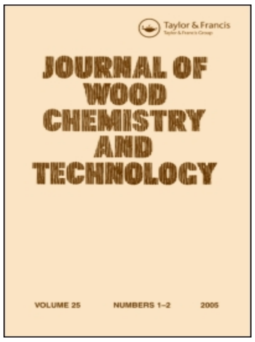

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HEAT TREATMENT EFFECT ON LIGNIN AND CARBOHYDRATES IN CORSICAN PINE EARLYWOOD AND LATEWOOD STUDIED BY PY–GC–MS TECHNIQUE

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Lignin-derived degradation products from non-treated (NT) and heat-treated (T) Corsican pine (*Pinus nigra* subsp. *laricio*) obtained by pyrolysis–gas chromatography–mass spectrometry (Py–GC–MS) were investigated, whereby the earlywood (EW) and latewood (LW) parts of the annual ring were considered separately. The data evaluation was done by principal component analysis (PCA) and the Kruskal–Wallis test. There are no differences in the pyrolysis products composition between EW and LW, but NT and T samples were discernible by PCA applied to Py–GC–MS data. Less phenols with longer chains (4-vinylguaiacol, and *trans*-isoeugenol) than those with shorter chains (guaiacol, 4-methylguaiacol) and an increase of anhydrosugar (AHS) were found among the pyrolysis products after heat treatment. These signs for autocondensation and side chain cleavages in the lignin during heat treatment were more evident in the EW than in the LW and for the crystallization of cellulose. A slight decrease of the carbohydrate/lignin ratio (C/L) after heat treatment indicates a greater degradation of carbohydrates compared to lignin. The relation of pyrolysis products of lignin and mechanical properties of wood was evaluated by regression analysis. An inverse correlation between short-chain phenols and MOE and a direct correlation between long-chain phenols and compression strength was found in case of NT wood, while a weak positive correlation could be observed between short-chain phenols and the density in T wood.

KEYWORDS. Wood, PCA, mechanical properties, sapwood, lignin, carbohydrates, thermowood

INTRODUCTION

The mechanical properties of wood including shrinkage, oxidation, and mechanical strength are heavily influenced by the composition of the cell wall, but also by the ratios of earlywood (EW) and latewood (LW) of wood.[1,2] At the cell wall level, the lignin part plays a pivotal role in terms of mechanical properties.[1,3] Concerning micromorphological details (such as EW and LW), pyrolysis–gas chromatography–mass spectrometry (Py–GC–MS) is an established rapid analytical screening tool[4] with low sample demand, which gives rapid information about the chemistry of the cell wall in general and the lignin composition in particular. The material amount needed for Py is around 30 μg and previous lignin isolation is not necessary to obtain lignin related data. Py–GC–MS studies about archaeological wood, degraded wood, and industrial products are frequently reported,[5–7] such as about characterization of wood from different geographical provenances[8,9] and climates[10] under consideration of growth conditions[11] and the sampling place within the tree.[12]

Unlike for lignin, the analysis of results from analytical pyrolysis of carbohydrates is more difficult for several reasons concerning the

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separation and identification of the large number of degradation products.[13] Nevertheless, Py–GC–MS has been used to characterize cellulose and hemicelluloses[14,15] and has been successfully applied to the analysis of carbohydrates in the Kraft delignification process.[16]

The physical and mechanical properties of EW and LW affect the wood density.[17,18] As well known, the ratio between EW and LW is related to the climate and forest site conditions, i.e., also to the dimensions of silviculture. The chemical differences between EW and LW are seldom investigated.

Heat treatment is an environmentally benign process to improve wood durability[19–21] and wood color,[22–25] reducing significantly wood hygroscopicity[26–28] as well as shrinkage/swelling.[29–32] Heat treatment modifies the relative composition of the wood by hemicelluloses degradation leading to an apparently higher lignin content.[33,34] One of the major disadvantages of heat treatment is the decrease of dynamic mechanical properties, which is influenced by the raw material and the parameters of the heat treatment process.[20,22,28,35,36] The effect of heat treatment on the chemical structures in wood has been frequently reported.[37–39] Even though it is accepted that intra-ring differences of chemical components (i.e., lignin, cellulose and hemicellulose) are found regarding their relative quantity, not in their chemical structures, some studies showed consistent variations on the dynamic deposition of lignin[40,41] as well as on its chemical structure as showed in S/G ratio variation in Komine maple.[42] In these studies, analytical pyrolysis was never used and neither possible effects of intra-ring differences on industrial processes such as heat treatment were investigated.

Py–GC–MS is a convenient screening method with low material demand and little sample preparation, which not only gives exact information about the chemical structure of the degraded wood, but allows first rough estimations of relative changes in the wood composition. Even if the results obtained by Py–GC–MS are more significant for lignin than for polysaccharides, additional information about the modifications in heat-treated (T) wood can be acquired by analysis of the pyrolysis products of carbohydrates. The present paper is a continuation of the work of Romagnoli et al.[28] and its first aim is to investigate qualitative differences in lignin and carbohydrates structure in EW and LW in the sapwood of *Pinus nigra* subsp. *laricio* before and after heat treatment. The study has been performed on EW and LW, because the width of both tissues has a relevant effect on many other physical wood properties such as density, shrinkage and swelling, hardness and mechanical parameters, which change after wood heat treatment.[28]

The second aim was the correlation of the pyrolysis products deriving from lignin and carbohydrates to some important physical and mechanical wood properties in the context of heat treatment.

MATERIAL AND METHODS

Samples were collected from Corsican pine (*P. nigra* subsp. *laricio*) located in the mixed reforest site of Poggio Nibbio in the Cimini Mountains (Viterbo, Italy). These trees show large ring widths with ca. 8.35 mm, with the LW being approx. 3.90 mm. A total of 20 sapwood specimens were considered, which were obtained from 10 different trees. Ten boards were cut to prepare samples for both physical and mechanical characterizations according to UNI technical standards (Figure 1). For each board, the left-hand side served as control, while the right-hand side was subjected to heat treatment (20 samples). The heat treatment was performed according to the protocol of VTT Research Center in Finland (180°C in the presence of steam) in an industrial plant. The following parameters were determined: total shrinkage coefficients (βt, βr), density, axial compression strength, and MOR (modulus of rupture in bending) and MOE (modulus of elasticity). For further details on the sample preparation and the test conditions, see Romagnoli et al.[28]

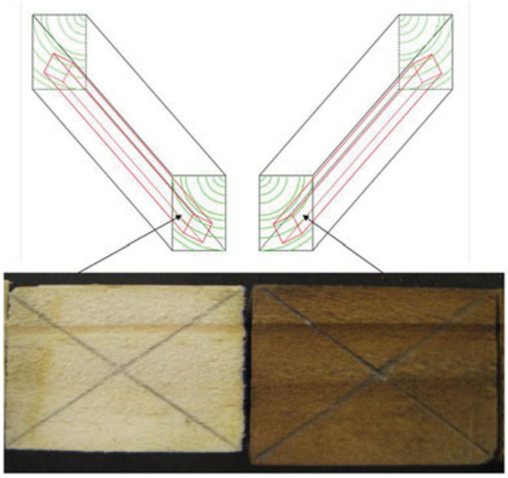

FIGURE 1. Plan of the sampling by the same board Pinus samples. One sample was left non-treated, the twin one was heat treated.

Separation of Earlywood (EW) and Latewood (LW)

The separation was done with a hammer and chisel. The EW and LW samples from 1 complete ring were crushed separately by means of a mechanical mill equipped with a 0.4-mm hole size filter. The final 40 samples (including 20 EW and 20 LW, both from non-treated (NT) and T) consisted of 1.5–2.0 mg of fine wood powder and each were pressed into a pellet using a special syringe.

Py–GC–MS Analysis

These pellets were then directly applied to a microfurnace pyrolyzer (Pyrojector II, SGE) coupled to a GC–MS system (HP 5971 GC-MS, Agilent; EI mode at 70 eV at 180°C, mass range 50–500 *m*/*z*, total ion current was obtained with a frequency of 2.0 scan s^{-1}). Each sample was pyrolyzed in duplicate at 450°C. The GC instrument (HP 5890) was equipped with a Restek Rtx 1701 column (30 m × 0.25 mm ID). The stationary phase consists of 0.25 μm film thickness, 14% cyanopropylphenyl, 86% dimethyl polysiloxane.

The carrier gas was He (233 kPa in the pyrolyzer and at 200 kPa in the GC). Injector 250°C; split ratio 20:1. Temperature program: 40°C (4 min) → 6°C min^{-1} up to 250°C (5 min). Substance identification was based on libraries included in the management software of a mass spectrometer (NIST 08 and Wiley 6.0), and on interpretations of mass spectra and relative retention times available in the literature.[13,43–45] The relative area of the peaks for individual compounds was calculated using Agilent software based on GC/MS data.

Statistical Analysis

The pyrograms of 40 samples were normalized. The data (relative peak areas of pyrolysis products from lignin and carbohydrate wood components) were then subjected to principal component analysis (PCA) and the Kruskal–Wallis test (statistical programs: R package (version 4.0), and Systat, respectively). PCA was performed on the total samples and separately on the T and NT ones. The Kruskal–Wallis test was applied on NT and T samples. Linear regression analyses were performed to compare all the Py–GC–MS data with those of physical and mechanical properties.

RESULTS AND DISCUSSION

The Py–GC–MS data evaluation was focused on 14 identified phenolic peaks of 20 EW and 20 LW samples (Table 1)[12,46,47] and on 31 carbohydrate derivatives.[14,15,48,49]

The relative content of carbohydrate and lignin in wood was expressed as the ratio of the average sum of relative peak areas of carbohydrate and lignin pyrolysis products (C/L). C/L decreased by 3.86%, from 4.14 in NT to 3.98 in T wood, which can be explained by a degradation of carbohydrate, principally hemicellulose, during heat treatment. This finding is in good agreement with many studies.[29,50–54] Several authors have suggested that lignin undergoes polycondensation reactions with other cell wall components, resulting in further cross-linking and increasing the apparent lignin content.[48]

Lignin

All detected phenols are from guaiacol (G-type) origin in agreement with the G lignin type in softwoods. Similarly to the suggestion of Kim et al.,[34] the phenols were divided into 3

TABLE 1. Compounds obtained by Py–GC–MS with the molecular weight, retention time and the formula

Peak	Compound	Formula	Molecular weight	Type	Retention time (s)
A	Guaiacol	$C_7H_8O_2$ (G)	124	G/SC	6.9
B	4-Methylguaiacol	$G–CH_3$	138	G/SC	7.9
C	4-Ethylguaiacol	$G–CH_2CH_3$	152	G/SC	8.7
D	4-Vinylguaiacol	$G–CH{=}CH_2$	150	G/SC	9.3
E	Eugenol	$G–CH{=}CHCH_3$	164	G/LC	9.5
F	Catechol	$C_6H_6O_2$	110	G/SC	9.7
G	cis-Isoeugenol	$G–CH{=}CHCH_3$ (Z)	164	G/LC	10.0
H	trans-Isoeugenol	$G–CH{=}CHCH_3$ (E)	164	G/LC	10.5
I	Vanillin	G–(CHO)	152	G/OC	10.7
J	Homovanillin	$G–CH_2–(CHO)$	166	G/OC	11.2
K	Acetoguaiacone	$G–(CO)–CH_3$	166	G/OC	11.4
L	Guaiacyl acetone	$G–CH_2–(CO)–CH_3$	180	G/OC	11.8
M	Coniferyl alcohol	$G–CH{=}CHCH_2OH$	180	G/OC	12.1
N	Coniferaldehyde	G–CH=CH(CHO)	178	G/OC	13.7

To each compound, a letter is assigned for the next processing. SC = short chain, LC = long chain, OC = oxygenated chain.

categories (Table 1): those having no side chain or a short side chain of 1 or 2 carbons (designated SC group consisting of the phenols A, B, C and D), those having a long side chain of 2 carbons (designated LC group consisting of phenols E and H), and those having an oxygenated functional group (designated OC group consisting of phenols K and L). The score plot in Figure 2a shows a remarkable distinction between the T and NT samples. In combination, PC1 and PC2 account for 68.8% of the entire variance observed, with PC1 representing 47.0% and PC2 21.8%. Furthermore, PC1 describes the distribution of samples between the T and NT groups. The variation observed in PC1 is due to the contribution of phenols A (guaiacol) and B (4-methylguaiacol) from the SC group, and H (*trans*-isoeugenol) and E (eugenol) from the LC group. While phenols A and B are positively correlated with PC1, phenols H and E are negatively correlated (Figure 2b). Thus, the SC phenols increase in the T samples, so as LC phenols increase in NT samples. These results are consistent with those of Kim et al.[34] where short-chain phenols produced by lignin pyrolysis accounted for the majority of the difference between the $T_{200°C}$ and NT samples.

PCA was then applied to distinguish between NT samples (Figure 2c) and T samples (Figure 2d), focusing on the influence of the EW and LW origin. Score plots show that the relative yields of phenols are very similar in EW and LW regardless of the NT or T origin. EW and LW were not yet compared based on Py–GC–MS of lignin studies. Rather, differentiation between EW and LW is possible comparing the carbohydrate composition of hemicelluloses and pectins as shown by Bertaud and Holmbom.[55]

After heat treatment, the EW and LW samples belonging to the same block (see *Materials and Methods* section), appear very close to each other (Figure 2d) compared to NT wood (Figure 2c). Specifically, the samples 1E and 1L, 3E and 3L, 6E and 6L, 9E and 9L, 10E and 10L and 14E and 14L are located very close in the score plot.

The results of the Kruskal–Wallis statistical test also indicated that the most abundant products in both the NT wood and T_{EW} and T_{LW} samples are the following: guaiacol (A), 4-methylguaiacol (B), 4-vinylguaiacol (D) and trans-isoeugenol (H) (Figure 3, Table 1). Moreover, there was a difference in the yields of phenols of T_{EW} and T_{LW} samples. Concerning the NT_{EW} and T_{EW} samples (Figure 3a), 4 phenols exhibited significant changes. An increase in phenol B (4-methylguaiacol, $p = 0.028$) and decrease in phenols E (eugenol, $p = 0.049$), G (*cis*-isoeugenol, $p = 0.028$), and H (*trans*-isoeugenol, $p = 0.034$) were seen. Similarly, 3 phenols were found to vary significantly before and after the treatment in LW_{NT} and LW_T samples (Figure 3b). According to

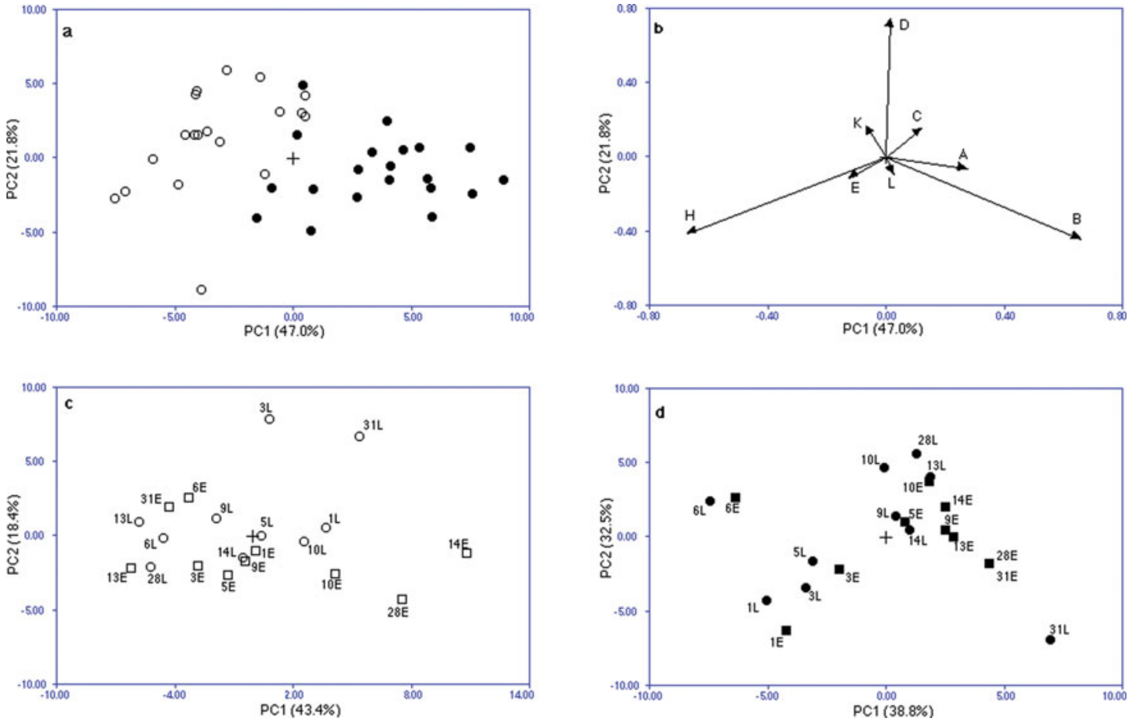

FIGURE 2. PCA analysis of lignin pyrolysis products. (a) Score plot of all samples; black circles: heat-treated samples, white circles: non-treated samples. (b) Loading plot. (c) Score plot of non-treated samples; white circles: latewood samples, white squares: earlywood samples. (d) Score plot of treated samples; black circles: latewood samples, black squares: earlywood samples.

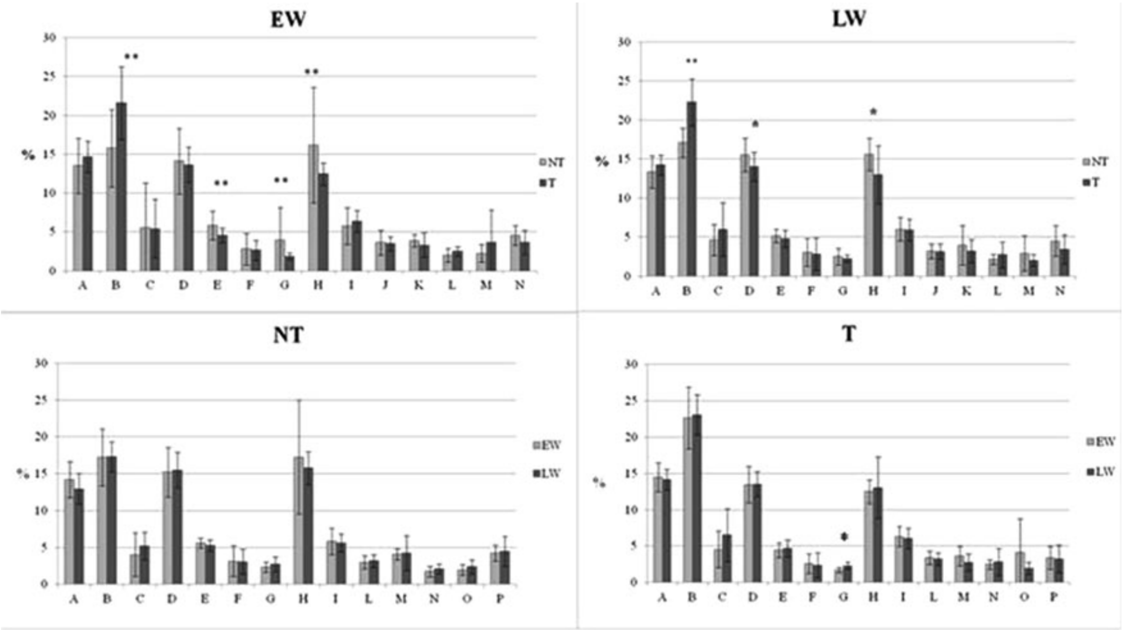

FIGURE 3. Kruskal–Wallis analysis. (a) Earlywood samples, the bars are related to non-treated and treated wood. (b) Latewood samples, the bars are related to non-treated and treated wood. After the treatment, there is a significant variation of the phenols B, E, G and H in earlywood and B, D and H in latewood, *$p > 95\%$, **$p > 99\%$, ***$p > 99.9\%$. In panel (c), are reported close together the bars of earlywood and latewood in non-treated wood samples. In panel (d), there are the bars of the phenols of earlywood and latewood in treated samples. No significant difference was found between earlywood and latewood in non-treated samples. In latewood, only a weak difference is found for phenol G, which is present in a low amount.

the Kruskal–Wallis test, phenol B content (4-methylguaiacol, $p = 0.01$) increased and the content of phenols D (vinylguaiacol, $p = 0.049$) and H (*trans*-isoeugenol, $p = 0.023$) decreased.

The Kruskal–Wallis test revealed common trends in the variations of phenols yields regarding their origin from LW_{NT} and EW_{T} (Figure 3a and b), confirming the results of PCA. First, yields of phenols A (guaiacol) and B (4-methylguaiacol) increased, while in contrast larger peaks of phenols with longer side chains were observed, such as phenol E (eugenol), G (*cis*-isoeugenol) and H (*trans*-isoeugenol). Kim et al.[34] and Rousset et al.[56] made similar observations. Heat treatments with temperatures greater than 200°C lead to condensation and cross-linking reactions that enrich resistant interunit bonds in lignin which make lignin more similar to the structure of char.[29,34,51–53,56,57] In addition, pyrolytic cleavage of linkages between aromatic units and propanoic side chains (e.g., $C\alpha$–$C\beta$–$C\gamma$) could lead to the enrichment of phenolic products with shorter side chains. Thus, the yield of more complex phenolic compounds with longer side chains (e.g., phenols E, G and H) must be necessarily reduced.

However, the Kruskal–Wallis analysis indicated a slightly different behavior of EW and LW samples. The yields of phenols B (4-methylguayacol) and H (*trans*-isoeugenols) changed in both EW and LW samples, while phenol D only exhibited significant changes in the LW samples and phenols E and G only changed significantly in the EW samples. Our interpretation is that lignins in EW are more susceptible to T than those in LW. This result might find a biological explanation, concerning the dynamic of lignin deposition in the cell walls.[58]. Lignification in early and late xylem at cell maturation stages was found to occur with different rates and with opposite trends. Lignin deposition during EW (slower) and LW (faster) formation has different rates and it might be a result of (1) the heterogeneity of lignin precursors, (2) the conditions of monolignol condensation and (3) the nature of the carbohydrate matrix in which the polymerization of phenylpropanoid units occurred.[41]. This phenomenon has been observed also in beech where lignification of the fiber cell walls proceeds more slowly in the initial part of the growth ring than in the terminal part.[59,62]. Lignification depends on temperature and environmental conditions[60] affecting the lignification rate.

Carbohydrates

In Table 2, the list of carbohydrate pyrolysis products is reported. Similarly to Grinins et al.[48] and Dizhbite et al.,[49] carbohydrates were merged in 6 representative groups (Table 2) namely AAE = aliphatic acids and esters, AAAK = aliphatic alcohols, aldehydes and ketones, FD = furan derivatives, CPD = cyclopentane derivatives, PD = pyran derivatives and AHS = anhydrosugars. The 6 groups were used as variables to perform PCA analysis (Figure 4) on the whole 40 samples. In combination, PC1 and PC2 account for 94% of the total variance observed, with PC1 representing 86.6% and PC2 7.4%. Furthermore, PC2 describes the distribution of samples between the T and NT groups (Figure 4a). In the loading plot (Figure 4b), it is shown as the variance between NT and T samples is described by AHS and aliphatic alcohol, aldheydes and ketons (AAAK) group on one hand and all the other groups on the other hand. Comparing the score plots of NT and T samples (Figure 4c and d), no separation can be detected between EW and LW samples. After heat treatment, the most samples belonging to the same analyzed block (see *Materials and Methods* section) appear very close to each other (Figure 4d), confirming the results obtained by PCA of the lignin pyrolysis products (Figure 2d).

Regarding the histograms of the carbohydrates pyrolysis products (Figure 5), we can assess no significant difference according to the Kruskal–Wallis test in EW comparing NT and T (Figure 5a) and the same result was found for the LW samples (Figure 5b). No significant differences were found regarding the carbohydrates pyrolysis products of EW and LW considering both the NT and T samples (Figure 5c and d).

TABLE 2. Compounds obtained by Py–GC–MS with the molecular weight, retention time and the formula. Peak no 12. is composed by two compounds, the corresponding formulas, base peaks and Molecular Weights are indicated in the table by a + symbol

Peak no	Name of compound	Retention time (min)	Formula	Base peak (*m/z*)	MW	Group
1	Propanal-2-one	1.67	$C_3H_4O_2$	43	72	AAAK
2	2,3-Butanedione	2.08	$C_4H_6O_2$	43	86	AAAK
3	Hydroxyacetaldehyde	2.58	$C_2H_4O_2$	31	60	AAAK
4	Formic acid	2.83	CH_2O_2	46	46	AAE
5	Acido acetico	3.18	$C_2H_4O_2$	45	60	AAE
6	Hydroxypropanone	3.71	$C_3H_6O_2$	43	74	AAAK
7	1,2-Dihydroxyethene	4.35	$C_2H_4O_2$	31	60	AAAK
8	3-Methylfuran	5.15	C_5H_6O	82	82	FD
9	2-Propenoic acid methyl ester	5.77	$C_4H_6O_2$	55	86	AAE
10	3-Hydroxypropanal	6.65	$C_3H_6O_2$	43	74	AAAK
11	3-Butenal-2-one	6.91	$C_4H_4O_2$	84	84	AAAK
12	(2H)-Furan-3-one + 3-Furaldehyde	7.55	$C_4H_4O_2$ + $C_5H_4O_2$	84 + 95	84 + 96	FD
13	Butanedial	8.01	$C_4H_6O_2$	58	86	AAAK
14	2-Hydroxy-3-oxobutanal	8.3	$C_4H_6O_3$	43	102	AAAK
15	2-Furaldehyde	8.55	$C_5H_4O_2$	95	96	FD
16	2,3-Dihydro-5-methylfuran-2-one	10.09	$C_5H_6O_2$	55	98	FD
17	2-Fufuryl alcohol	10.49	$C_5H_6O_2$	98	98	FD
18	1-Acetyloxypropane-2-one	10.82	$C_5H_8O_3$	43	116	AAAK
19	Dihydromethylfuranone (isomer of compound no. 16)	11.15	$C_5H_6O_2$	98	98	FD
20	Methoxy-dihydrofuran	11.68	$C_5H_8O_2$	69	100	FD
21	4-Cyclopentene-1,3-dione	11.76	$C_5H_4O_2$	42	96	CPD
22	Dihydromethylfuranone (isomer of compound no. 16)	13.08	$C_5H_6O_2$	98	98	FD
23	Dihydromethylfuranone (isomer of compound no. 16)	13.73	$C_5H_6O_2$	39	98	FD
24	5-Methyl-2-furaldehyde	13.87	$C_6H_6O_2$	110	110	FD
25	(5H)-Furan-2-one	14.98	$C_4H_4O_2$	55	84	FD
26	4-Hydroxy-5,6-dihydro-(2H)-pyran-2-one	15.79	$C_5H_6O_3$	114	114	PD
27	Methyldihydro-(2H)-pyran-2-one	16.72	$C_6H_8O_2$	55	112	PD
28	2-Hydroxy-1-methyl-1-cyclopentene-3-one	16.94	$C_6H_8O_2$	112	112	CPD
29	g-lactone derivative	21.4	Unknow	85	116	FD
30	4-Hydroxy-3-methyl-(5H)-furanone	25.41	$C_5H_6O_3$	56	114	FD
31	5-Hydroxymethyl-2-furaldehyde	28.57	$C_6H_6O_3$	41	126	FD
32	2-Hydroxymethyl-5-hydroxy-2,3-dihydro-(4H)-pyran-4-one	30.53	$C_6H_8O_4$	87	144	PD
33	1,6-Anhydro-β-D-mannopyranose	36.81	$C_6H_{10}O_5$	60	162	AHS
34	1,6-Anhydro-β-D-glucopyranose (levoglucosan)	38.91	$C_6H_{10}O_5$	60	162	AHS

Each compound is inserted into a group of carbohydrates; AAE = aliphatic acids and esters; AAAK = aliphatic alcohols, aldehydes and ketones; FD = furan derivatives; CPD = cyclopentane derivatives; PD = pyran derivatives; AHS = anhydrosugars.

By observing closely Figure 5a and b, it became evident that heat treatment produces the same variation (increasing and/or decreasing) of carbohydrates products by pyrolysis in EW and in LW, even if the variation is very low for some samples. Noteworthy, the group AAK decreases both in EW and in LW after heat treatment. Grinins et al.,[48] on the contrary, found a considerable increase in the AAK content using pyrolysis, which was ascribed to an oxidative transformation component of the hydrothermal modification (HTM). However, the different results could be related to different heat treatment process conditions.

PD compounds, deriving from hemicelluloses, were reported to decrease after heat

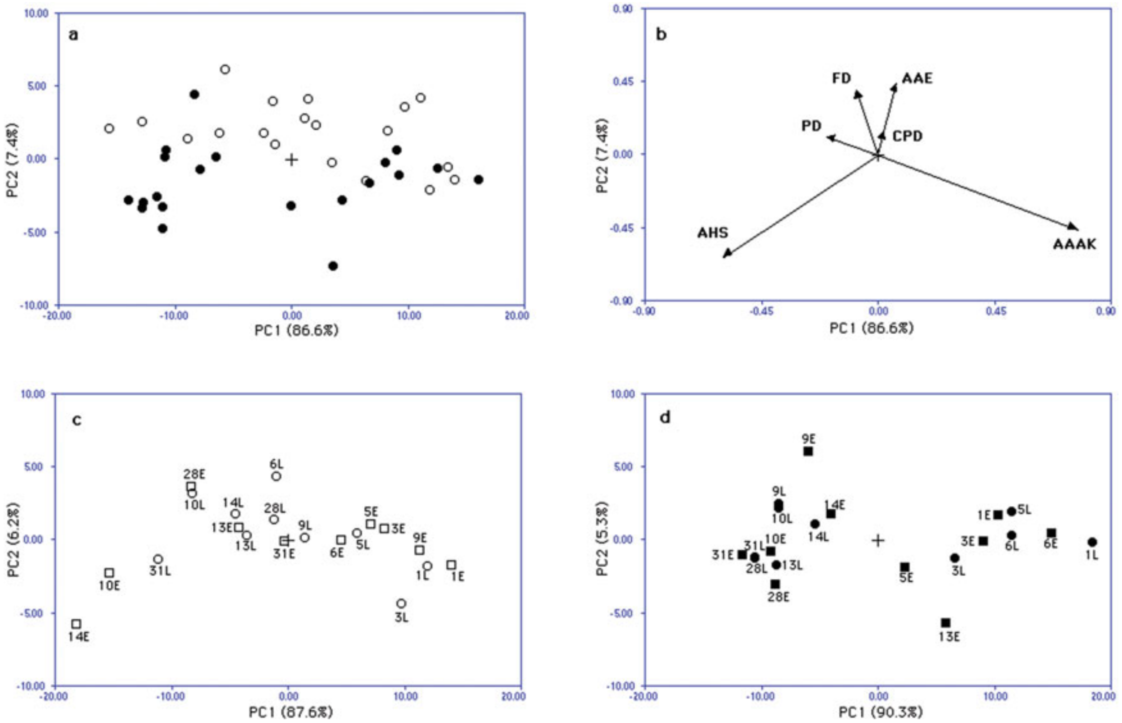

FIGURE 4. PCA analysis of carbohydrate pyrolysis products. (a) Score plot of all samples; black circles: heat-treated samples, white circles: non-treated samples. (b) Loading plot. (c) Score plot of non-treated samples; white circles: latewood samples, white squares: earlywood samples. (d) Score plot of treated samples; black circles: latewood samples, black squares: earlywood samples.

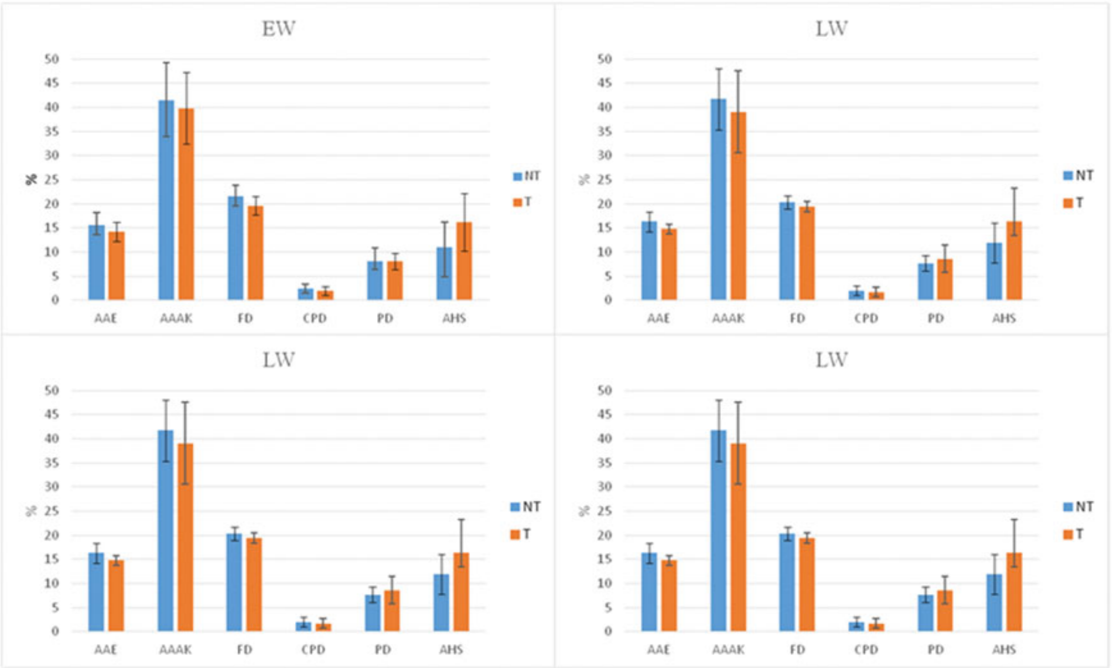

FIGURE 5. Kruskal–Wallis analysis. In panel (a), for earlywood samples, the bars are related to non-treated and treated wood. In panel (b), the same is for latewood samples. After the treatment, there is no significant variation of the group of carbohydrates. In panel (c), are reported close together the bars of earlywood and latewood in non-treated wood samples. In panel (d), the bars of the groups of carbohydrates of earlywood and latewood in treated samples are shown. No significant difference was found between earlywood and latewood in non-treated and treated samples.

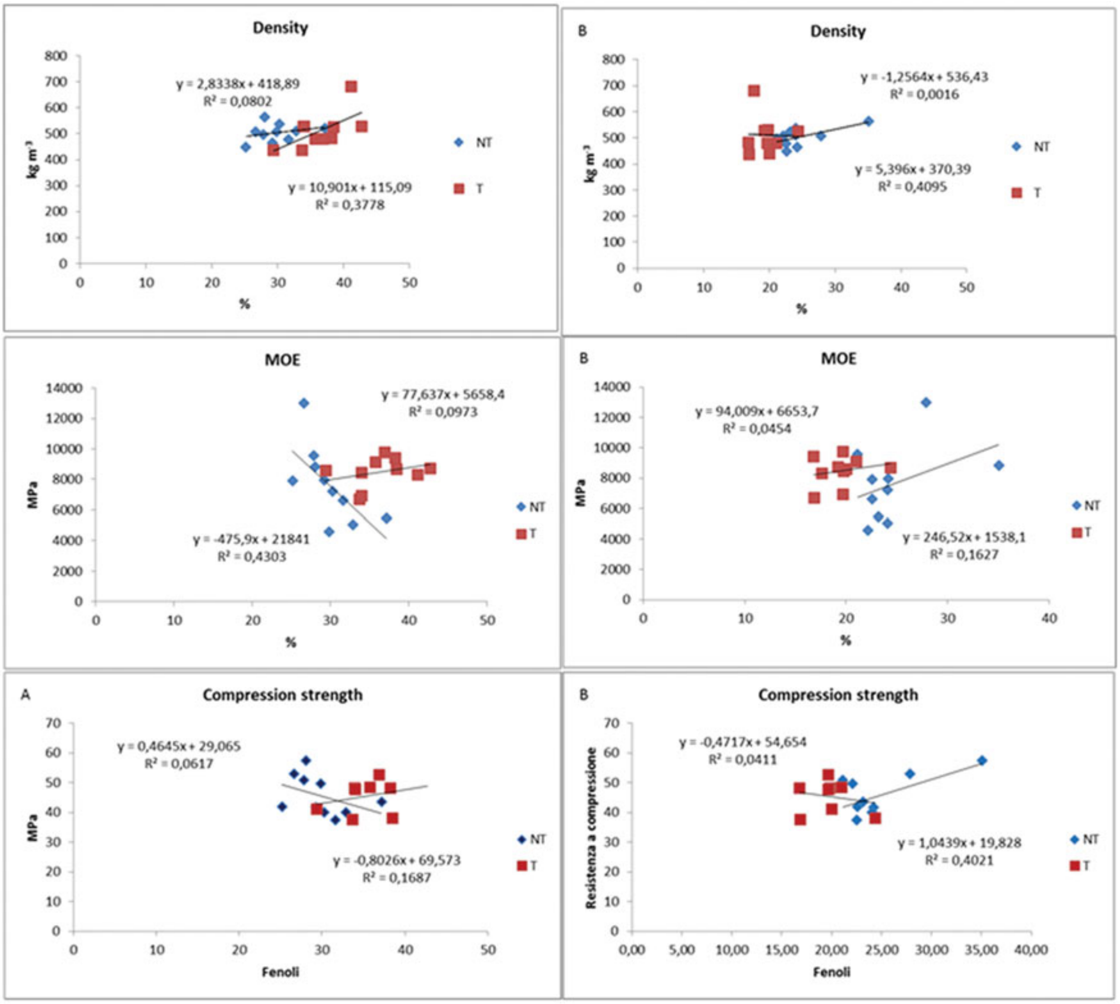

FIGURE 6. Regression analysis of physical–mechanical parameters density, MOE and compression strength according to the amount (in %) of the sum of phenols A + B (column A) and E + G + H (column B). The regression analysis is performed on the same graph in non-treated and treated samples.

treatment.[14,15,48] However, in our experiments, we could not observe any significant changes. The different heat treatment time and temperature could be considered as reasons for our differing results as well as the fact that the investigated species of Grinins et al.[48] were hardwoods.

By the heat treatment, both in EW and LW, there is a remarkable increase of AHS, in agreement with the results of Grinins et al.[48]

The AHS compounds are produced by cellulose depolymerization after severe heat treatment[36] where levoglucosan is the primary product of cellulose pyrolysis, which is a precursor of other chemical species formed by secondary reactions during pyrolysis.[14,15] Moreover, the microcrystalline nature of cellulose, which has been showed to increase after heat treatment,[29,37,53,61] has been reported to facilitate the levoglucosan formation.[14]

Comparing Figure 5c and d, no remarkable difference can be assessed between EW and LW comparing both NT and T cases. In NT samples (Figure 5c), there is a slight variability in carbohydrates pyrolysis products in EW and LW, but the variability flats after heat treatment (Figure 5d). Regarding carbohydrates, a significant difference was reported in the distribution of hemicellulose sugars between EW and LW in conifers by Bertaud et al.[55] who found that spruce LW contained clearly more galactoglucomannan than EW and conversely less pectins. Since we could not find such evidence in NT, it could be concluded that Py–GC–MS is not the most suitable method to show changes in hemicelluloses.

Correlation of Pyrolysis Products with Mechanical Properties

As shown in Figure 6a, a noteworthy regression coefficient was associated with the negative correlation observed between the short side chain phenols (e.g., A and B) and MOE in NT wood. On the contrary, the long-chain phenols (E, G and H) are positively correlated with compression strength. However, after heat treatment, the regression coefficient of MOE and compression strength was lower (Figure 5, column b). This is an indirect indication between the changes in the supramolecular architecture of the cell wall after heat treatment including hemicelluloses degradation and the increment of the polymerization degree and cross-linking density of the lignin moiety on the one hand and the physical properties on the other hand. Romagnoli et al.[28] demonstrated that heat treatment increases compression strength in Corsican pine. The same authors also showed MOE increment after heat treatment. No remarkable correlation was found with other lignin pyrolysis products or with carbohydrates (data not shown).

CONCLUSIONS

Py–GC–MS do not show reliable differences between EW and LW considering both lignin- and carbohydrates-derived pyrolysis products. The data scattering is due to tree to tree variations, which is more evident in T samples both by lignin and carbohydrates pyrolysis products analysis. Heat treatment causes a modification of the main components and changes the chemical composition of wood as described in previous studies leading to changes in the relative quantities of pyrolysis products from lignin increasing the yield of phenols with a shorter side chains (and lowering the yield of phenols with longer side chains).

There is a slight difference in carbohydrates pyrolysis products due to the heat treatment regarding AHS compounds.

The very well-known increased stability in T samples regarding lower hygroscopicity can further explained the observed flattening of the variability in the chemical compounds after the heat treatment as assessed by Py–GC–MS analysis and PCA. Heat treatment leads to lignin condensation and cellulose crystallization, which renders the polymers much more stable and uniform.

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