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Research article

The behavior of thermally modified wood after exposure in maritime/industrial and urban environments

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ABSTRACT

Natural and thermally modified Pine, Ash, and Acacia woods were exposed in two different environments: urban and maritime/industrial. The weathering effects were evaluated during 24 months regarding color, chemical, and structural changes. In all wood species, thermal modification induced color, chemical, and structural changes. All woods became darker (Pine ΔL*: −32.01; Ash ΔL*: −36.83; Acacia ΔL*: −27.50), total extractives content increased (Pine: 19 %; Ash: 32 % and Acacia: 18 %), and the samples presented deformation and damaged cells. Total lignin was not significantly changed, although there were detected changes in lignin, namely the reduction of G-units in Pine (≈2 %) and reduction of S/G ratio in Acacia (≈0.04 %). Ash remained almost the same. After weathering, modified woods suffered fewer color changes, indicating that the thermal modification could improve the resistance to color change. Acacia wood, when exposed to maritime/industrial conditions, revealed a higher color change (ΔE: 35.7 at 24 months) when compared with urban conditions (ΔE: 23.5 at 24 months). Delignification, possibly caused by photodegradation, occurred in all wood samples, and the loss of extractive happened, perhaps caused by rain. Modified woods were slightly less resistant to weathering in maritime/industrial environments. Some structural damage, namely cracked cells, the appearance of molds, blue staining, and particle deposition, was observed. The thermal modification enables color stabilization but does not seem to improve the weathering resistance in all studied wood species. Exposure to the different environments did not lead to significant differences in the morphology and chemical composition of the three natural and modified wood species.

1. Introduction

Due to the continuous urban development and growth of cities, architects, engineers, and constructors have chosen sustainable materials. Wood is a natural, sustainable, and low-carbon material. It has a wide variety of applications, and nobody questions the value of the products made of wood, namely for building materials, including indoor and outdoor products, such as structural frames,

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window and door frames, floors, and facade systems [1–7]. However, the environment in which timber is exposed greatly influences its performance in service conditions, as exposure to water or water vapor profoundly affects timber performance. Wood is a hygroscopic material due to the abundance of hydroxyl groups associated with the cell wall polymers. The material exhibits dimensional changes with variations in moisture content (MC) and atmospheric relative humidity [8].

Weathering describes the slow degradation that occurs by combining different biotic and abiotic agents [9–11]. Understanding the mechanisms of natural weathering, the role of the altering factors, and their effect on the anatomical, chemical, and physical properties of wood is fundamental to assessing the actual conditions of timber artefacts. It is also crucial to predict their performance and potentially ensure long-term protection and maintenance [12]. Therefore, some outdoor exposure tests have already been conducted to understand the degradation mechanisms of different wood species under different climatic conditions [6,13].

After exposure, the first phenomenon is the color change caused by UV radiation. Wood can become pale or greyish, yellowish or darkened depending on its chemical compounds, especially extractive ones [11]. Besides the photodegradation of these compounds, UV radiation can also cause the degradation of wood's main structural compounds. It is also known that salt water (seawater and other salinity sources) can be corrosive to wood. These phenomena happen when the wood is exposed to wetting cycles that promote tracheid defibration or “fuzzy wood,” which can sometimes be confused with wood decay [9,14,15].

Thermally modified wood has been one of the alternatives to improve wood durability, namely the increase in biodegradation resistance [16–18]. Even though there are some enhanced properties, thermally modified wood is still subject to surface degradation during weathering [19–21]. The treatment uses only heat to proceed with the modification, with temperatures between 180 and 230 °C and water uptake, which helps to protect wood against fungi growth [22].

This study evaluated the degradation caused by natural weathering in maritime/industrial and urban environments to natural and thermally modified wood considering three different wood species: Australian blackwood *(Acacia melanoxylon),* Maritime Pine (*Pinus pinaster*) *and* Ash (*Fraxinus excelsior*).

2. Materials and methods

2.1. Raw material and thermal modification

Wood boards of *Acacia melanoxylon* were provided by Parques de Sintra – Monte da Lua, Sintra, Portugal. *Pinus pinaster* and *Fraxinus excelsior* woods were supplied by the company Santos & Santos Madeiras. All samples were thermally modified by Santos & Santos Industry, using a temperature between 210 and 215 °C, for approximately 6 h (Atlanticwood ® process). The thermal modification is according to the Thermowood ® process, using Thermo-D conditions [18].

2.2. Wood density measurement

The measurement of wood density was assessed at 12 % moisture content for both natural and thermally modified woods, according to the standard ISO 13061–2:2014 [23].

2.3. Natural weathering exposure

The specimens for natural exposure had two different sizes, 100 × 320 × 20 mm and 100 × 320 × 40 mm (width x length x thickness), based on standard EN 927–3:2019 [24], with the difference in the length that it was based on standard ISO 13061–3:2014 [25], where the length is based on thickness, for posterior tests. The thickness was chosen based on the average thickness used in outdoor applications. To compare the degradation in different environments, they were exposed in two locations in Portugal, Lumiar

Table 1
Climate characterization of the two natural exposure testing sites, considering the exposure period between October 2019 and November 2021.

	Location	
	Sines	Lumiar
Latitude	37.95°N	38.77°N
Longitude	8.88°W	9.17°W
Altitude (m)	17	116
Temperature (°C)	16.4 ± 2.5	17.0 ± 3.9
Global radiation (J cm^{-2})	1663.3 ± 477.7	2177.2 ± 1036.4
Relative humidity (%)	85.3 ± 17.9	69.0 ± 6.6
Rain (mm)	24.4 ± 31.4	54.0 ± 48.4
Air pollutants deposition (mg day^{-1} mm^{-2})		
SO_2	36.0 ± 25.9	8.8 ± 5.2
Cl^-	116.3 ± 70.2	17.5 ± 16.0
Environment type	Maritime/Industrial	Urban
Corrosivity category for steel[a]	C5 (very high)	C2 (low)

[a] According to ISO 9223: 2012 [26].

(Lisbon) and Sines (Table 1), between October 2019 and November 2021. All wood samples were exposed at 45°, according to EN 927–3:2019 [24]. The weathering effect was evaluated according to the corrosivity scale for steel according to ISO 9223:2012 [26].

During natural exposure, samples were taken at different times: 9, 12, and 24 months, for monitorization of physical (color change), morphological, and chemical changes (total extractives, total lignin holocellulose, and ashes content, FTIR-ATR spectroscopy, and SEM/EDS) in the three wood species, with and without thermal modification.

2.4. *Color measurement*

A portable spectrometer (X-RITE SP 78) was used to measure the color *in situ* of all wood samples submitted to weathering. Five measurements of each wood sample were taken in a direction parallel to the wood grain. The color was measured in the CIELab color space using the D65 standard illuminant and a 10° observer. In this system, color is represented by three coordinates: L*, a*, and b*. L* axis represents the lightness, and these values vary between 100 (white) and 0 (black); the a* axis represents the variation between green (-a*) and red (+a*), while the b* axis varies between blue (-b*) and yellow (+b*). The following formula was used to calculate the color changes (ΔE*):

$$\Delta E^{*} = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}}$$

where ΔL*, Δa* and Δb* are the color parameter changes.

2.5. *Chemical characterization*

2.5.1. *Chemical analysis*

The summative chemical analysis was determined in the wood samples' 40–60 mesh fraction after collecting a complete longitudinal sample of the boards used for the modification and exposition. Ash content was determined according to TAPPI standard T15 os-58. Extractive content was obtained by sequential extraction in dichloromethane, ethanol, and water in a Soxhlet apparatus, with cellulose extraction thimbles, for <16 h with each solvent. After extraction with each solvent, the extractives content was determined by weight variation of the oven dry thimble. Klason and acid soluble was determined in the extractive-free material, following TAPPI standard T222 om-88 and UM250 om-83. Holocellulose content was determined by difference using the data from extractive content, total lignin, and ashes content.

2.5.2. *Analytical pyrolysis (Py-GC/MS)*

An aliquot of extractives-free samples used in chemical analysis (just the samples from time 0 with and without modification and those after exposition of 24 months) were used for the analytical pyrolysis. The samples were prepared: milled in a Retsch MM20 mixer ball mill for 10 min, then dried in a vacuum oven under phosphorus pentoxide overnight at 35 °C. Then, around 0.10 mg of the sample was weighted and pyrolyzed at 550 °C (for 1 min) in a platinum coil Pyroprobe connected to a CDS 5150 valved interface linked to the GC-MS (Agilent 7890B & 5977B). The volatiles were separated in a fused-silica capillary column (ZB-1701: 60 m × 0.25 mm i.d. x 0.25 μm film thickness) under the following chromatographic conditions: 40 °C (held for 4 min), 20 °C min^{-1} to 100 °C, 6 °C min^{-1} to 270 °C (held for 5 min). The temperatures applied were 270 °C (injector) and 280 °C (MS interface). The electron ionization energy was at 70 eV, and helium was used as the carrier gas (total flow of 1 mL/min). The compounds were identified by comparing their mass spectra with Wiley NIST2014 and personal database. The total area of the pyrogram was obtained automatically, and the percentage area of each compound identified was calculated; S/G and C/L ratios and the relation between the lignin monomers (H:G:S) were calculated.

2.5.3. *FTIR – ATR spectroscopy*

FTIR-ATR spectroscopy analyzed the surface chemical changes of the wood samples associated with thermal modification and weathering. FTIR-ATR spectra were obtained using a PerkinElmer Spectrum Two, equipped with a UATR Two accessory with the diamond crystal at 4 cm^{-1} resolution and with 8 scans. Baseline correction was made in three points, and after that, spectra were normalized to the maximum band around 1031 cm^{-1}, using the same method by other authors [27]. Difference spectra were calculated to compare the modified and unmodified samples, with and without exposition. Data processing was made with Spectragryph 1.2.15 software. Spectra were analyzed in the range 1800-800 cm^{-1}, as this region's most pronounced changes were noticed.

2.6. *Morphological characterization by SEM*

Small wood pieces were taken from the surface with a 5 × 5 mm razor blade for morphological evaluation under the Scanning Electron Microscope Hitachi TM Plus (SEM) at 5 kV. A Phillips Scanning Electron Microscope, Model XL 30 FEG, coupled to an Energy Dispersive Spectrometer (SEM/EDS) at 15 kV, was used for the elemental characterization of particles found on the weathered wood sample surfaces. For SEM/EDS, the small pieces were dried for 12 h under a vacuum and then coated with gold for better conduction in the Emitech K575× turbo sputter coater.

3. Results and discussion

3.1. Color changes

3.1.1. Thermal modification effects

Table 2 presents the CIELab color coordinates of the wood measured before and after thermal modification and the respective differences.

Thermal modification caused color variations in the three species of wood. All species became darker (-ΔL*) due to the higher temperatures. Pine and Ash became redder (+Δa*) and Acacia greener (-Δa*). The reddening of modified treated wood results from a combination of different chemical alterations, such as the oxidation of phenolic compounds, the caramelization of holocellulose compounds, and the degradation products of the quinone and quinone methide types [28]. This degradation occurred in all wood species studied by these authors [28], namely in *Fraxinus excelsior*, *Chlorophora excelsa*, *Pinus sylvestris,* and *Picea orientalis*.

3.1.2. Natural weathering effects

During the natural exposure, samples suffered changes in color since wood is susceptible to photodegradation [6,9–11,19,20,29]. Because both locations present high irradiation values, it was expected that the color change would occur in all samples caused by the environmental conditions and chemical changes on the wood surface caused by weathering, namely the reactions in lignin [21]. According to the literature and our results in Fig. 1a-c, photochemical degradation makes the wood yellowish or brownish, leading to eventual greying [30].

The modified woods presented a high resistance to color change over time, provided by thermal modification, as reported by other authors [20,21,29,31]. This was reflected in ΔL* values during the first month of exposition: while natural wood became darker (-ΔL*), the modified wood became lighter (positive values of ΔL*). The appearance of molds or blue staining can also contribute to the wood surface darkening, which was noticed in Pine and Ash woods. Acacia was the exception, where non-modified and modified woods presented positive ΔL* values (≈4 and ≈ 18), suggesting a low growth of molds or blue staining [32]. In the case of Δa* results, all wood samples became greener (negative values in the range of ~ -1 and ≈-11). Comparing wood without and with thermal modification, the latter became greener, except for Acacia, which revealed the opposite behavior. For Δb*, all exposed wood samples became bluer, with Pine and Ash becoming bluer than Acacia, likely because they can be more susceptible to mold and low-staining growth [31,33]. Pine already showed the presence of blue staining, so the weathering samples were expected to become bluer. All results of ΔL* (Fig. S1), Δa* (Fig. S2), and Δb* (Fig. S3) are presented in the ESI).

Overall, Pine and Ash in both natural and modified woods behave similarly in marine/industrial and urban environments. This does not seem to happen with natural Acacia, where the marine/industrial environment leads to a more significant color change, which does not occur in an urban setting (Fig. 1c). Fig. 2 shows the exposed wood samples' appearance in both locations.

3.2. Chemical characterization

3.2.1. Summative chemical composition

3.2.1.1. Thermal modification effects. Heat treatment promotes an average mass loss in all woods, where hardwoods presented the highest values of mass loss in accordance with the literature [34]. The weight loss is mainly due to the degradation of hemicelluloses, the most thermally labile polymers [34]. The basic density after thermal treatment decreased from 620.7 kg m^{-3} to 577.7 kg m^{-3}, 731.9 kg m^{-3} to 648.2 kg $m^{-3,}$ and 669.8 kg m^{-3} to 599.0 kg m^{-3}, respectively, for Pine, Ash, and Acacia. Fig. 3 presents the chemical composition before and after thermal modification.

Thermal treatments affect the chemical compositions of the wood. Compared with natural timber, thermal wood increased total extractives content, mainly in Ash and Acacia (19 % *vs.* 32 % and 9 % *vs.* 18 %, respectively). In comparison, total lignin content remained partially constant for Pine and Ash but increased by 34 % for Acacia wood. This apparent increase in lignin may be attributed to lignin itself and degradation products such as extractives [35]. It was found in *Eucalyptus* species that lignin suffers depolymerization and condensation reactions after wood thermal modification, which could also explain its apparent increase in the summative analysis [35], and in this case, could be promoted by the rise in Klason lignin increase (Table S1 of the ESI). Holocellulose content was reduced

Table 2
Color coordinates of the wood before and after thermal modification and color difference.

Parameters		L*	a*	b*	ΔE*
Pine	**Wood**	73.70 ± 2.86	7.68 ± 0.59	23.76 ± 0.74	–
	Thermal wood	41.69 ± 1.41	10.36 ± 0.58	18.60 ± 0.81	–
	Difference	−32.01 ± 2.93	2.69 ± 0.49	−5.16 ± 1.12	32.56 ± 2.89
Ash	**Wood**	77.47 ± 1.74	4.49 ± 0.42	16.19 ± 0.34	–
	Thermal wood	40.64 ± 0.91	9.28 ± 0.19	15.70 ± 0.63	–
	Difference	−36.83 ± 2.03	4.78 ± 0.43	−0.50 ± 0.70	37.15 ± 2.04
Acacia	**Wood**	62.20 ± 3.89	13.54 ± 2.70	21.87 ± 1.23	–
	Thermal wood	34.70 ± 1.12	6.43 ± 0.70	9.54 ± 1.58	–
	Difference	−27.50 ± 4.28	−7.12 ± 2.51	−12.33 ± 2.32	31.07 ± 4.73

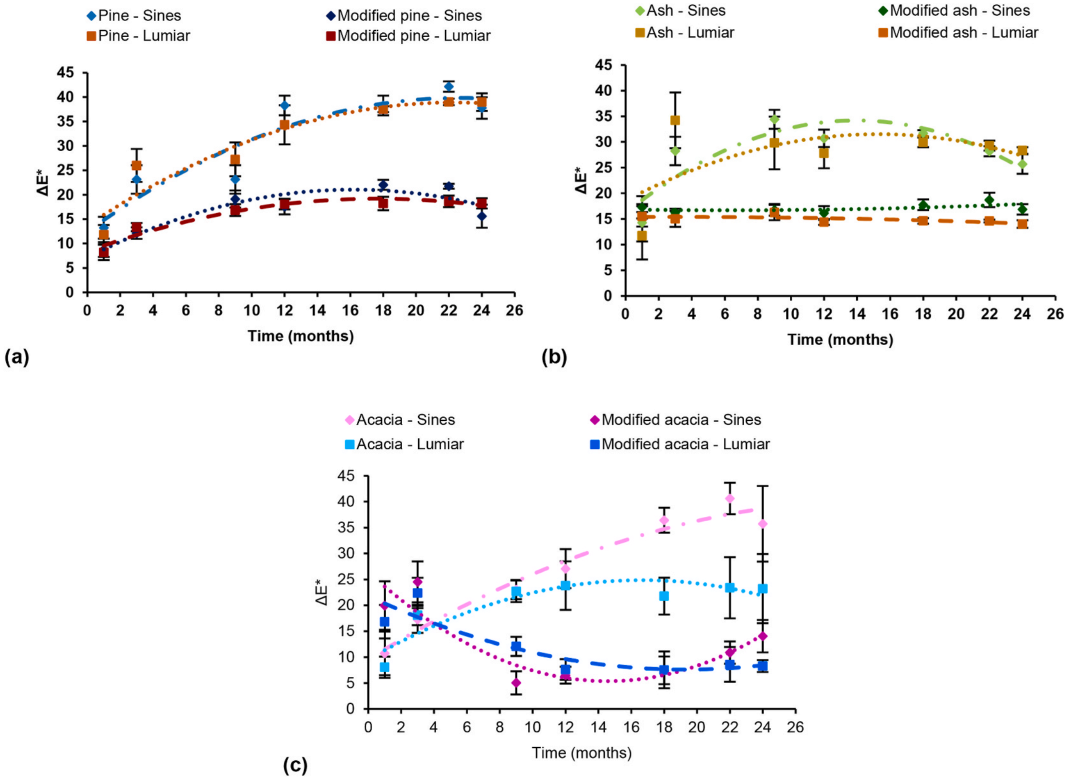

Fig. 1. Color changes (ΔE*) over time in wood samples: (a) Pine, (b); Ash; (c) Acacia. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

by 25 % in Pine, 20 % in Ash, and 17 % in Acacia. These results partially agree with the alterations when the wood is subjected to thermal treatment (below 250 °C), where hemicelluloses are severely degraded, but the cellulose maintains relative stability [34,36,37]. The same chemical degradation in the thermally modified wood of *Quercus robur* [38], *Eucalyptus* species [37,39], and *Pinus oocarpa* [40] was reported.

3.2.1.2. Natural weathering effects. The chemical composition of the exposed wood samples (with and without thermal modification) in the two environmental conditions, maritime/industrial and urban, are presented in Fig. 4. The wood samples showed similar behaviors in both exposure sites over the 24 months. Extractives were the main compounds to be degraded by climatic conditions. However, the *t*-Student statistical analysis ($p < 0.05$) revealed no significant differences between the two test sites for the three species thermally modified. The loss of extractives can also contribute to color change because of the erosion caused by rain, wind, and photodegradation. Extractive loss on weathered wood has also been reported in the literature [9,11,20,40,49]. For instance, in recent studies, authors reported this phenomenon on thermally modified woods of *Pinus sylvestris*, *Picea abies*, and *Fraxinus excelsior* [50] and in *Cunninghamia lanceolate* [51]. The lignin content remained practically constant, while the holocellulose underwent slight changes. However, there are differences between the three species evaluated in this work. Pine presented significant alterations, i.e., loss of extractives (approximately 80 % for Pine and 78 % for Modified Pine) and increased holocellulose content. Ash and modified Ash did not suffer pronounced chemical differences. Acacia holocellulose decreased with the exposure time, and lignin remained constant. Acacia's extractive content increased when exposed to Lumiar conditions, while in Sines, they remained steady. Wood basic density does not change substantially during weathering: Pine wood initially presented 621 kg m^{-3}, while after 24 months, the values were 625 and 586 kg m^{-3} in Lumiar and Sines, respectively. In turn, MPine with 578 kg m^{-3} presented at the end, 567 (Lumiar) and 558 kg m^{-3} (Sines). The same trend was observed for Ash wood (732 kg m^{-3}), which had 678 kg m^{-3} in Lumiar and 681 kg m^{-3} in Sines; MAsh (648 kg m^{-3}) changed to 618 kg m^{-3} (Lumiar) and 641 kg m^{-3} (Sines); Acacia (670 kg m^{-3}) presented 627 and 659 kg m^{-3} respectively after Lumiar and Sines exposition. MAcacia started with 599 kg m^{-3}, and after 24 months, the values were 533 *vs* 517 kg m^{-3} attained in wood from Lumiar and Sines.

3.2.2. Analytical pyrolysis

A summary of results from pyrolysis analysis is presented in Table 4, showing differences between species regarding their lignin monomeric composition. Pine is a softwood species, rich in guaiacyl units (19.1 %) and a few H units (0.3 %) but no syringyl units. In contrast, Acacia and Ash are both hardwoods, where lignin has more S-units (12.2 vs. 14.2 %) than G-units (6.6 vs. 6.8 %) and presented an S/G ratio of 1.85 and 2.09 respectively.

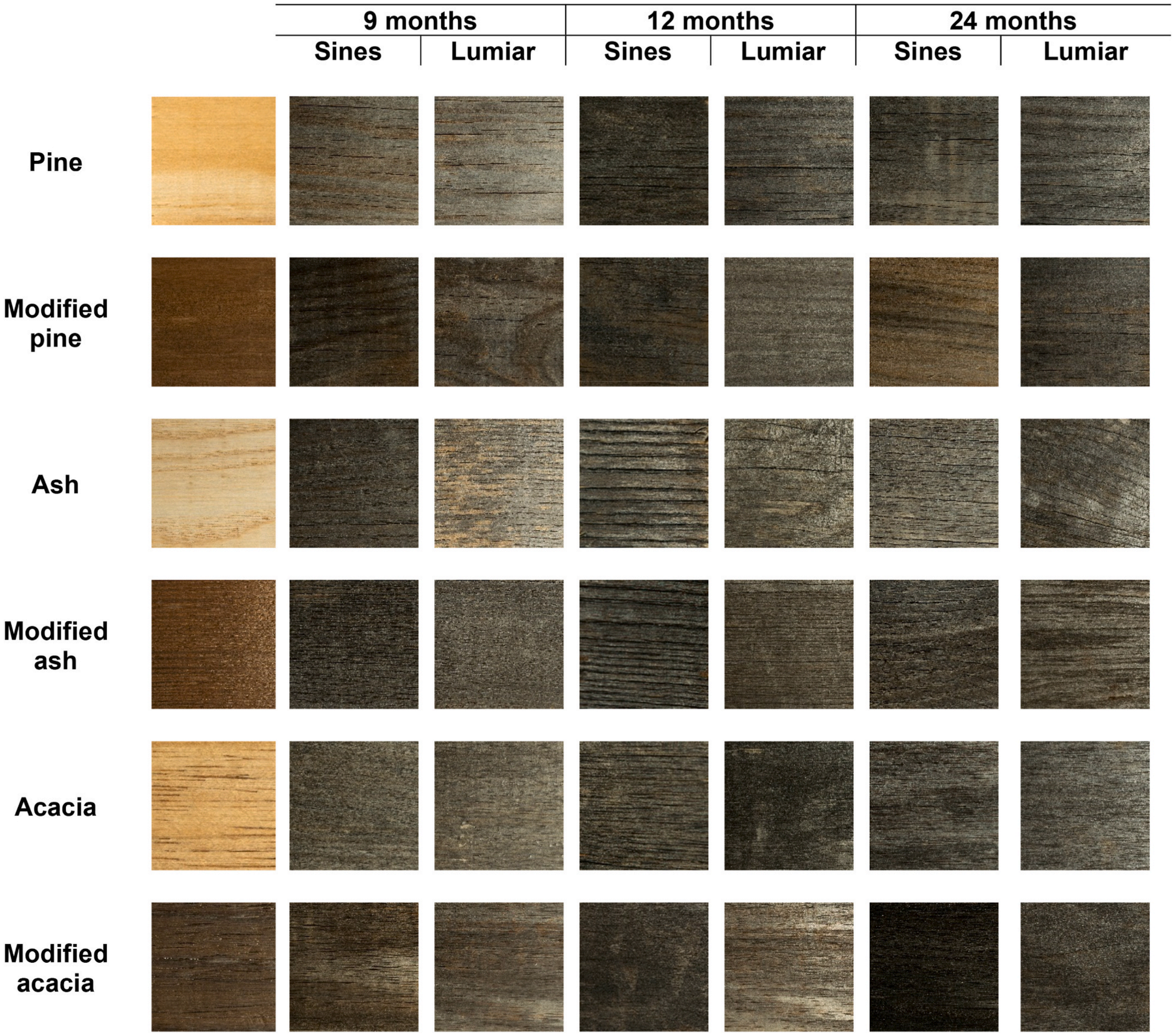

Fig. 2. Color change evolution during 9, 12, and 24 months of exposure in both locations. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

3.2.2.1. Thermal modification effects. The thermo-modification induced a reduction of total lignin (L) and an increase of the carbohydrates (C), as shown in the rise of the C/L ratio in all the species: 2.0 *vs*. 2.6 (pine), 2.3 *vs*. 3.6 (Acacia), 1.7 *vs*. 2.1 (Ash), which is in contrast to the data of chemical analysis. This may be explained as follows: the thermo-modification of wood, even at not so high temperatures, such as those mentioned here, can still induce some degradation of the lignin polymer: depolymerization and condensation reactions [35]. Therefore, lignin condensation may explain the data of chemical analysis (an increase of Klason lignin shown in Table S2 of the ESI), and the fact that lignin suffered depolymerization is only noticed by pyrolysis analysis. MPine shows a reduction of guaiacyl units (19.1 *vs*. 17.1 %), and MAcacia a reduction in both guaiacyl and syringyl units, slightly decreasing the S/G ratio (1.85 *vs*. 1.81). Ash presented slightly decreased syringyl units but an increase of guaiacyl units, which almost maintained the S/G ratio (1.96 *vs*. 2.09). All identified compounds on natural and modified woods are presented in Table S3 in the ESI.

3.2.2.2. Natural weathering effects. In both sites, the untreated woods presented a decrease in lignin, higher in an urban environment for Pine and Ash, with slightly more degradation of G-units (difference of 1.5–2.9 % for Pine, 0.4–1.6 % in Ash); the increase of carbohydrates was similar in both sites for both species. There was no variation of lignin content in Acacia wood, but carbohydrates increase more in maritime/industrial environments (43.5 *vs*. 49.3 %) compared to urban (43.5 *vs*. 45.2 %). In the modified woods, these alterations were not so pronounced. The difference in lignin content was about 1.4 % in MAsh (more or less degradation of G and S-units) but low value for the MPine and in MAcacia, the lignin slightly increased (≈0.4 %). Regarding carbohydrates, the differences between wood exposed for 2 years and not exposed occurred mainly in maritime/industrial environments, in about 4.5 %, 3.9 %, and

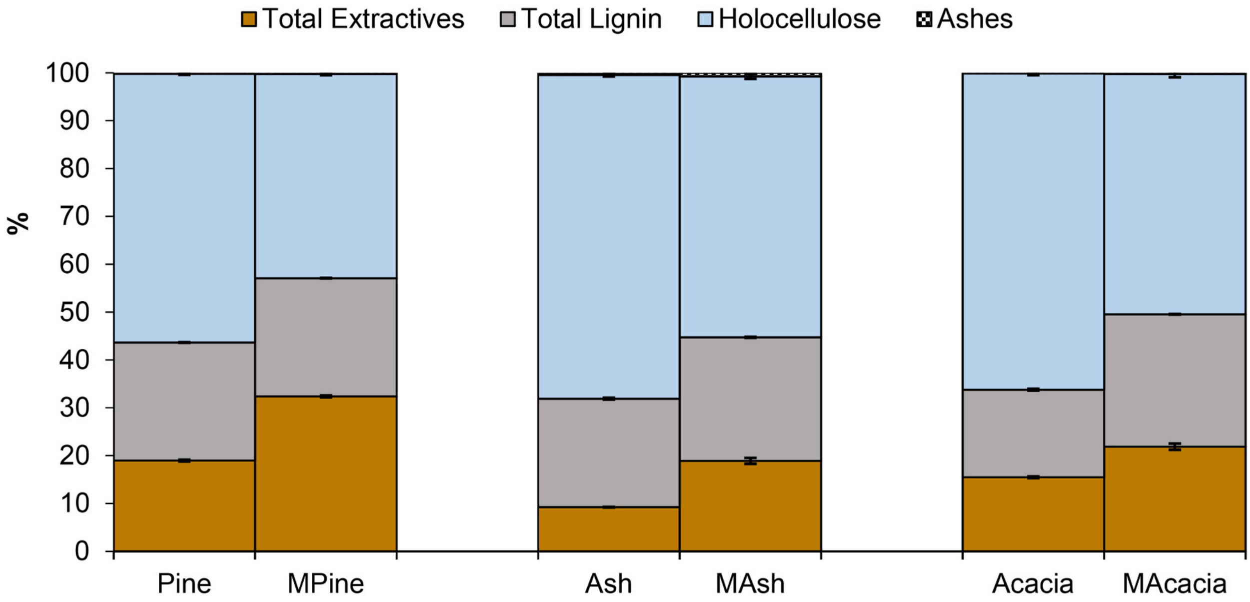

Fig. 3. The wood's chemical composition (% o.d. material) before and after thermal modification. *Legend:* Modified Pine (MPine), Modified Ash (MAsh), and Modified Acacia (MAcacia).

0.8 % for MAcacia, MPine, and MAsh, respectively. Overall, the modified woods were less resistant to weathering in this environment compared to urban (slight difference: 2.4 %, 1.1 %, and 1.5 % for MAcacia, MPine, and MAsh). Table 3 presents a summary of the pyrolysis analysis results.

All identified compounds on all exposed samples of Lumiar (Table S4) and Sines (Table S5) are presented in the ESI.

3.2.3. *FTIR-ATR analysis*

The assignment bands of the FTIR spectra are made in Table 4.

3.2.3.1. Thermal modification effects. Fig. 5 presents the FTIR-ATR spectra difference between wood and modified wood to observe the chemical changes due to thermal modification.

In both MAcacia and MAsh, the bands related to carbohydrates and lignin functional groups increased. There was a positive intensity of bands at 1605 cm^{-1} (syringyl lignin) and 1515 cm^{-1} (guaiacyl lignin), maybe due to condensation reactions in the lignin polymer, as shown in eucalyptus species [35,48], but also at 1460 cm^{-1} (lignin and xylans), and band 1203 cm^{-1} attributed to cellulose. However, in MAcacia, all the bands were higher than in MAsh; an exception was made at the 1000-985 cm^{-1} band that had a pronounced decrease, while in MAsh, there was a negative intensity in this same region, plus the bands at 1104 cm^{-1} (cellulose) and 1054-1052 cm^{-1} (carbohydrates) which reflect more degradation of carbohydrates in Ash compared to Acacia. In all modified samples, the band at 893 cm^{-1} slightly decreased, possibly due to a degradation of the amorphous cellulose [44]. Similar results were reported in Ash wood modified at different temperatures [43] and some other hardwoods, namely in *Eucalyptus camaldulensis* [41], *Eucalyptus globulus* [54], and *Quercus robur* [38]. Modified Pine presented opposite results: decrease of intensity in the regions related to C=O stretching in unconjugated groups not only in hemicelluloses but also in lignin (1730-1724 cm^{-1}), meaning that both were more affected by wood modification in the case of Pine compared to the hardwood species (Acacia and Ash). Also, a decrease in the bands related to G-lignin (1515-1506 cm^{-1}) was observed, consistent with the Py-GC/MS results (decrease in guaiacyl units after wood modification). Moreover, the decrease in the band associated with cellulose (1110-1104 cm^{-1}) was noticed, which may reflect some alteration of this polymer in the case of Pine. The band 1506 cm^{-1} is a characteristic band for C=C stretching in the aromatic ring, showing changes in lignin polymer as already [35,48]. Literature is not conceptual regarding the influence of the softwoods' modification, possibly due to differences in the applied conditions. Some studies reported similar behaviors for Scots pine (*Pinus sylvestris*) and Oriental spruce (*Picea orientalis*) [48]. Still, others attain an increase of intensities in these same bands, such as the case for Maritime pine [54] and Spruce [55].

3.2.3.2. Natural weathering effects. Fig. 6 shows the spectral changes of wood and modified wood after exposure in Sines and Lumiar for 12 and 24 months.

In all Pine samples, bands decreased in the regions 1605-1598 cm^{-1}, 1515-1506 cm^{-1}, and 1266-1261 cm^{-1} (Fig. 6a), which are associated with lignin, suggesting its degradation by UV light; this radiation interacts with the chromophore's groups of lignin, photo-oxidation reactions occur contributing for the depolymerization of lignin, posterior lixiviation by rain and wood discoloration [30,56]. This phenomenon is the cause of the color change in Pine samples. Lignin degradation has another impact: the exposition of celluloses

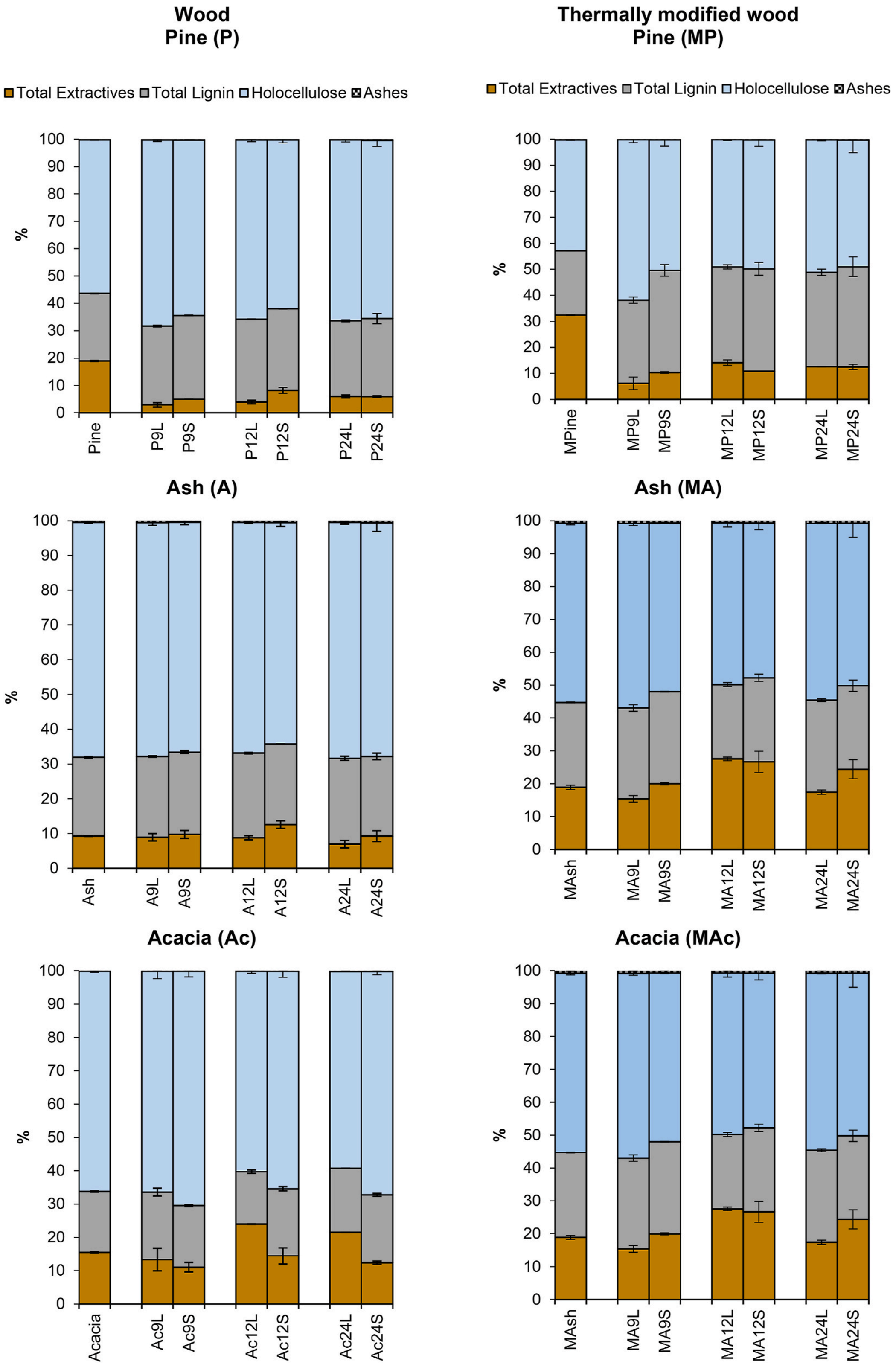

Fig. 4. Chemical composition of all exposed wood samples. *Legend:* Pine (P), Ash (A), Acacia (Ac), Modified Pine (MP), Modified Ash (MA), and Modified Acacia (MAc) at 9, 12, and 24 months of exposure time in Lumiar (L) and Sines (S).

Table 3
Summary of the pyrolysis analysis results for the wood and modified wood from the three species (time 0) and after natural weathering (24 months exposition). Values as a percentage of total pyrogram area.

		Total carbohydrates		Total lignin		H-lignin		G-lignin		S-lignin		S/G ratio		C/L ratio	
Sines		0	24	0	24	0	24	0	24	0	24	0	24	0	24
	Pine	38.8	44.5	19.4	17.8	0.3	0.3	19.1	17.6	0.0	0.0	0.0	0.0	2.0	2.5
	MPine	44.5	48.4	17.3	16.0	0.3	0.4	17.1	15.6	0.0	0.0	0.0	0.0	2.6	3.0
	Acacia	43.5	49.3	18.9	19.0	0.1	0.2	6.6	5.6	12.2	13.1	1.85	2.34	2.3	2.6
	MAc	52.4	56.9	14.5	15.1	0.2	0.3	5.1	5.3	9.2	9.5	1.81	1.81	3.6	3.8
	Ash	36.4	44.7	21.1	22.2	0.1	0.2	6.8	7.2	14.2	14.8	2.09	2.05	1.7	2.0
	MAsh	44.4	45.3	20.8	22.1	0.2	0.2	7.0	7.4	13.7	14.5	1.96	1.97	2.1	2.0
Lumiar		**0**	**24**	**0**	**24**	**0**	**24**	**0**	**24**	**0**	**24**	**0**	**24**	**0**	**24**
	Pine	38.8	44.4	19.4	16.4	0.3	0.3	19.1	16.1	0.0	0.0	0.0	0.0	2.0	2.7
	MPine	44.5	45.6	17.3	17.0	0.3	0.4	17.1	16.6	0.0	0.0	0.0	0.0	2.6	2.7
	Acacia	43.5	45.2	18.9	19.2	0.1	0.2	6.6	7.0	12.2	12.0	1.85	1.71	2.3	2.4
	MAc	52.4	54.8	14.5	14.9	0.2	0.3	5.1	5.1	9.2	9.5	1.81	1.86	3.6	3.7
	Ash	36.4	44.4	21.1	18.3	0.1	0.2	6.8	5.2	14.2	12.9	2.09	2.48	1.7	2.4
	MAsh	44.4	46.0	20.8	19.4	0.2	0.2	7.0	6.1	13.7	13.0	1.96	2.13	2.1	2.4

Table 4
Assignment of FTIR bands of principal chemical components in wood in the region 1800-800 cm^{-1}.

Wavenumber (cm^{-1})	Assignment	References
1750–1720	C═O stretching in conjugated ketones, carbonyls, aldehydes, and ester group	[41]
1724–1730	Free carbonyl groups, C═O Stretching of acetyl or carboxylic acid (hemicellulose and lignin)	[21,42–44]
1605–1598	C═C Aromatic ring stretching in lignin (syringyl lignin)	[21,38,41,44–46]
1515–1506	C═C stretching of the aromatic ring in lignin (guaiacyl lignin)	[21,42,44,46]
1470–1460	C–H deformation (asymmetric) (lignin and xylan)	[21,27,41,42,44,46]
1430–1420	Aromatic skeletal vibration (lignin) and C–H deformation (cellulose)	[21,41,44]
1370–1365	CH_2 bending in cellulose and hemicelluloses	[21,44]
1330–1320	C–H vibration in cellulose and C–O vibration in syringyl and guaiacyl rings	[44,47,48]
1266–1261	Guaiacyl ring breathing with CO-stretching (lignin and hemicelluloses) and esters	[21,44,45]
1240–1220	Syringyl ring and C–O stretch in lignin and xylan	[27,41,44,49]
1210–1201	OH-bending (cellulose), aryl aldehyde, a- and unsaturated aldehyde, lactones, phenols, and diaryl ethers. Associated with crystallized and amorphous cellulose	[21,48]
1155–1159	C–O–C vibration in cellulose and hemicellulose is also associated with crystallized and amorphous cellulose	[21,41,48,50]
1104–1110	OH association (cellulose)	[21,48]
1054–1052	C–O deformation in aliphatic alcohols and ethers (carbohydrates)	[21]
1051–1023	C–H and C–O deformations (polysaccharides and cellulose)	[21,41,48,49]
1000–985	C–O valence vibration (cellulose)	[51–53]
898–897	C–H deformation of glucose ring in cellulose and hemicellulose	[21,41,44,45,48]

and hemicelluloses to weathering [52]. Therefore, it was also noticed a decrease in the C═O band at 1723 cm^{-1} attributed not only to carbonyl groups in lignin but also to the cleavage of acetyl groups in hemicelluloses during weathering, as also reported in the literature [44]. However, the Modified Pine exposed during 24 months in Sines showed a pronounced increase in the 1105-1098 cm^{-1} region, while at 24 months in Lumiar, it was in 1000-985 cm^{-1}. In the case of Ash samples, the decrease of lignin bands also occurred, as well as the increase in cellulose bands, but at a lower level when compared to Pine. The less degradation of Ash and MAsh woods (Fig. 6b) could explain the observed constant color over time after the first month of exposure. Acacia wood samples (Fig. 6c) also suffered delignification detected by the intensity decrease in the correspondent bands regions, such as regions 1515-1506 cm^{-1} in Modified Acacia, exposed in Sines for 24 months. A noted reduction in the carbonyl peak at 1725 cm-1 was observed in Pine and Ash, reflecting hemicelluloses degradation during weathering. The carbohydrate bands in the regions 1052-1054 cm^{-1} and 1000-985 cm^{-1} increased. This could be promoted by the delignification of the wood surface caused by depolymerization and demethoxylation of lignin [21]. The spectrum of Acacia wood exposed in Sines for 12 months shows a pronounced increase of the at band ≈1632 cm^{-1}, which is probably caused by adsorbed water, that might be due to the enrichment of cellulose in wood during weathering because lixiviation of lignin occurs [21]. An increase in a band around 1300 cm-1 was noticed in all species, confirming the increase in condensed structures [44]. Other studies found similar results concerning chemical changes on the surface of woods, namely lignin degradation [21,57], and they confirmed that lignin is the main structural component that suffers from weathering, as the same happened in our study. FTIR-ATR showed the band's shifting from 1500 to 1512 cm^{-1}, which shows demethoxylation of the lignin [44]. However, a decrease in the band related to acetyl groups was also seen, showing degradation in hemicelluloses due to the cleavage of these groups [44]. Cellulose was less degraded in all the woods, as demonstrated by the slight decrease of band 893 cm^{-1} (degradation of amorphous cellulose).

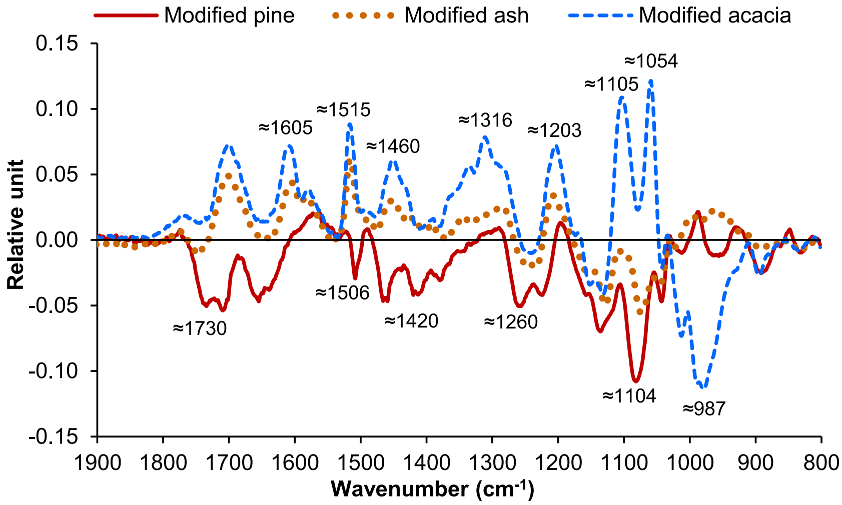

Fig. 5. FTIR-ATR difference spectra of modified wood relative to wood.

3.3. *Morphological characterization*

3.3.1. *Thermal modification effects*

Fig. 7 presents SEM micrographs of three wood species before and after thermal modification. SEM analysis showed that thermal modification caused changes in the morphological structure of all three wood species, *e.g.,* in Pine (Fig. 7a), damage in tracheid's walls (Fig. 7b), in Ash, a ring-porous wood (Fig. 7c), reduction of the diameter of the vessels by deformation of their cell walls, mainly in the large vessels of the spring wood (Fig. 7d) and Acacia, a diffuse – porous wood (Fig. 7e), occurrence of micro-cracks in vessels and a sort of a detachment of the fibers near vessels, were noticed on a radial section (Fig. 7f). Cracks, broken cells, and deformations in the wood cell wall are also reported in recent studies in *Pinus radiata* [58], *Pinus taeda, Eucalyptus grandis* [59], and *Pinus oocarpa* [40]. According to the same authors, these alterations of the wood's cellular structures, namely hemicellulose, cellulose, and lignin, are probably caused by the chemical changes during thermal modification.

3.3.2. *Natural weathering effects*

Micro-cracks were observed in the weathered wood samples of 9, 12, and 24 months. Fig. 8(a–b) shows some examples of the wood surface structure in both locations after 24 months of exposure. The modified wood samples showed more cracks on the surface, probably because modified wood samples presented a surface fragility caused by thermal modification. According to the literature, this injury on the wood surface contributes to increased wood roughness [21] and can be caused by UV radiation and surface erosion [21, 56]. This was confirmed by FTIR-ATR results, where it was possible to establish the degradation of lignin, the principal component sensible to photodegradation and lixiviation.

Apart from the anatomical changes due to the weathering, i.e., micro-cracks in cell walls, the deposition of particles was also observed in these samples (Fig. 8), probably an effect of marine aerosol and industrial pollution. The encrusted dust particles into the empty spaces in cracks and micro-cracks were also mentioned by Mamoňová et al. [60] when they studied the effect of naturally and artificially weathered surfaces of different tropical hardwoods. Still, the authors did not characterize the particle composition.

Using SEM/EDS, it was possible to know the chemical elements of these particles and if some of these elements could contribute to wood surface degradation. The samples exposed in Sines showed the presence of Si, Al, Fe, Na, and Cl. Sines's environment is identified as maritime/industrial, so the appearance of these elements in wood is not surprising. NaCl crystals were only identified in wood samples after 9 months of exposure (Fig. 9a). These elements were not observed for 12 and 24 months, or only trace elements were noticed, perhaps because the samples were taken out after a rainy period.

It was difficult to confirm if salt crystals contributed to wood surface degradation. It was known through different studies that salt can cause severe damage to wood [14,15], but this degradation is sometimes confused with wood decay [14,15]. In this case, the wood was never directly exposed to salty water, they were only exposed to a maritime aerosol.

The surface of wood samples in Lumiar (urban environment) presented mainly particles silicium (Fig. 9b). Concerning weathered wood, no study was found where SEM with EDS has been used to characterize chemically the particle deposition.

4. Conclusions

This experimental work allowed us to draw the following conclusions:

Thermal modification caused:

- Color changes due to chemical changes;

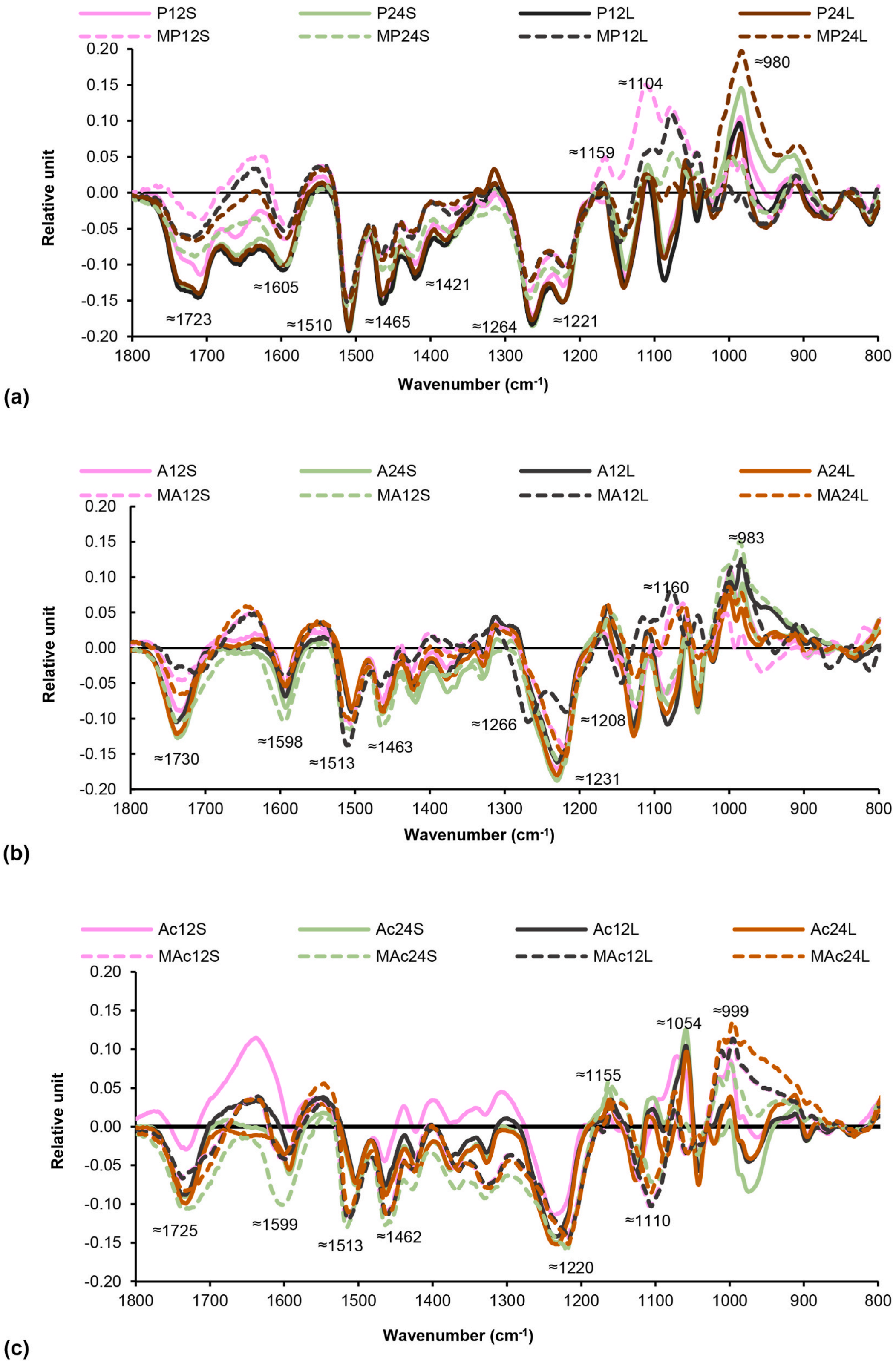

Fig. 6. FTIR-ATR difference spectra of all exposed wood samples: (a) Pine; (b) Ash; (c) Acacia. *Legend:* Pine (P), Ash (A), Acacia (Ac), Modified Pine (MP), Modified (MA), and Modified Acacia (MAc), at 12 and 24 months of exposure time in Lumiar (L) and Sines (S).

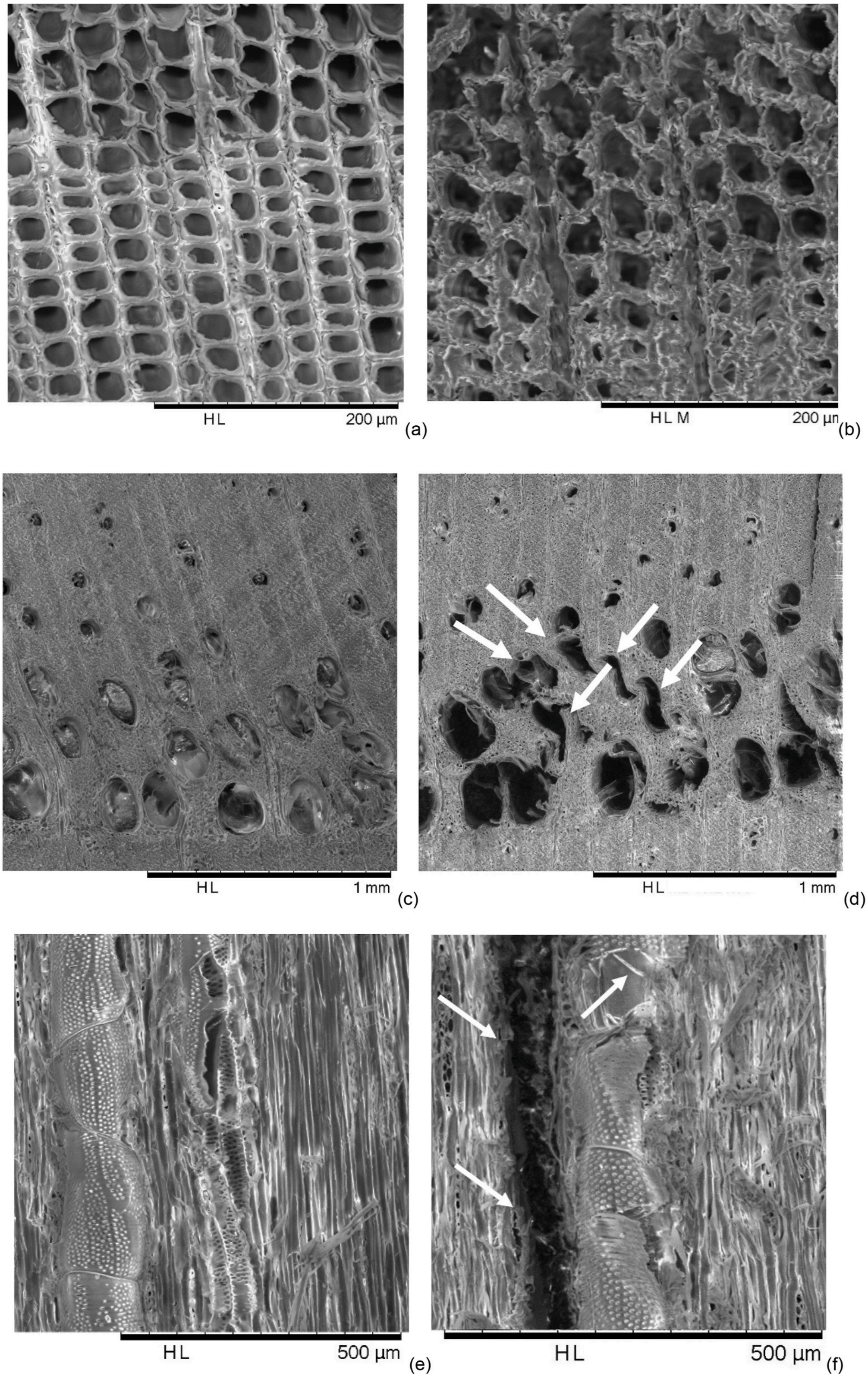

Fig. 7. SEM micrographs of transversal cuts of natural (a) and thermally modified pine wood (b); transversal cuts of natural (c) and modified ash wood (d): deformation of vessel cell walls (arrows); tangential cuts of natural (e) and modified acacia wood (d).

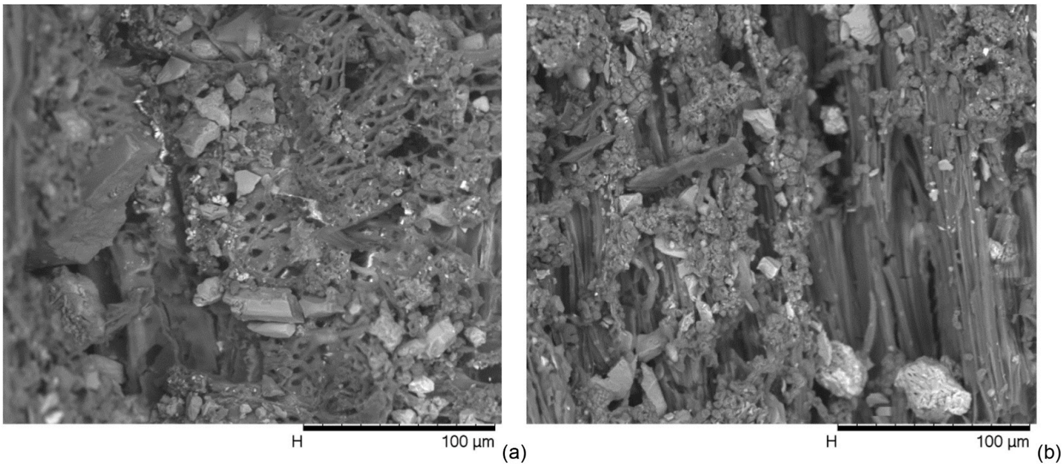

Fig. 8. SEM picture of modified acacia wood exposed during 24 months in Lumiar (a) and modified acacia wood exposed during 24 months in Sines (b).

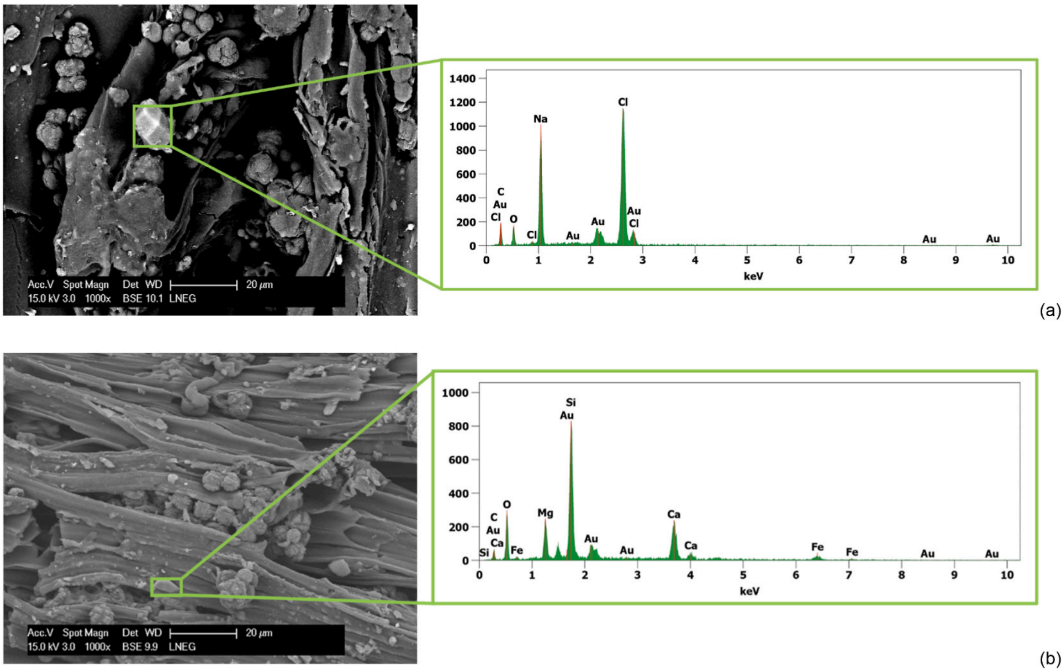

Fig. 9. SEM/EDS images and spectrums of modified acacia wood exposed for 9 months exposed in Sines, (b) modified acacia wood exposed for 9 months in Lumiar.

- Chemical changes in all wood species, namely an increase in total extractive content and total lignin due to the thermal degradation of hemicellulose and cellulose;
- Some damage in the wood cell structure, namely small cracks and cell deformation.

Natural weathering in maritime/industrial and urban environments has led to the following changes:

- All thermally modified woods suffered fewer color changes, but modified ash was the most stable of the tree wood species.
- All wood samples lost extractives because of lixiviation caused by rain, particularly Pine and MPine. This also may have contributed to the color changes observed in the wood samples;
- Py-GC/MS analysis revealed a reduced lignin content in the wood samples after thermal modification, with some alterations in its monomeric composition (slightly decrease of S/G ratio in MAsh and MAcacia).

- FTIR-ATR studies showed a decrease in lignin in all wood samples after exposition, possibly caused by lignin photodegradation. These results also showed that thermal modification did not contribute to lignin protection.
- In all wood sample structures, the appearance of cracks occurred, which indicates that surface erosion occurs. This appearance was more noticeable in thermally modified woods with structural damage caused by thermal modification.
- The only wood species that presented some difference was Acacia, which showed the color difference between the two locations with greater color change in maritime/industrial conditions. The extractive content difference could cause this, and Acacia wood exposed to Sines had similar behaviors to modified Acacia. Sine's environment presented the highest relative humidity, time of wetness, and atmospheric contaminants. This also could explain why Acacia became darker in Sines than in Lumiar, which could promote mold and blue staining growth. Acacia wood seems to be more sensitive to environments with different atmospheric conditions.
- Thermal modification enables color stabilization but does not seem to promote weathering resistance in both environments.

No morphological or chemical evidence demonstrates that marine/industrial or urban environments lead to woods (without and with thermal modification) having different weathering resistance. However, further studies with a higher exposure period are needed to understand if the wood samples will show another behavior between the two different environments.

Author contributions

Conceptualization, DG, TQ, TCD, and JG; methodology, DG, SdOA, CF, AL, TQ, TCD, and JG; formal analysis, DG, CF, and AL; writing—original draft preparation, DG; writing, review and editing, CF, AL, SdOA, TQ, TCD, and JG; supervision, TQ, TCD, and JG. All authors have read and agreed to the published version of the manuscript.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.heliyon.2024.e25020.

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