, *22*, 1182–1197. [[CrossRef](#)]
42. Cui, C.; Sadeghifar, H.; Sen, S.; Argyropoulos, D.S. Towards thermoplastic lignin polymers; Part II: Thermal & polymer characteristics of kraft lignin & derivatives. *BioResources* **2012**, *8*, 864–886. [[CrossRef](#)]
43. Patil, S.V.; Argyropoulos, D.S. Stable Organic Radicals in Lignin: A Review. *ChemSusChem* **2017**, *10*, 3284–3303. [[CrossRef](#)]

44. Kubovský, I.; Kačíková, D.; Kačík, F. Structural Changes of Oak Wood Main Components Caused by Thermal Modification. *Polymers* **2020**, *12*, 485. [[CrossRef](#)]
45. Faix, O. Classification of lignins from different botanical origins by FTIR spectroscopy. *Holzforschung* **1991**, *45*, 21–27. [[CrossRef](#)]
46. Lisperguer, J.; Perez, P.; Urizar, S. Structure and thermal properties of lignins: Characterization by infrared spectroscopy and differential scanning calorimetry. *J. Chil. Chem. Soc.* **2009**, *54*, 460–463. [[CrossRef](#)]
47. Gerardin, P. New alternatives for wood preservation based on thermal and chemical modification of wood—a review. *Ann. For. Sci.* **2016**, *73*, 559–570. [[CrossRef](#)]
48. Nada, A.M.A.; Youssef, M.A.; Shaffei, K.A.; Aalah, A.M. Infrared spectroscopy of some treated lignins. *Polym. Degrad. Stab.* **1998**, *62*, 157–163. [[CrossRef](#)]
49. Zhang, P.; Dong, S.J.; Ma, H.H.; Zhang, B.X.; Wang, Y.F.; Hu, X.M. Fractionation of corn stover into cellulose, hemicellulose and lignin using a series of ionic liquids. *Ind. Crop. Prod.* **2015**, *76*, 688–696. [[CrossRef](#)]
50. Méndez-Mejías, L.D.; Moya, R. Effects on density, shrinking, color changing and chemical surface analysis through FTIR of *Tectona grandis* thermo-treated. *Sci. For.* **2016**, *44*, 811–820. [[CrossRef](#)]
51. Popescu, M.C.; Popescu, C.M.; Lisa, G.; Sakata, Y. Evaluation of morphological and chemical aspects of different wood species by spectroscopy and thermal methods. *J. Mol. Struct.* **2011**, *988*, 65–72. [[CrossRef](#)]
52. Esteves, B.; Marques, A.V.; Domingos, I.; Pereira, H. Chemical changes of heat treated pine and eucalypt wood monitored by FTIR. *Maderas Cienc. Tecnol.* **2013**, *15*, 245–258. [[CrossRef](#)]
53. Liu, C.; Wang, X.; Lin, F.; Zhang, H.; Xiao, R. Structural elucidation of industrial bioethanol residual lignin from corn stalk: A potential source of vinyl phenolics. *Fuel Process. Technol.* **2018**, *169*, 50–57. [[CrossRef](#)]
54. Liu, C.; Hu, J.; Zhang, H.; Xiao, R. Thermal conversion of lignin to phenols: Relevance between chemical structure and pyrolysis behaviors. *Fuel* **2016**, *182*, 864–870. [[CrossRef](#)]
55. Kotilainen, R.; Toivannen, T.; Alén, R. FTIR monitoring of chemical changes in softwood during heating. *J. Wood Chem. Technol.* **2000**, *20*, 307–320. [[CrossRef](#)]
56. Vartanian, E.; Barres, O.; Roque, C. FTIR spectroscopy of woods: A new approach to study the weathering of the carving face of a sculpture. *Spectrochim. Acta Part A* **2015**, *136*, 1255–1259. [[CrossRef](#)]
57. Özgenç, Ö.; Durmaz, S.; Boyaci, I.H.; Eksi-Kocak, H. Determination of chemical changes in heat-treated wood using ATR-FTIR and FT Raman spectrometry. *Spectrochim. Acta Part A* **2017**, *171*, 395–400. [[CrossRef](#)] [[PubMed](#)]
58. Li, M.Y.; Cheng, S.C.; Li, D.; Wang, S.N.; Huang, A.M.; Sun, S.Q. Structural characterization of steam-heat treated *Tectona grandis* wood analyzed by FT-IR and 2D-IR correlation spectroscopy. *Chin. Chem. Lett.* **2015**, *26*, 221–225. [[CrossRef](#)]
59. González-Peña, M.M.; Curling, S.F.; Hale, M.D. On the effect of heat on the chemical composition and dimensions of thermally modified wood. *Polym. Degrad. Stab.* **2009**, *94*, 2184–2193. [[CrossRef](#)]
60. Popescu, M.C.; Froidevaux, J.; Navi, P.; Popescu, C.M. Structural modifications of *Tilia cordata* wood during heat treatment investigated by FT-IR and 2D IR correlation spectroscopy. *J. Mol. Struct.* **2013**, *1033*, 176–186. [[CrossRef](#)]
61. Rodrigues, J.; Faix, O.; Pereira, H. Determination of lignin content of Eucalyptus globulus wood using FTIR spectroscopy. *Holzforschung* **1998**, *52*, 46–50. [[CrossRef](#)]
62. Müller, G.; Schöpfer, C.; Vos, H.; Kharazipour, A.; Polle, A. FTIR-ATR spectroscopic analysis of changes in wood properties during particle and fibreboard production of hard and softwood trees. *BioResources* **2009**, *4*, 49–71. [[CrossRef](#)]
63. Zhang, P.; Wei, Y.; Liu, Y.; Gao, J.; Chen, Y.; Fan, Y. Heat-Induced Discoloration of Chromophore Structures in Eucalyptus Lignin. *Materials* **2018**, *11*, 1686. [[CrossRef](#)] [[PubMed](#)]
64. 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](#)]
65. Cheng, X.Y.; Li, X.J.; Xu, K.; Huang, Q.T.; Sun, H.N.; Wu, Y.Q. Effect of Thermal Treatment on Functional Groups and Degree of Cellulose Crystallinity of Eucalyptus Wood (*Eucalyptus grandis* × *Eucalyptus urophylla*). *Forest Prod. J.* **2017**, *67*, 135–140. [[CrossRef](#)]
66. Watkins, D.; Nuruddin, M.D.; Hosur, M.; Tcherbi-Narteh, A.; Jeelani, S. Extraction and characterization of lignin from different biomass resources. *J. Mater. Res. Technol.* **2015**, *4*, 26–32. [[CrossRef](#)]

67. Erdocia, X.; Prado, R.; Corcuera, M.Á.; Labidi, J. Effect of different organosolv treatments on the structure and properties of olive tree pruning lignin. *J. Ind. Eng. Chem.* **2014**, *20*, 1103–1108. [[CrossRef](#)]
68. Ion, S.; Opris, C.; Cojocaru, B.; Tudorache, M.; Zgura, I.; Galca, A.C.; Bodescu, A.M.; Enache, M.; Maria, G.M.; Parvulescu, V.I. One-Pot Enzymatic Production of Lignin-Composites. *Front. Chem.* **2018**, *6*, 124. [[CrossRef](#)]
69. Ragauskas, A.J.; Beckham, G.T.; Biddy, M.J.; Chandra, R.; Chen, F.; Davis, M.F.; Davison, B.H. Lignin Valorization: Improving Lignin Processing in the Biorefinery. *Science* **2014**, *344*, 1246843. [[CrossRef](#)] [[PubMed](#)]



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