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Chemical composition and hygroscopicity of thermally modified *Eucalyptus grandis* wood in closed and open systems

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Abstract. Thermal modification is a sustainable approach to improve the properties of juvenile wood, including hygroscopicity, dimensional stability, and biological durability. This study evaluated the effects of thermal modification in closed and open systems on the chemical composition and hygroscopicity of juvenile *Eucalyptus grandis* wood. Untreated wood and thermally modified wood produced in closed systems at 150, 160, and 170 °C and in open systems at 170, 190, and 210 °C were investigated. Process performance was characterized by final moisture content, duration, and corrected mass loss (CML). Chemical composition was determined by wet chemical analysis, including alpha-cellulose, hemicelluloses, total lignin, and extractives, and Fourier transform infrared spectroscopy. Crystallinity was assessed by X-ray diffraction, while hygroscopicity was evaluated through equilibrium moisture content (EMC) and moisture exclusion efficiency (MEE). Thermal modification in closed system resulted in higher CML, even at lower temperatures. Significant changes in chemical composition were observed in all treatments except 170 °C in the open system. For similar CML, the closed system produced higher alpha-cellulose and extractive contents, whereas the open system retained more hemicelluloses and dichloromethane-soluble extractives. All treatments reduced hygroscopicity, with the greatest effect observed for the open-system treatments at 190 and 210 °C.

Keywords: Thermal modification; Wet chemistry; Corrected mass loss; Crystallinity index; FTIR.

Introduction

Thermal modification of wood involves applying heat between 140 and 240 °C under controlled conditions, which causes chemical changes in the main constituents of the cell wall and extractives [1]-[3]. Cellulose exhibits greater thermal resistance than hemicelluloses, undergoing degradation primarily in its amorphous regions. When subjected to prolonged heating, cellulose chains break down, forming alkali-soluble oligosaccharides, accompanied by a decrease in the degree of polymerization and an increase in crystallinity, especially above 150°C, in which this degradation is intensified in the presence of oxygen [4], [5]. At higher temperatures, its decomposition produces levoglucosan, along with other anhydroglucoses, furans, and their derivatives [6]. Due to their predominantly amorphous nature, hemicelluloses have the most considerable fraction of accessible hydroxyl groups in the cell wall, which makes them chemically more reactive and thermally less stable compared to cellulose and lignin [1], [5], [7], [8]. The degradation of hemicelluloses forms acids, mainly acetic acid, which catalyze the hydrolysis of carbohydrates, resulting in the production of furfural and hydroxymethylfurfural, less hygroscopic compounds that reduce the moisture absorption of wood [6], [9], [10].

Lignin, despite its greater thermal stability than carbohydrates, also degrades under thermal conditions [11]-[13]. The rupture of ether bonds, particularly β -O-4 bonds, results in the formation of free phenolic and carbonyl groups, which favor cross-linking reactions through the formation of methylene bridges [14]. Additionally, demethoxylation occurs in the aromatic rings of the guaiacyl and syringyl units, generating new reactive sites that promote condensation reactions [15]. Volatile extractives tend to disappear, while new compounds arise from the degradation of structural polymers [1], [9], [14]. The presence and quantity of these new extractives in the final wood products depend significantly on the process conditions.

This process enhances the desirable properties of wood, including reduced hygroscopicity, increased dimensional stability, and resistance to decay fungi [2], [3], [9], [10], [16]. The effect, however, depends on the process used; nowadays, there are mainly two industrial systems: the closed system and the open system [1]. In a closed system, also known as a pressurized system, the retention of volatiles and the homogeneous distribution of heat favor the retention of chemical compounds in the wood, making the process more efficient and less energy-intensive. In open systems, such as ThermoWood®, thermal treatment is carried out at atmospheric pressure, which favors the volatilization of degradation compounds and can result in less uniform modification of the wood [17], [18].

Eucalyptus grandis is widely cultivated in Brazil for its rapid growth, high productivity, and adaptability, making it one of the primary species used by the forest industry [19]. However, the adoption of short-rotation cycles leads to a predominance of juvenile wood, which differs from mature wood in that it has lower density, reduced dimensional stability, and greater susceptibility to defects and biological degradation [20], [21]. Despite these limitations, *E. grandis* exhibits remarkable technological potential, and thermal modification processes have proven effective in enhancing the physical and biological properties of its wood [16], [22]-[24].

Accordingly, the objective of this study was to evaluate the effect of thermal modification in closed and open systems on the chemical composition and hygroscopicity of juvenile *Eucalyptus grandis* wood.

The hypothesis is that the closed system will result in greater retention of extractives and lower hygroscopicity than the open system.

Materials and methods

Material collection and preparation

The *E. grandis* W. Hill ex Maiden wood came from a plantation in the municipality of Fundão, Espírito Santo, Brazil, with no age control. Samples measuring 30 x 120 x 650 mm (radial x tangential x longitudinal) were taken from wood that had been dried naturally under cover, with an average moisture content (MC) of 12% ($\pm 0.6\%$). The samples were distributed evenly across the treatments, with 10 per treatment.

Thermal modification

In addition to untreated wood, six thermal modification treatments were evaluated, as shown in Table 1. Thermal modification was performed at Göttingen University in a 65-liter pilot reactor manufactured by Wood Treatment Technology (Jyllandsvej, Denmark). The equipment can operate in a closed (pressurized) or open (atmospheric pressure) system, simulating the FirmoLin® and ThermoWood® industrial processes, respectively.

Table 1 Parameters of the thermal modification processes: temperature (°C), max pressure (MPa), relative humidity (RH, %), final MC (%), process duration (h:min), and corrected mass loss (CML, %). Coefficient of variation (%) in parentheses.

Treatment	Temperature (°C)	Max pressure (MPa)	RH (%)	Final MC (%)	Process duration (h:min)	CML (%)
Closed system						
150CS	150	0.48	100	4.6 (0.2)	16:54	5.8 (41.0)
160CS	160	0.60	100	5.4 (17.5)	17:58	13.1 (20.8)
170CS	170	0.80	100	4.9 (12.6)	19:21	14.9 (21.3)
Open system						
170OS	170	Atmospheric	-	2.9 (16.0)	32:07	6.1 (21.6)
190OS	190	Atmospheric	-	2.3 (24.6)	36:52	11.7 (24.7)
210OS	210	Atmospheric	-	1.5 (25.3)	37:27	13.8 (13.8)

The closed system process program was carried out in three stages: heating at a rate of 12 °C per hour until the final process temperature was reached, coinciding with the maximum pressure (Table 1); maintaining the final temperature for 3 hours; and cooling at a rate of -20 °C per hour to 65 °C. The open system process program was carried out in five stages: heating at 12 °C per hour to 100 °C; heating at 2 °C per hour to 130 °C; heating at 12 °C per hour until the final process temperature (Table 1); maintaining the final temperature for 3 hours; cooling at -20 °C per hour until 65 °C.

The 150CS and 160CS treatments were selected based on Wentzel et al. [18]. Specifically, for the latter, the CML (18.6%) was comparable to that observed at 210 °C (18.7%) under open system conditions. Although 170 °C is relatively low for open-system processes, this condition was adopted to enable a direct comparison with the closed system at the same final temperature. The 190OS and 210OS

treatments correspond to final temperatures similar to those used in the Thermo-S and Thermo-D standards for hardwoods in the ThermoWood® process [25]. Furthermore, the 210OS treatment is directly related to 160CS.

Corrected mass loss

The CML caused by thermal modification was calculated according to the method described by Gomes et al. [26], considering the extractive-free mass before and after thermal modification. This excludes the effect of the extractives that remain in the wood after the thermal modification process. To calculate the CLM, it was necessary to estimate the oven-dry mass of the pieces in the initial (MEi, g) and thermally modified (MEtm, g) conditions (Eq. 1 and 2). To do this, before each thermal modification load, two 10 mm-long samples were cut from the ends of each piece and used to determine the initial MC (MCi, %) by the gravimetric method. After thermal modification, two additional 10 mm-long samples were cut from the ends of each piece to determine the final MC (MCf, %).

$$MEi = \frac{100Mi}{100 + MCi} \quad (1)$$

$$MEtm = \frac{100Mtm}{100 + MCf} \quad (2)$$

Where – Mi: initial mass of the slat (g); Mtm: mass of the slat after thermal modification (g).

Wet chemistry analysis

To prepare the material for wet-chemistry analysis (Table 2), a 15-mm-long sample was cut from one end of each piece. The samples were ground in a knife mill equipped with a 1.0 mm sieve, using only the sawdust that passed through the 40-mesh sieve and was retained on the 60-mesh sieve. Subsequently, the sawdust was conditioned at 20 ± 2 °C / $65 \pm 5\%$ RH before analysis.

Table 2 Summary of wet chemical analyses.

Chemical component	Observation	Reference
Alpha-cellulose	Obtained from sodium hydroxide (17.5%)	T 203 cm-99 [27]
Holocellulose	Obtained from sodium chlorite and acetic acid	Wise et al. [28]
Lignin	Klason lignin insoluble in sulfuric acid (72%)	Gomide and Demuner [29]
	Acid-soluble lignin	Goldschmid [30]
Total extractives	Use of toluene instead of benzene	T 264 cm-97 [31]
Extractives	Extraction with acetone and dichloromethane	T 204 cm-97 [32]

The chemical analyses were performed in triplicate, except the total extractives analyses, which were performed in six replicates. This exception was necessary for the preparation of extractive-free material used in the analysis of alpha-cellulose, holocellulose, and lignin. The total lignin content was calculated by summing the soluble and insoluble lignin contents. The hemicellulose content was determined by the difference between the holocellulose and alpha-cellulose contents.

Identification of functional groups

FTIR analysis was performed to detect possible changes in the functional groups of thermally modified wood. For this analysis, sawdust retained on a 60-mesh sieve and conditioned was used. FTIR spectra were obtained using an FTIR spectrometer (model DairyQuant-P, Stengårdsvej, Denmark) in the wavelength range of 500 to 4,000 cm⁻¹, with a resolution of 4 cm⁻¹ and 32 scans accumulated. Three spectra were obtained for each treatment.

Crystallinity index

XRD analysis was performed to determine the crystallinity index (CI) of the cell wall. The material used in this analysis passed through a 60-mesh sieve (fine fraction). The test was performed on a diffractometer (Rigaku, MiniFlex model, Tokyo, Japan) equipped with copper (Cu) K α radiation ($\lambda = 1.54 \text{ \AA}$). The samples were analyzed in the 2θ range from 5° to 70°, with a scanning rate of 2°/min and a step size of 0.02°. Three replicates were performed for each treatment. The CI was calculated according to Segal et al. [33].

Hygroscopicity test

Thirty test specimens (10 x 10 x 10 mm³) per treatment were conditioned at $20 \pm 2 \text{ }^\circ\text{C} / 65 \pm 5\% \text{ RH}$ in a 115 L climatic chamber. The mass of the test specimens was monitored by weighing them every 24 hours to the nearest 0.001 g. Equilibrium was considered to be reached when the difference between two consecutive weighings was less than 0.2%. Finally, the test specimens were dried in an oven at $105 \pm 3 \text{ }^\circ\text{C}$ to determine their oven-dry mass. The equilibrium moisture content (EMC, %) was calculated using Eq. 3 as a measure of the hygroscopicity of the wood, and the moisture exclusion efficiency (MEE, %) was calculated using Eq. 4 as a measure of the efficiency of the thermal modification process.

$$\text{EMC} = \frac{m - m_0}{m_0} \cdot 100 \quad (3)$$

$$\text{MEE}_i = \frac{(\text{EMC}_u - \text{EMC}_{\text{tmi}})}{\text{EMC}_u} \cdot 100 \quad (4)$$

Where – m: mass in equilibrium in the climatic chamber (g); m₀: anhydrous mass (g); EMC_u: EMC of the untreated (%); EMC_{tmi}: EMC of the thermally modified wood from treatment i (%).

Statistical analysis

Statistical analysis was performed using a completely randomized design, with a significance level of 5% for all tests. Quantitative data from the process analysis and qualitative data from the FTIR analysis were not subjected to statistical analysis. The Dunnett test was used to compare the results of each thermal wood modification treatment with those of the untreated wood. Regression analysis was employed to compare temperatures within the same system, and a Student's t-test was used to compare temperatures across different thermal modification systems. Pearson's correlation test was performed between the quantitative data obtained in the different tests. Statistical analysis and all graphs were performed using RStudio software version 2024.04.2 (Posit Software, PBC, Boston, USA).

Results and discussion

Analysis of the thermal modification process

The final MC (Table 1) was lower in the open system treatments than in the closed system. This behavior can be attributed to the presence of water vapor in the reactor atmosphere of the closed system, which promotes moisture retention in the wood. During the cooling phase, the RH in the closed system remains high. Consequently, the samples remain relatively moist compared with those in the open system, where no external moisture source is available for adsorption. As this condition is absent in the open system, a consistent decrease in final MC was observed with increasing temperature.

Within one system (closed or open), the CML increased with temperature and process duration. Note that at the same temperature (170 °C), the CML was 8.8 percentage points (p.p.) higher for the closed-system process (14.9%) than for the open-system process (6.1%), despite the shorter process duration. It was also observed that the 160CS and 210OS treatments had similar CML (0.7 p.p. difference). However, the closed system process lasted about 20 hours less than the open system process. This demonstrates the importance of the process environment, in which pressure and high RH enhance the thermal degradation of wood. This is due to the higher MC and accumulation of carboxylic acids in the wood of closed systems, which leads to faster degradation mechanisms [17], [34].

Wet chemistry analysis

Table 3 presents the results of the wet-chemistry analysis and the Dunnett test. Treatment 170OS stood out as the only one that did not differ significantly from the untreated for alpha-cellulose, total lignin, and acetone extractives. This is related to its low CML, which indicates lower process severity. In contrast, treatment 150CS had an even lower CML (5.8%), but differed statistically from the untreated, suggesting that closed and open systems promote chemical changes of different natures.

The alpha-cellulose content increased significantly from 48.8% (untreated) to 53.7% (150CS) due to hemicellulose degradation, making cellulose proportionally more abundant. In a closed system, a progressive reduction in this content was observed with increasing temperature (Fig. 1a), whereas in an open system, the behavior was parabolic, with an optimum point and a drop at higher temperatures (Fig. 1b), suggesting thermal degradation of the cellulose chain under more severe conditions.

Due to the heteroscedasticity of the data, it was not possible to adjust the regression model for hemicelluloses. Therefore, a descriptive analysis of the results was performed. The untreated wood presented the highest content (30.8%, Table 3). In the closed system, the reduction was more pronounced, reaching 8.85% in 160CS. In contrast, in the open system, the highest average was observed in 170OS (23.3%), indicating less thermal degradation of the wood than in the other treatments. In the open system, a gradual reduction trend was also observed with increasing temperature, alongside an increase in CML (Table 1). During the thermal modification process, acetic acid is released from the degradation of hemicelluloses, which acts as a catalyst in the acid hydrolysis of the hemicelluloses themselves and the amorphous regions of the cellulose [35].

Table 3 Results of wet chemistry analysis: comparison between the means of TMW and the untreated wood.

Treatment	Alpha-cellulose (%)	Hemicelluloses (%)	Total lignin (%)	Total extractives (%)	Acetone extractives (%)	Dichloromethane extractives (%)
untreated	48.8 (0.3)	30.8 (0.1)	31.8 (0.4)	6.7 (1.6)	2.9 (3.7)	1.5 (1.3)
150CS	53.7* (0.2)	9.9 (0.2)	33.2* (0.8)	14.6* (1.7)	7.2* (3.4)	2.5* (0.8)
160CS	53.0* (0.3)	8.9 (1.2)	36.0* (2.1)	14.3* (1.0)	8.8* (5.2)	2.7* (1.5)
170CS	50.4* (0.7)	10.8 (2.3)	37.2* (0.9)	12.9* (0.9)	7.3* (1.7)	2.9* (1.5)
170OS	49.1 ^{ns} (0.4)	23.3 (1.2)	32.6 ^{ns} (2.1)	4.8* (3.5)	2.8 ^{ns} (2.1)	1.7* (1.0)
190OS	50.5* (0.3)	16.3 (0.9)	34.8* (0.4)	8.7* (1.7)	4.0* (1.7)	4.6* (1.7)
210OS	50.2* (0.2)	14.2 (0.1)	35.6* (0.9)	8.7* (1.9)	4.4* (2.3)	5.9* (0.7)
Bartlett's test	4.31 ^{ns}	16.96*	8.36 ^{ns}	3.94 ^{ns}	11.41 ^{ns}	6.96 ^{ns}
Fc	240.40*	-	59.50*	3477.00*	382.70*	4144.00*

Coefficient of variation (%) in parentheses. ns: not significant ($P > 0.05$). *: significant at 5% probability ($P \leq 0.05$).

Fig. 2 shows the Pearson correlation matrix between the quantitative results obtained in this study. Only “strong” ($r > 0.60$) and “very strong” ($r > 0.81$) correlations that were significant at 5% probability ($P \leq 0.05$) are shown in this matrix. It is noted that hemicelluloses were the most closely related to the other variables analyzed, with four very strong correlations (with alpha-cellulose, CI, total extractives, and acetone extractives) and two strong correlations (with CML and total lignin). The negative correlations indicate that these variables increase with the degradation of hemicelluloses, reinforcing their importance for thermal modification.

Lignin increased significantly in all treatments compared with the untreated (31.8%), except in 170OS (32.6%), with the highest value in 170CS (37.2%). This apparent increase, as shown in Fig. 1c and Fig. 1d, is related to the greater thermal stability of lignin, condensation reactions, and the degradation of hemicelluloses [11]-[13]. This was also observed in Fig. 2, where lignin content showed a very strong and negative correlation with hemicelluloses content ($r = -0.76^*$). The results obtained for the structural components of the cell wall (cellulose, hemicelluloses, and lignin) were similar to those reported by Wentzel et al. [18], who evaluated thermally modified *E. nitens* wood in closed and open systems.

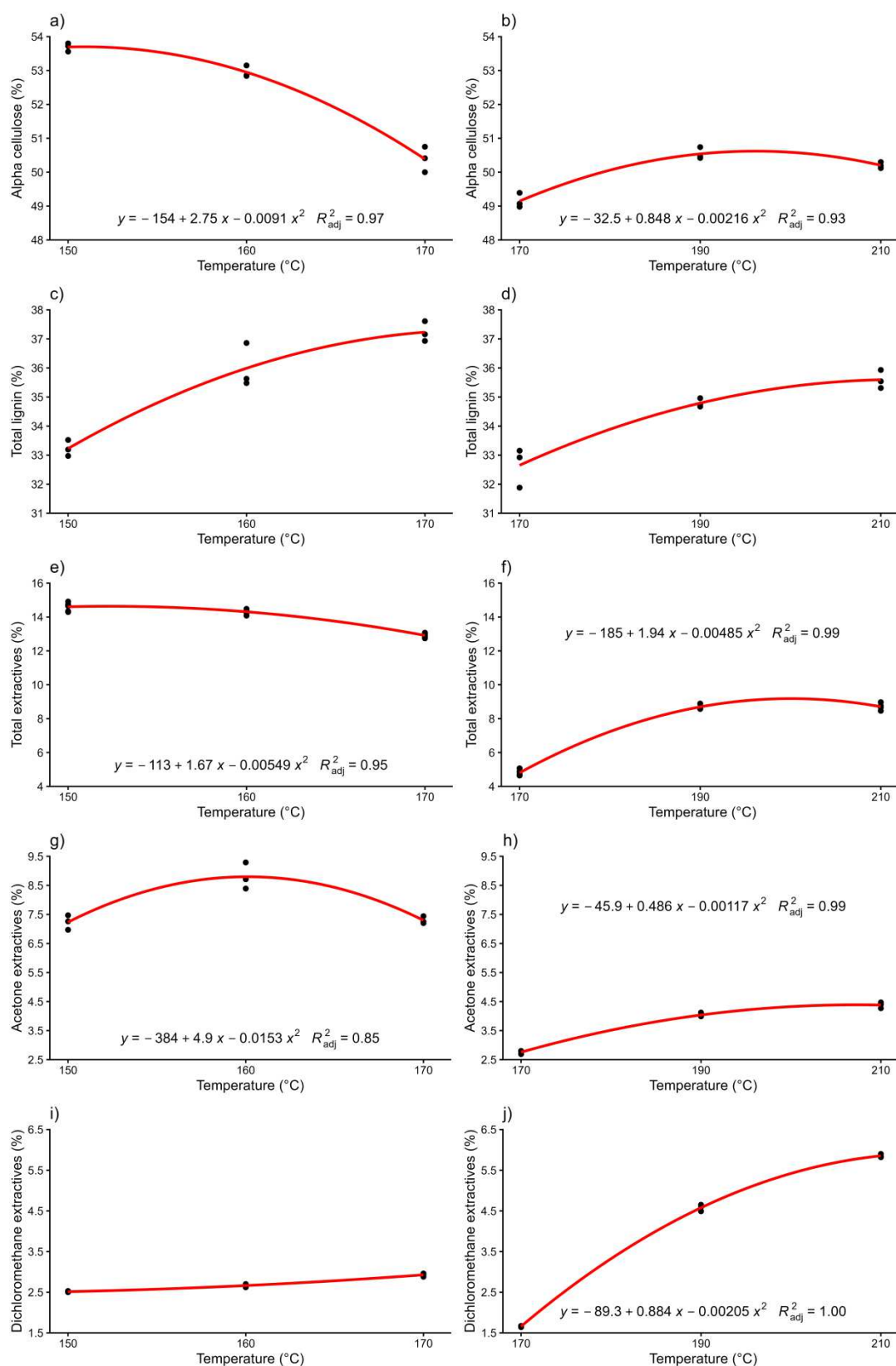


Figure 1 Effect of temperature on alpha cellulose content (a, b), total lignin (c, d), total extractives (e, f), acetone (g, h) and dichloromethane extractives (i, j) of TMW in closed (a, c, e, g, i) and open (b, d, f, h, j) systems. The parameters of the equations were significant at a 5% probability level, except for c, d, and i.

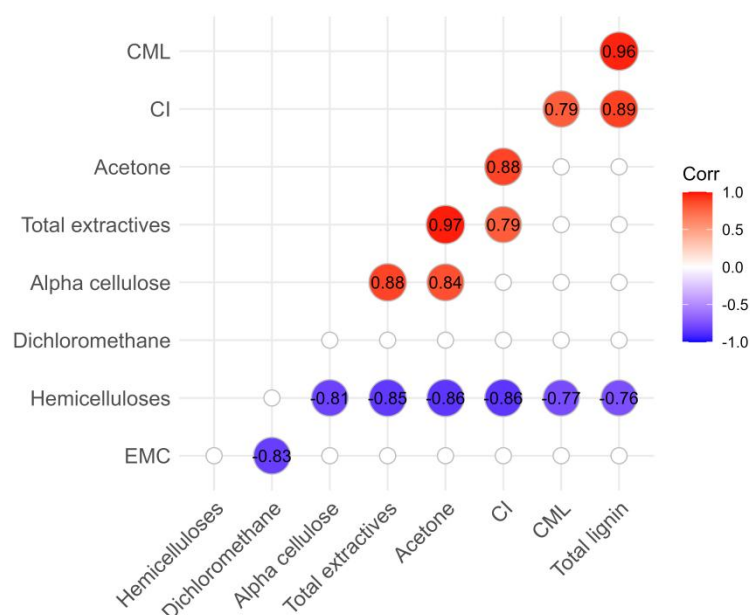


Figure 2 Pearson correlation matrix.

According to the literature, nearly all of the original wood extractives are lost, and new compounds form as a result of the degradation of hemicelluloses and lignin [1], [9], [14]. Total extractives and acetone extractives had a very strong correlation with hemicellulose content ($r = -0.85^*$ and -0.86^* , respectively) (Fig. 2). The negative relationship indicates that the amount of these extractives increases with the degradation of hemicelluloses. Total extractives showed different behavior between the systems. In the closed system, the averages were higher, with 150CS standing out (14.6%), followed by decreasing values with increasing temperature (Fig. 1e). In the open system, the values were closer to the untreated, with 170OS standing out (4.8%), below the untreated value (6.7%). The parabolic curve (Fig. 1f) suggests a downward trend in the total extractives amount at higher temperatures.

The same trend was observed for the acetone extractives (polar solvent). A significant increase was observed in all treatments except 170OS (2.8%), which did not differ from the untreated (2.9%). The highest value was obtained in 160CS (8.8%, Table 3), and the behavior in a closed system indicated the existence of an optimum temperature for the preservation of these compounds (Fig. 1g). In an open system, the contents increased with temperature, reaching 4.38% in 210OS (Fig. 1h). A similar trend was observed by Wentzel et al. [18], who reported an increase in the extractive content of *E. nitens* extracted with hot water up to a specific temperature (160 °C for the closed system and 210 °C for the open system) and then a decrease. Esteves et al. [11] also observed this trend for *E. globulus*, where treatments with higher temperatures and higher process durations (200 °C in an autoclave and 190 °C in an oven) had the lowest extractive contents (in dichloromethane, ethanol, and water). This difference may result from longer reaction times for the formation of degradation products or from their vaporization at high temperatures [18].

The dichloromethane extractives (nonpolar solvent) also increased in relation to the untreated (1.5%). The tendency to increase with temperature was observed in both systems (Fig. 1i, j), although the parabolic curve in the open system indicates a maximum solubilization limit. The highest averages were obtained in the open system, especially at 210°C (5.9%). This again suggests that the nature of

chemical changes in wood may differ depending on the type of system. Esteves et al. [11] evaluated thermally modified *E. globulus* wood in both an autoclave and an oven, observing that the composition of the dichloromethane extract was similar in both systems. However, in oven-treated samples, small amounts of certain pyrolysis-derived compounds were identified that were not detected in autoclave reactions.

The comparison between treatments at 170 °C (Table 4) revealed significant differences across all constituents, with lower hemicelluloses contents in 170CS (10.8%) than in 170OS (23.3%), and higher cellulose, lignin, and extractive contents in the closed system. This condition was more severe, as reflected by higher CML (14.9% vs. 6.1%; Table 1) and shorter process duration, highlighting the role of pressure and RH. This same trend was reported by Wentzel et al. [18] for *E. nitens* wood thermally modified at 160 °C in closed and open systems, in which, except for hemicelluloses content, all other analyses showed higher means for the treatment in the closed system.

Table 4 Comparison between treatments at 170 °C in closed and open systems.

Treatment	Alpha-cellulose (%)	Hemicelluloses (%)	Total lignin (%)	Total extractives (%)	Acetone extractives (%)	Dichloromethane extractives (%)
170CS	50.4 (0.7)	10.8 (2.3)	37.2 (0.9)	12.9 (0.9)	7.3 (1.7)	2.9 (1.5)
170OS	49.1 (0.4)	23.3 (1.2)	32.6 (2.1)	4.8 (3.5)	2.8 (2.1)	1.7 (1.0)
Bartlett's test	0.47 ^{ns}	0.02 ^{ns}	0.67 ^{ns}	0.44 ^{ns}	0.87 ^{ns}	1.10 ^{ns}
tc	4.96*	-56.51*	10.45*	97.63*	56.36*	48.65*

Coefficient of variation (%) in parentheses. ns: not significant ($P > 0.05$). *: significant at 5% probability ($P < 0.05$).

Processes from different systems with similar CMLs, 160CS (13.1%) and 210OS (13.8%), are compared in Table 5. Mass loss is a crucial tool for quality control in thermal modification processes and has been studied by several authors [17], [18], [26], [36]. There was no significant difference between the means for total lignin only. The hemicelluloses content was lower for 160CS, while the total extractives and acetone extractives were higher. The content of dichloromethane extractives was higher for the 210OS treatment, as previously mentioned. Closed system processes have higher RH, which intensifies acid hydrolysis compared to open system processes, resulting in greater degradation of wood polymers [35]. Wentzel et al. [18] observed the same trend when comparing treatment in a closed system at 160 °C and in an open system at 210 °C for *E. nitens* wood.

Identification of functional groups

Fig. 3 shows the FTIR spectra of *E. grandis* wood from different treatments. The band around 3350 cm⁻¹, attributed to O–H stretching of hydroxyl groups in alcohols, phenols, and carboxylic acids, showed a reduction in intensity with increasing temperature in both systems, consistent with the decrease in hemicellulose content (Table 3). However, in sample 170CS, an intensification of this band was observed, possibly due to the higher apparent lignin content (37.2%, Table 3), since the degradation of

carbohydrates increases the relative proportion of O–H groups in phenolic structures. Another relevant point is that the broad band observed between 3200 and 3600 cm^{-1} is also associated with the O–H stretching vibration of water. The higher intensity of this band in samples 150CS and 170CS may be related to their final MC (4.6 and 4.9%, respectively; Table 1), which was higher in the closed system treatments compared to those in the open system.

Table 5 Comparison between treatments with similar CML in closed and open systems.

Treatment	Alpha-cellulose (%)	Hemicelluloses (%)	Total lignin (%)	Total extractives (%)	Acetone extractives (%)	Dichloromethane extractives (%)
160CS	52.95 (0.3)	8.85 (1.2)	35.99 (2.1)	14.31 (1.0)	8.80 (5.2)	2.66 (1.5)
210OS	50.20 (0.2)	14.23 (0.1)	35.59 (0.9)	8.70 (1.9)	4.38 (2.3)	5.85 (0.7)
Bartlett's test	0.63 ^{ns}	3.11 ^{ns}	1.11 ^{ns}	0.14 ^{ns}	2.75 ^{ns}	0.001 ^{ns}
tc	24.30*	-86.34*	0.84 ^{ns}	63.54*	16.37*	-95.22*

Coefficient of variation (%) in parentheses. ns: not significant ($P > 0.05$). *: significant at 5% probability ($P < 0.05$).

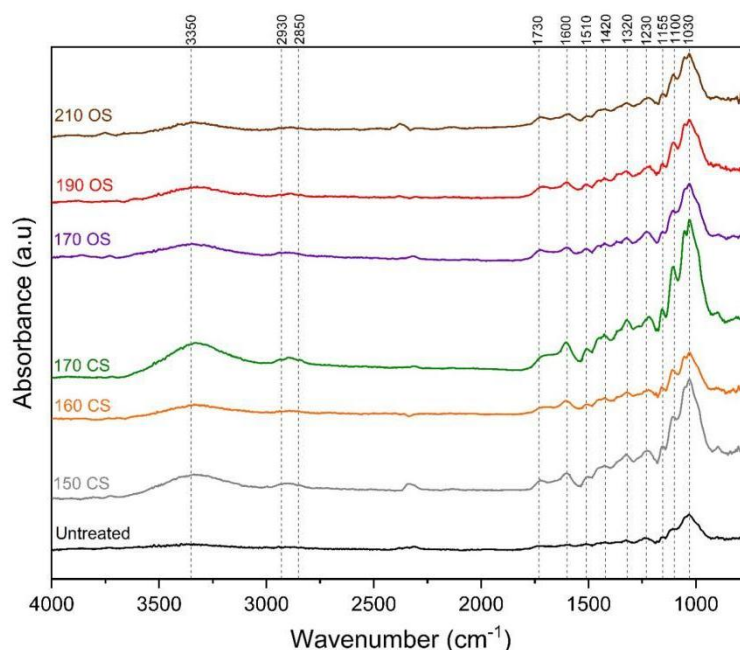


Figure 3 FTIR spectra of differently thermally modified *E. grandis*.

In the range of 2930–2850 cm^{-1} , associated with the stretching of C–H bond in $-\text{CH}_3$ and $-\text{CH}_2-$ groups, treatments 150CS and 170CS showed significant intensification compared to the untreated, indicating reorganization of the alkyl groups and changes in the relative proportion of lignin, which contains methoxyl ($-\text{OCH}_3$) groups [37]. This behavior could also be related to an increase in cellulose crystallinity due to thermal dehydration, influencing the C–H and O–H stretching vibrations [38], [39].

The region between 1750 and 1700 cm^{-1} corresponds to C=O stretching, especially of the acetoxy groups of xylans, in band 1730 cm^{-1} [40]. Absorbance was higher across all treatments than in untreated wood, and it decreased with increasing temperature within the same system, especially in open systems, the same as reported by Wentzel et al. [41]. In closed systems, 170CS stood out, suggesting the formation of thermal oxidation products, such as acids, aldehydes, and ketones [40], resulting from the degradation of hemicelluloses.

The bands at 1600 and 1510 cm^{-1} , attributed to the aromatic ring of lignin, showed slight variations in intensity across treatments, corroborating their greater thermal stability relative to carbohydrates. In closed systems, there was a slight intensification associated with the relative increase in lignin due to hemicelluloses degradation. The 1320–1230 cm^{-1} bands, associated with syringyl and guaiacyl units, showed subtle changes, consistent with the results of Esteves et al. [42] and Wentzel et al. [41]. The bands at 1155 and 1100 cm^{-1} , also attributed to lignin, were less intense in the modified treatments, suggesting changes in structural integrity. The band at 1030 cm^{-1} , associated with ether bonds (C–O–C) in cellulose and hemicellulose, also decreased, indicating degradation via hydrolysis or oxidation.

Cellulose crystallinity index and hygroscopicity

Table 6 presents the results of the CI, EMC, and MEE, along with the Dunnett test. The untreated wood showed a CI of 51.3%, which is close to that reported by Morais et al. [43] for *E. grandis*. Among the treatments, only 170OS did not differ significantly from the untreated, coinciding with the highest hemicellulose content (23.3%) and the absence of differences in alpha-cellulose (Table 3). In the others, thermal modification increased CI due to the degradation of amorphous fractions, especially hemicelluloses, which have lower thermal stability [3], [9]. The removal of these less organized fractions favors the rearrangement of cellulose chains, resulting in a relative increase in the crystalline fraction [4], [5].

Table 6 Results of the cellulose CI by XRD analyses and hygroscopicity.

Treatment	CI (%)	EMC (%)	MEE (%)
untreated	51.3 (4.4)	10.0 (2.1)	-
150CS	57.4* (1.5)	7.9 (9.1)	20.5
160CS	61.6* (1.7)	7.7 (13.4)	23.1
170CS	63.4* (0.8)	6.6 (8.9)	33.6
170OS	53.5 ^{ns} (0.7)	6.1 (10.8)	39.0
190OS	54.7* (1.3)	4.5 (11.7)	55.3
210OS	57.6* (1.6)	3.8 (6.1)	61.8
Bartlett's test	6.86 ^{ns}	82.38*	-
Fc	45.8*	-	-

Coefficient of variation (%) in parentheses. ns: not significant ($P > 0.05$). *: significant at 5% probability ($P \leq 0.05$).

The CI increased with temperature in both systems, following the same trend reported by Wentzel et al. [41]. This increase was more pronounced in the closed system (Fig. 4a) than in the open system (Fig. 4b), even at lower temperatures, which may be related to the higher RH of the process, which favors the crystallization of amorphous cellulose [4].

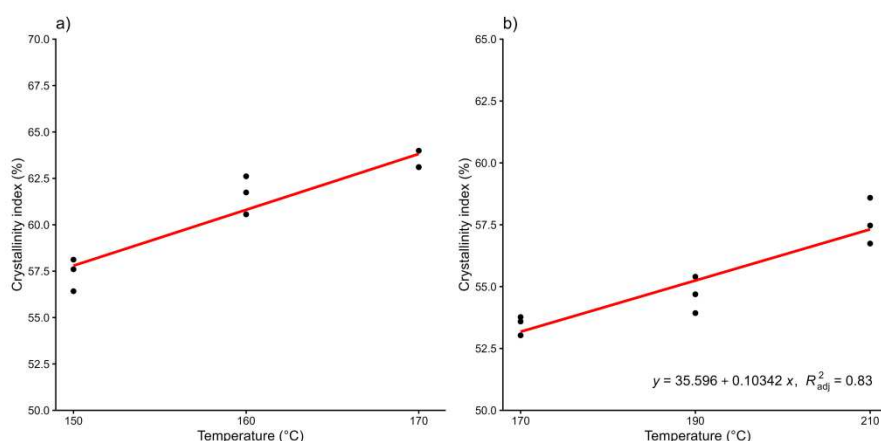


Figure 4 Effect of temperature on the CI of TMW cellulose in closed (a) and open (b) systems. The parameters of the equation in b were significant at a 5% probability level.

The X-ray diffractogram (Fig. 5) confirms this result, showing increased peak intensities attributed to the crystalline regions of cellulose. The peaks in the treated samples (especially 160CS and 170CS) are more intense and better defined than in the untreated samples. The main peak ($\sim 22^\circ 2\theta$), associated with the 002 plane of cellulose, is more pronounced in samples with higher CI, indicating greater structural organization. The reduction of the broad peak at 18° (associated with the amorphous region) in TMW also confirms the decrease of the amorphous fraction.

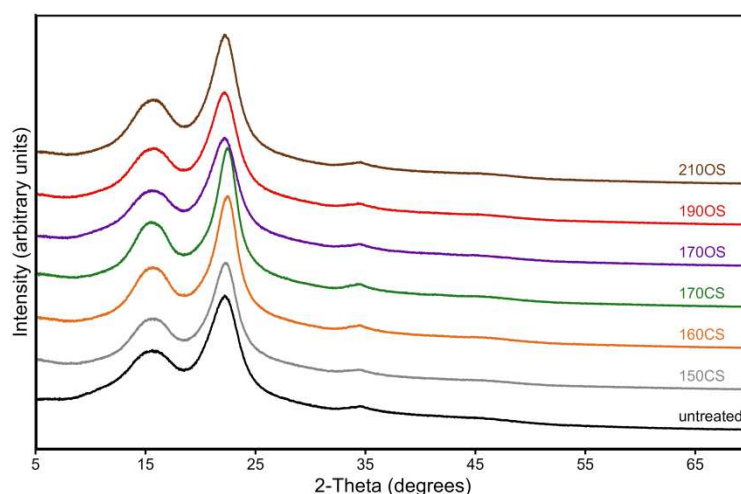


Figure 5 X-ray diffractogram of the untreated and thermally modified *E. grandis* wood.

Due to heteroscedasticity in the data, it was not possible to perform a Dunnett test on the EMC results (Table 6), so only a descriptive analysis was conducted. The hygroscopicity results indicate that

EMC decreases with increasing temperature in both systems. Even at 150°C, there was a 20.5% reduction compared to the untreated, associated with the removal of hydroxyl groups from hemicelluloses (Table 3). However, in equivalent treatments, such as 170°C and 170°C, the EMC was lower in the open system (6.1% vs. 6.6%), despite the closed system being more severe. Comparing similar CML treatments (160°C and 210°C), the EMC was about 50% lower in the open system. Wentzel et al. [34] also reported higher EMC averages for *E. nitens* wood after modification at 100% RH than after modification in an open system. Esteves et al. [44], when evaluating *E. globulus* and *Pinus pinaster* wood modified in an autoclave under different RH conditions (35, 65, and 85%), reported higher average EMC for treatments at higher RH.

When measuring EMC in TMW, accumulated degradation products are present in the samples, providing additional sorption sites for water [34]. In fact, although closed system treatments generally have higher MC and lower hemicelluloses content, they also have higher total extractives and acetone extractives (Table 3). These results indicate that these extractives are hygroscopic, thereby increasing the hygroscopicity of TMW in a closed system.

On the other hand, EMC had a very strong correlation with the content of dichloromethane extractives ($r = -0.83^*$, Fig. 2). This indicates that the increase in nonpolar extractives in wood contributes to the reduction in hygroscopic water sorption. Esteves et al. [11] reported the presence of glycerol, fatty acids, phenolic compounds, and sterols in dichloromethane extracts from thermally modified *E. globulus* wood, most of which have low affinity to water. However, in this study, these compounds could not be identified, and further analysis is needed.

Conclusions

At the same temperature (170 °C), despite the shorter duration, the corrected mass loss was greater in the closed system, indicating that high relative humidity and pressure promote the thermal degradation of wood. Except for the treatment at 170 °C in an open system, the contents of alpha-cellulose, cellulose, total lignin, and extractives (total, in acetone, and dichloromethane) were significantly altered by thermal modification in closed and open systems. Thermal modification across all processes effectively reduced the hygroscopicity of wood. In the same system, hygroscopicity decreases with increasing temperature.

Data availability

The data presented in this study are available on request from the corresponding author.

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Author Contributions

Conceptualization, DCB, MW, CB, HM, MFCS; Methodology, DCB, ACOR, MSR, BLCP, LGV; Software, ACOR, BLCP, LGV; Validation, DCB, MW, CB, HM, DG, MFCS; Formal analysis, DCB, ACOR, MSR, BLCP, LGV; Investigation, DCB, ACOR, MSR; Data curation, DCB, MW, CB, HM, DG, MFCS; Writing-original draft preparation, ACOR; Writing-review and editing, DCB, MW, CB, HM, DG, MFCS; Supervision, DCB, HM, MFCS; Project administration, DCB; Funding acquisition, DCB.

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Competing Interests

The authors declare that they have no competing interests.