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CHARACTERIZATION OF THERMALLY MODIFIED WOOD AT DIFFERENT INDUSTRIAL CONDITIONS

*In this study European ash wood (*Fraxinus excelsior* L.) was modified at 192°C and 202°C in Thermo-Drewno®, Poland; and at 212°C in Termogenik®, Spain. After modification, samples were characterized by wet chemistry according to standard methods (TAPPI) and by instrumental methods (FT-IR); in addition, surface and physical properties were measured (density, acidity, moisture, water uptake, contact angle, colour) in order to quantify changes due to treatment and temperature. The results showed that chemical composition of modified wood presents a gradual variation according to the heating regime, regardless of the industrial process applied; the greatest differences were obtained in treatment at 212°C compared to untreated wood. Furthermore, the density ($< 0.68 \text{ g}\cdot\text{cm}^{-3}$) of modified wood decreased proportionally to treatment temperature. Colour measurements showed proportional changes to darker colours depending on the treatment temperature. On the other hand, some physical properties did not vary significantly between treatments, obtaining similar values of contact angle (97°-99°) and of moisture content (<7%).*

Keywords: thermal modification, physicochemical properties, European ash wood

Introduction

Thermally modified wood has been widely used and established by several companies and patents because of the improvements gained, such as durability, hydrophobicity and dimensional stability, while the use of chemical products is minimized [Welzbacher and Rapp 2007]. The modification process has different variants, but all involve controlled pyrolysis performed at temperatures ranging from 170°C to 240°C and within a specific atmosphere (steam, oil, vacuum or inert gas) [Esteves and Pereira 2008a].

The thermally modified wood features are well accepted by researchers and companies due to the improved dimensional stability and restricted accessibility

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to fungal activity and degrading agents [Brischke and Rapp 2006; Junghans et al. 2005]. These modifications prolong the service life of wood and wood-based materials and enlarge the range of outdoor applications [Militz 2002].

The changes occurring in the chemical structure of wood during thermal modification, are mainly due to the autocatalytic reactions of the cell wall constituents [Shen, et al. 2010]. Initially carbonic acids will be formed as a result of cleavage of the acetyl groups of particular hemicelluloses, subsequently the monomeric sugar units will be dehydrated to aldehydes [Hakkou et al. 2005]. The lignin complex reacts in small proportions, the reactivity increases only at high temperatures, then the lignin disintegrates into highly concentrated phenol groups, and several condensation reactions with aldehydes occur [Boonstra and Tjeerdsma 2006].

Together with the chemical reconfiguration, the decrease of cell wall microvoids plays an important role on the interactions between water and substrate by reducing water sorption. The microvoids matrix contains hydroxyl groups that absorb water through hydrogen bonds that expand the cell wall to the point where it becomes saturated with water, and therefore changes the moisture content [Yildiz et al. 2004].

On the other hand, due to the chemical reconfiguration of wood some mechanical properties decrease slightly. Thermally modified wood shows a reduction in impact toughness, modulus of rupture, work to fracture and abrasion resistance, and is not suitable for structural applications [Epmeier et al. 2004, Boonstra et al. 2007].

Regarding the industrial methods of modification, the physicochemical changes are produced by the heating regime, process steps and time of treatment. This work analyses the physicochemical differences and the surface properties of European ash wood industrially treated at three different temperatures.

Materials and methods

Wood and industrial treatment

European ash wood (*Fraxinus excelsior L.*) samples were thermally modified according to the industrial production standards of Thermo-Drewno® (Poland) and Termogenik® (Spain). The modification process begins with a fast increase of chamber temperature up to 100°C which allows the wood to dry to within 3-4% of moisture content. Subsequently steam is sprinkled in order to avoid damage to the wood and the temperature in the chamber is raised to its maximum level (192°C, 202°C, 212°C respectively); the last stage is the cooling down and stabilizing of the samples at 25°C (about 24 hours). The processes are similar for the two companies and both use steam. The differences are in the specific schedule that they each use to run the modification steps and to achieve the maximum temperature. Untreated samples were used to compare all analytical characterizations.

Wood macromolecular composition

The chemical analysis of modified wood and control samples was done by wet chemistry according to the standard methods with samples milled through a 4 mm mesh sieve; ashes (TAPPI T211 om-12), ethanol-toluene soluble extract content (TAPPI T264 cm 07), lignin (TAPPI T222 om-02), holocellulose [Wise et al. 1946], cellulose [Rowell 1984] and hemicelluloses as the difference between holocellulose and cellulose. All analyses were carried out three times.

Physicochemical characterization of modified wood

The investigated properties were measured using solid or milled samples depending on the performed test. The moisture content was done in accordance with UNE-EN 13183-1 (oven dry basis), and the basic density (oven dry weight and volume) according to ASTM D2395-14. The water uptake test was performed calculating the weight of water absorbed (%WWA) on samples submitted to a vacuum of 7 mbars for 15 minutes and introduced into a vessel filled with deionized water and maintained fully submerged for 96 hours. The weight of samples was measured at the beginning and after submersion at oven-dry state and at different times (4, 8, 24, 48, 72 and 96 hours) of the experiment. WWA was calculated as shown in Equation 2, where w_i is the initial weight and w_f is the weight after each period of impregnation.

$$\text{WWA (\%)} = ((w_f - w_i) / w_i) \times 100 \quad (1)$$

Moreover, wood pH was measured using 1.25 g of sawdust suspended in 25 mL of distilled water and stirred for 24 hours; after that the pH of the suspension was measured with a CRISON- Basic 20 pH meter. The wood acidity was obtained according to a procedure described by Matsuda [1987], adding 1 mL of 0.1 M HCl to the mixed sample and titrated using 0.01 M NaOH with phenolphthalein as the indicator. The amount of NaOH required to reach the neutralization point was used as a measure for the acidity of dry wood (meq NaOH g⁻¹); then the following equation was obtained.

$$A \text{ (meq/g dry wood)} = (v - v_0) \times 10^{-2} m^{-1} \quad (2)$$

Where v is the volume (mL) of 0.01 M NaOH titration solution used for a wood sample, v_0 the volume (mL) of 0.01 M NaOH solution used for neutralizing 1 mL of 0.1 M HCl diluted in 25 mL of distilled water and m the sample mass (g) used for titration.

In addition, FT-IR spectroscopy was used to analyse the structure of wood components and the chemical changes induced by the treatment. Infrared spectra were collected using the PerkinElmer Spectrum Two FT-IR Spectrometer equipment, by direct transmittance equipped with a Universal Attenuated Total

Reflectance accessory with internal reflection diamond crystal lens. The defined range was from 800 cm^{-1} to 4000 cm^{-1} with 32 scans and a resolution of 8 cm^{-1} .

Wood surface evaluation

To determine the impact of hydrothermal treatment on the wood surface, samples were cut with the following dimensions: $25\text{ mm} \times 25\text{ mm} \times 60\text{ mm}$ (tangential, radial and fibre directions), and the contact angle (OCA System 20 goniometer, provided by Data Physics Co.) was measured using distilled water, ethylene glycol and methylene iodide as reference liquids. The test was performed by the sessile drop technique with single drops of $10\text{ }\mu\text{L}$ dispensed on surface points and the shape recorded with a digital camera during the first second (25 frames per second); after measurements, the surface free energy of each sample were calculated based on Young's equation:

$$\gamma_s = \gamma_{SL} + \gamma_L \cos \theta \quad (3)$$

Where γ is the surface tension (mJ m^{-2}) of the solid ($_s$), the solid-liquid ($_{SL}$), and the liquid ($_L$) interface, respectively.

The optical appearance of modified samples was analysed with a Konica Minolta CM-2600d device and expressed using the CIE-Lab colour space coordinate system L^* , a^* , and b^* (lightness, red-green-axis, and yellow-blue axis). The overall colour change (ΔE^*) was also calculated from the L^* , a^* , and b^* values for each coating system (Eqn. 3). The surface specular gloss at the incidence angles of 20, 60 and 85 was measured using a gloss meter (Konica-Minolta Multi Gloss 268 plus).

$$\Delta E^* = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \quad (4)$$

Results and discussion

The analysis of the structural components of wood (hemicelluloses, cellulose and lignin) and low molecular mass compounds (ethanol-toluene extractives) was done to quantify the influence of treatment on the macromolecular composition of wood. The results obtained (tab. 1) show that macro constituents of European ash wood were gradually altered during the hydrothermal modification according to the treatment intensity.

The proportion of wood components showed remarkable differences compared to untreated wood samples and these differences increased with the treatment temperature. Treatment at 192°C present an increase in extractives of up to 30% and a decrease of about 13% in hemicelluloses, meanwhile the cellulose and lignin show only slight differences. Increasing the temperature of treatment by 10°C (202°C) causes the proportion of extracts to increase by up to

72% and the content of hemicellulose decreases to 39% whilst at the same time the lignin proportion increases by 22%.

At maximum heating regimen (212°C) the differences were intensified between modified and unmodified wood with an increase of over 100% in extractives and 23% in lignin, while the hemicelluloses content decreases by up to 44% and the cellulose content starts to degrade by reducing by 16% compared to the other treatments and control.

Table 1. Changes in the macromolecular composition of wood

Analysis [%]	Hemicellulose	α -Cellulose	Lignin	Extracts	Ash
<i>F.excelsior</i>	18.61 \pm 0.52	45.38 \pm 0.14	28.88 \pm 1.29	4.69 \pm 0.43	1.27 \pm 0.12
<i>F.excelsior192</i>	16.29 \pm 0.22	43.81 \pm 0.61	29.13 \pm 1.11	6.11 \pm 0.93	1.89 \pm 0.10
<i>F.excelsior202</i>	11.44 \pm 0.23	43.93 \pm 0.66	35.12 \pm 1.42	8.06 \pm 0.38	2.16 \pm 0.21
<i>F.excelsior212</i>	10.47 \pm 0.14	38.14 \pm 0.46	35.54 \pm 1.99	9.49 \pm 0.53	2.19 \pm 0.18

Following the results, the hemicelluloses are degraded to a much greater extent than cellulose; however, the extracts and lignin apparently increase and these differences were specifically highlighted in treatments over 200°C. According to the grade of degradation of the macromolecular components of wood, it is possible to classify the intensity of treatment as mild (192°C), intermediate (202°C) and strong treatment (212°C) depending on the heating regimen used.

The hygrothermal modification of wood degraded the hemicelluloses to a greater proportion compared to other components, even with the mild treatment, being the most thermally labile component of wood. One of the main reasons for this behavior is the presence of acetyl groups in the hemicelluloses which are thermally labile causing acid-catalysed degradation of these components [Herrera et al. 2014]. Moreover, the degradation of hemicelluloses involves dehydration reactions that reduce the hydroxyl groups, with a direct effect on the moisture content of thermally modified wood [Korkut et al. 2012].

A relative stability of the cellulose fraction was observed with slight changes in mild (192°C) and intermediate treatments (202°C) but with noticeable degradation on the strong treatment (212°C); a possible reason for this effect is the high degradation of hemicelluloses at this treatment temperature which leads to increases in the crystalline fraction of wood, diminishing the amorphous cellulose which is unstable [Carvalho et al. 2008].

On the other hand, a significant increase of the lignin content and ethanol-toluene extractives was observed. In the case of lignin, the increment of phenolic-OH groups during treatment promoted free ortho-sites from the demethoxylation of guaiacyl and syringyl, allowing cross-linking with fragments of cellulose and hemicelluloses arising from the degradation of polysaccharides. The cross-linking of wood fragments has formed a lignin carbohydrate complex

(LCC) and thus the lignin proportion was established or increased [Choi et al. 2007].

In the case of ethanol–toluene extractives, during the modification process extracts such as fats, waxes and resin acids first migrated to the surface of the wood and above 180°C almost all of the original extractives disappeared from the surface, but new compounds are formed as a result of depolymerization reactions of the cell wall components. These extracts included phenolic-OH groups, monosaccharides and lignin derivatives which can be very soluble in ethanol–toluene mixture [Esteves et al. 2008b].

The physicochemical properties of thermally modified wood are presented in table 2. The results show significant changes in water and the water sorption mechanism with 50% to 60% reduced moisture content (MC) and 40% less water uptake than unmodified wood. This reduction effect is principally due to the removal of accessible water-sorption regions on the wood surface, related to a reduction of OH groups within the wood cell wall as a result of the degradation of macromolecular components [Wikberg and Manau 2004].

Table 2. Physicochemical characterization of modified wood

Analysis	Moisture content [%]	Density [g cm ⁻³]	Acidity [meq g _{dry wood}]	pH	WWA [%]
<i>F. excelsior</i>	11.08 ±0.71	0.69 ±0.04	6.74 10 ⁻²	4.55 ±0.06	54.65 ±1.95
<i>F. excelsior192</i>	5.58 ±0.72	0.68 ±0.04	4.35 10 ⁻²	4.55 ±0.09	34.59 ±0.42
<i>F. excelsior202</i>	4.67 ±0.24	0.65 ±0.02	2.79 10 ⁻²	4.75 ±0.05	33.13 ±0.51
<i>F. excelsior212</i>	4.47 ±0.07	0.63 ±0.02	1.59 10 ⁻²	5.32 ±0.08	33.03 ±0.36

In relation to the density decrease, it is possible to link the elevated degradation on hemicelluloses content into volatile products, which is higher in the intermediate and strong treatment, leading to a progressive diminishing of density in wood. Acidity values of wood decreased with the intensity of treatment, and it was verified by measuring the pH values (pH increased gradually). The most important changes affecting these properties are the decrease of carboxylic acid in the hemicelluloses fraction and the phenolic functions of lignin, showing decreasing acidity values [Willems 2014].

The chemical structure of wood was also characterized by FT-IR to visualize chemical changes caused by hygrothermal modification. The adjusted peaks and their assignments are listed in table 3, and the comparison between FT-IR spectra are presented in figure 3. The FT-IR showed some chemical modifications between treatments and unmodified wood, but their interpretation is very complex as there are several reactions occurring at the same time [Esteves et al. 2013].

There were changes found, however, from the mildest treatment at 192°C with peaks assigned to different stretching vibrations of groups from the main

wood components. Noticeable were the stretching vibrations of different groups O-H, C=O characteristic to carbohydrates (bands at 3340, 1740, 1375 and 1030 cm^{-1}) and stretching of different groups C-H characteristic to lignin (bands at 2897 and 1595 cm^{-1}) and the apparent displacement of groups C-O (1235 cm^{-1}) [Tjeerdsma and Militz 2005].

Table 3. Bands of wood FT-IR spectrum and assignments

Wavenumber [cm^{-1}]	Assignment	Short description
3340	O-H str. of bonded hydroxyl groups	Primary O-H
2942	CH stretching in $\text{CH}_2\text{-CH}_3$ groups	$\text{CH}_2\text{-CH}_3$ Lignin
2910	CH stretching in $\text{CH}_2\text{-CH}_3$ groups	$\text{CH}_2\text{-CH}_3$ Lignin
2897	CH stretching	CH aliphatic Lignin
2873	CH stretching	CH aliphatic Lignin
1740	Bond C=O stretching	Acetyl group Xylan
1734	Bond C=O str. non-conjugated	Carbonyl + esters
1716	conjugated carboxylic groups	Polysaccharides
1595	Aromatic skeletal. vibr. plus C=O str.	Lignin
1424	Aromatic skeletal. vibr. with $\text{CH}_2\text{-CH}_3$	Lignin
1375	C-H deformation vibration	Polysaccharides
1235	Syringyl ring plus C-O stretching	Lignin
1106	Ring asymmetric vibration	Polysaccharides
1030	C-O-C stretching	Polysaccharides

The FT-IR spectra of the intermediate treatment (202°C) showed a similar contour to that found in the mild treatment, with stretching vibrations of different groups O-H, C=O and conjugated carboxylic groups characteristic from carbohydrates (1740 cm^{-1} plus the same bands found in the mild treatment). Moreover, the smoothing of the bands at 1595 and 1235 cm^{-1} corresponds to vibrations in the aromatic ring of lignin and the contributions of syringyl and guaiacyl lignin, suggesting that there was a growth of structural diversity around the aromatic rings [Popescu et al. 2011].

Changes in the spectra of the strong treatment (212°C) are remarkable, and in addition to the differences above, reductions were found in peaks corresponding to hydroxyl groups and the overlapping of the stretch asymmetric and symmetric vibrations of methyl and methylene (2942, 2910, 2873 and 1424 cm^{-1}). The reduction of the intensity of these peaks indicates that in the modified wood less hydroxyl groups are accessible to be acetylated. Besides, the accessibility of hydroxyl groups for acetylation is highly correlated to the availability of water and leads to a drastic change in the hygroscopicity of wood [Pandey and Pitman 2003].

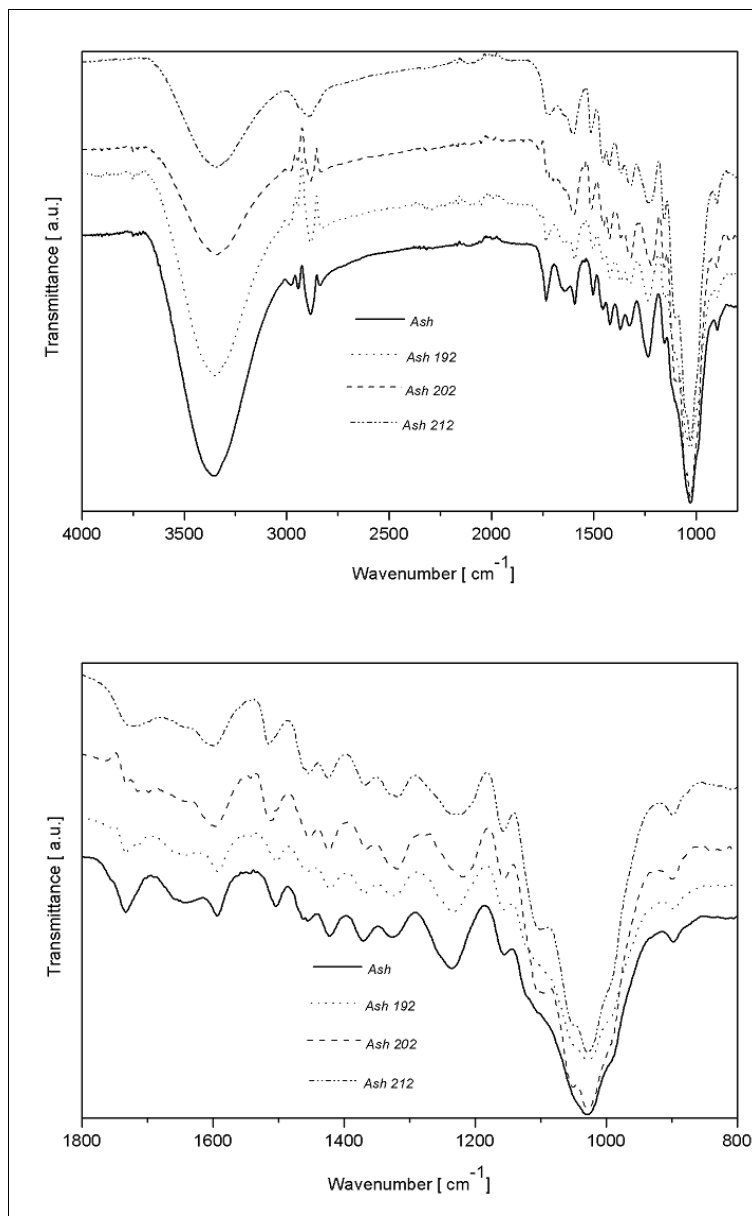


Fig. 1. FT-IR spectra of modified and control samples; above 4000-800 cm^{-1} and below the fingerprint region 1800-800 cm^{-1}

The displacement at 1106 cm^{-1} and the gradual C-O stretching at 1030 cm^{-1} , indicate an apparent modification in characteristic groups of carbohydrates, which is probably due to the modification of the crystallinity of cellulose which influences the CH and OH stretch frequencies [Akerholm et al. 2004].

The evaluation of the modified wood surface wettability was performed according to the results of the equilibrium contact angle with three liquids: water ($\gamma_{LV} = 72.8 \text{ mN/m}$; $\rho = 998 \text{ kg/m}^3$), ethylene glycol ($\gamma_{LV} = 47.7 \text{ mN/m}$; $\rho = 1113 \text{ kg/m}^3$) and methylene iodide ($\gamma_{LV} = 50.8 \text{ mN/m}$; $\rho = 3325 \text{ kg/m}^3$). In addition, the surface free energy was evaluated from the results of the different liquids tested and all the results are presented in table 4.

In general, the modified woods (from mild to strong treatment) showed higher hydrophobicity than untreated wood. The wettability of modified woods by water was drastically decreased by up to 50% and with ethylene glycol it decreased from 25% to 40%. On the other hand, with methylene iodide it showed an opposite trend increasing the wettability from 2% to 5%.

Table 4. Measured values of contact angles and surface free energy of wood

Samples	Contact angle [°]			Surface free energy [mJ m ⁻²]		
	Water	Ethylene glycol	methylene iodide	γ_s^p	γ_s^d	γ_s^T
<i>F. excelsior</i>	66.31 ±3.45	19.54 ±0.64	35.03 ±0.25	6.74	43.94	50.68
<i>F. excelsior192</i>	98.10 ±1.04	25.26 ±1.12	34.33 ±0.40	0.10	52.19	52.2
<i>F. excelsior202</i>	99.12 ±1.10	25.29 ±1.22	33.84 ±0.32	0.10	52.61	52.62
<i>F. excelsior212</i>	99.80 ±1.25	28.72 ±1.20	33.15 ±0.25	0.10	51.58	51.59

All the modification conditions (192°C, 202°C and 212°C) considerably improve the performance of wood against wettability increasing contact angles of water. This effect could be explained as a result of molecular reorientation of the surface functional groups and the cell micropores closure [Windeisen et al. 2007; Wiedenhoef and Miller 2005; Gérardin et al. 2007]. Moreover, the reductions in free reactive hydroxyl groups present in the hemicelluloses limit the wood wetting phenomena [Kocaefer et al. 2008]. Also, the migration of lignin compounds to the surface, creates a new hydrophobic layout cross-linked on the surface.

The results show decreasing contact angles of methylene iodide in the modified wood along with an increase in the disperse value of the surface energy. These results were somewhat expected, taking in to account that the contact angle of the polar liquid (water) was increased due to the thermal modification of the wood. Another theory relates to the chemical groups presented in the tested liquids that may also exist on wood surfaces, thus, interact with them in varying degrees depending on the surface modification [Cao and Kamdem 2007]. Several studies indicate a wetting behavior of this liquid used in thermally modified wood with values of contact angle near to 0° [Cao and Kamdem 2007; Kutnar et al. 2013; Piao et al. 2010].

The results of wood surface free energy revealed a relatively small polar component (acid-base component) compared to the disperse component, which

dropped drastically in modified wood and is probably caused by the removal of acid components during the acetylation in the modification process [Hochmanska et al. 2014]. The reduction of the acid-base component after thermal modification could be supported by the decrease of acidity and the increase of pH after modification [Gindl and Tschegg 2002].

The optical characterization of thermally modified wood has been defined by the CIE-Lab colour space and glossiness; the measured values are shown in table 5 and graphically in figure 2. A preliminary visual assessment exhibits gradual darkening of the original wood colour to the strong modification. This effect is due to oxidation of the degrading products during treatment [Korkut et al. 2012].

Colour values of untreated ash wood presented a lightness L^* of 82.52, a red/green hue a^* of 3.49, a yellow/blue hue b^* of 20.16, a chroma value C^* of 20.46 and a hue angle of 80.16. After the thermal treatment, the initial colour of ash wood became gradually darker (decreasing the L^* value) with a slight shift from yellow to red (increasing hue a^* and decreasing the hue angle).

The glossiness was measured perpendicular to the grain at 20°, 60° and 85° (tab. 5), and showed a remarkable decreasing trend of gloss at 60° up to 61.2% and at 20°, approximately 82.5% less. In the case of gloss at 85° the results are diverse. According to the results at 60°, the unmodified wood was classified as *half-matte* (15.50) and in all treatments it was changed to *matte* (6.87 to 6.04).

In several end-use applications the gloss values at an angle of 60° are very important, commonly used when lower than 90 gloss units. The values obtained across the grain section showed a good linear correlation between gloss at 60° and thermal modification. This tendency is similar to that found in some wood species after thermo-mechanical modification [Bekhta et al. 2014], showing that in general, the glossiness decreased with an increasing heating regime independent of the treated wood specie [Aksoy et al. 2011].

Table 5. Measured values of colour (CIE-Lab) and gloss on modified and control samples

Samples	Colour						Gloss			
	L^*	a^*	b^*	ΔE^*_{ab}	C^*	h	20°	60°	85°	classification
<i>F. excelsior</i>	82.52 ±5.67	3.49 ±0.54	20.16 ±1.02	–	20.46 ±2.65	80.16 ±4.67	8.86 ±0.25	15.5 ±0.64	5.86 ±0.36	<i>Half matte</i>
<i>F. excelsior</i> 192	55.15 ±2.31	10.75 ±1.04	25.12 ±1.77	30.21	27.33 ±2.36	66.83 ±2.69	1.21 ±0.14	6.87 ±0.22	1.89 ±0.10	<i>Matte</i>
<i>F. excelsior</i> 202	42.22 ±2.65	10.11 ±0.47	18.79 ±0.78	42.21	21.34 ±2.78	61.67 ±2.77	1.04 ±0.11	6.64 ±0.33	1.81 ±0.12	<i>Matte</i>
<i>F. excelsior</i> 212	37.91 ±2.01	8.94 ±0.54	14.28 ±0.71	46.57	16.86 ±1.77	57.89 ±1.99	2.13 ±0.17	6.04 ±0.31	5.88 ±0.10	<i>Matte</i>

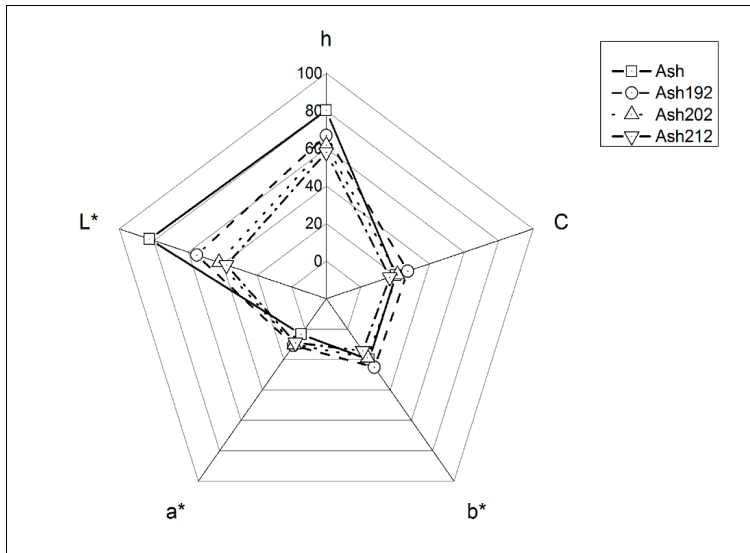


Fig. 2. Graphical representation of colour (CIE-Lab) measurements on modified and control samples

Conclusions

The European ash wood thermally modified at different industrial and heating conditions presented significant changes in the macromolecular composition induced by different physicochemical reactions occurring simultaneously. The modified samples were gradually altered during the hygrothermal modification according to the treatment intensity, resulting in a remarkable decrease in hemicelluloses content and an increase in extractives and lignin content. These structural components were altered, especially in treatments over 200°C and in a smaller proportion in the mildest treatment at 192°C; these alterations were evaluated by FT-IR spectra where the stretching of functional groups related to hemicelluloses were noticeable from the spectrum of the treatment at 192°C and the bands of groups associated as lignin components were changing in the spectrum of treatments at 202°C and 212°C.

The changes in physical properties were related to the chemical modifications that occur on wood during treatment. The darker colour after treatment, therefore, is caused by changes in the wood matrix when the treatment temperature is increased beyond 100°C. At this point, the content of hemicelluloses started to decrease, the lignin content increased and simultaneously the less stable extractive compounds were released from the wood. All these effects gradually change the pH and acidity of the wood, and are physically manifested by colour change to darker tones, meanwhile, the release of volatile compounds helps to reduce the free radicals able to attract water to the wood surface varying the acidity, pH and wettability of wood.

All treatments have a better dimensional stability and lower water affinity than unmodified wood, proved by wettability tests. The ash wood thermally modified at different temperatures, showed an interesting increase in quality characteristics, including colour and surface properties, which is an exceptional value in the solid timber market, and can be used as surface layers in outdoor applications as well.

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List of standards

TAPPI T211 om-12 – Ash in wood, pulp, paper and paperboard: combustion at 525°

TAPPI T264 cm-07 – Preparation of wood for chemical analysis

TAPPI T222 om-02 – Acid-insoluble lignin in wood and Pulp

Acknowledgements

The authors would like to thank the Basque Government (scholarship of young researchers training and project IT672-13) and the University of the Basque Country (US13/07) for financially supporting this research project. Special thanks to Poznan University of Life Sciences.

Submission date: 15.05.2015

Online publication date: 5.09.2016