Sorption and thermodynamic properties of wood of *Pinus canariensis* C. Sm. ex DC. buried in volcanic ash during eruption

Cristina Simón¹ · Luis García Esteban¹ ·
Paloma de Palacios¹ · Francisco García Fernández¹ ·
Alberto García-Iruela¹ · Raquel Martín-Sampedro² ·
María E. Eugenio²

Abstract The hygroscopicity and thermodynamic properties of *Pinus canariensis* wood buried in volcanic ash, dating from 1100 BC, were studied and compared with recently felled juvenile and mature wood of the same species. The sorption isotherms were obtained by the saturated salt method at 35 and 50 °C. The isotherms were fitted using the Guggenheim–Anderson–de Boer model. The thermodynamic parameters were determined following the Clausius–Clapeyron integration method. To understand the behaviour of each type of wood, the chemical composition, infrared spectra and X-ray diffractograms were determined for each sample. The mature wood has a higher sugar content and lower extractive content than the juvenile and the buried wood. For both temperatures, the isotherm of the mature wood is above the isotherm of the juvenile wood and this, in turn, is above the isotherm of the buried wood, primarily influenced by the higher cellulose and hemicellulose contents and lower extractives content in the mature wood, resulting in a higher number of accessible –OH groups. Degradation of the buried wood due to high temperatures explains why its isotherms are below the isotherms of the recent wood. The energy involved in the desorption process is greater than in adsorption. Similarly, more energy is involved in the mature wood than in the juvenile wood, and the energy involved in the juvenile wood is greater than in the buried wood.

✉ Cristina Simón
cristina.simon@upm.es

¹ Departamento Sistemas y Recursos Naturales. Cátedra de Tecnología de la Madera. Escuela Técnica Superior de Ingeniería de Montes, Forestal y del Medio Natural, Universidad Politécnica de Madrid, Ciudad Universitaria, 28040 Madrid, Spain

² Instituto Nacional de Investigación y Tecnología Agraria y Alimentaria, INIA, Carretera de la Coruña, km 7.5, 28040 Madrid, Spain

Introduction

Few studies have defined sorption behaviour in old and/or buried wood, but none have determined the hygroscopic behaviour of old wood that has been buried under volcanic ash. Knowing the hygroscopic response of these types of samples, subjected to extreme conditions, provides very valuable information for better understanding of the sorption mechanisms of wood.

The equilibrium moisture content (EMC) values are due, at least in part, to the number of –OH groups in the cell wall polymers and the accessibility of these groups (Rautkari et al. 2013, 2014). The chemical components of the cell wall undergo degradation, principally of the polysaccharides, during the ageing process of the wood (Fengel 1991). The same changes were found in wood that had been buried for 12,000 years (Iiyama et al. 1988). This circumstance explains the difference in the hygroscopic behaviour of old and/or buried wood compared to recent wood.

Several recent studies determined the hygroscopicity of old wood that forms part of historic objects. Bratasz et al. (2012) defined the behaviour of 21 species and Popescu and Hill (2013) studied samples of *Tilia cordata* Mill. of various ages. In both cases, the old wood came from historic objects which had been kept under room conditions. Popescu and Hill (2013) concluded that there was no correlation between the physical age of the historic samples and their sorption behaviour. However, other studies found differences between the hygroscopic response of old and recent wood. Esteban et al. (2006, 2008a) reported that old *Pinus sylvestris* L. wood describes a sorption isotherm above that of recent wood in both adsorption and desorption.

Esteban et al. (2009, 2010) also compared the sorption behaviour in wood of *P. sylvestris* L. aged 1170 ± 40 BP and *Quercus* spp. aged 5910 ± 250 BP that had been buried for a long time with the sorption behaviour of recently felled samples of the same species. The results showed higher EMC in the buried wood than in the recent wood caused by an increase in the amorphous zones.

Various authors found that wood exposed to high temperatures undergoes changes in the cell wall, which clearly affects the hygroscopic properties of this wood (Murata et al. 2013; Olek et al. 2013; Willems et al. 2013).

The finding of wood buried in volcanic ash after a deposit of pyroclastic materials during eruption made it possible to study a material subjected to exceptional natural conditions, outside the context of industrial processes or laboratory controlled experiments. It was a unique opportunity to compare this wood with a recently felled sample of the same species to determine whether any chemical modifications of the cell wall had occurred, if the hygroscopic response was different and whether the thermodynamic parameters associated with the sorption process differed between the two types of wood.

The buried wood had also been used to determine the most recently dated eruption on the island of Gran Canaria and was therefore a sample of very high scientific value.

The objective of this study was to compare for the first time the hygroscopic and thermodynamic behaviour of recently felled juvenile and mature wood of *Pinus canariensis* C. Sm. ex DC. with that of wood of the same species more than 3000 years old found buried under volcanic ash on the island of Gran Canaria (Spain). To do this, the 35 and 50 °C isotherms were plotted, the chemical composition was analysed, and infrared spectrum and X-ray diffractogram were used.

Materials and methods

The sample of old wood of *P. canariensis* C. Sm. ex DC. was obtained from the trunk of a tree that had been buried under volcanic ash discovered in 1966 in Cañada de las Arenas (Gran Canaria). The age of the tree was determined as 3075 ± 50 years BP, dating it to 1100 BC. Nogales and Schmincke (1969) described this tree.

The buried pine was discovered in 1966 at a quarry extracting volcanic ash (lapilli), commonly used as a construction material and in agriculture. The tree was found protruding about 5.5 m from the ashes, still in its original vertical position, although only the heartwood was conserved. The trunk diameter at the base was approximately 40 cm. It had no branches, as a result of the mechanical action of the falling lapilli. The same phenomenon was observed in 1949 during an eruption on the island of La Palma, where the Canary Island pines were not completely buried but were stripped of their branches by falling lapilli, giving them the appearance of posts (Nogales and Schmincke 1969). The sample was taken from a radial section at the top of the tree. As the growth tables for Canary Island pine compiled by Climent et al. (1993) estimated that for diameters of 40 cm the mean age of this species is about 100 years, the sample extracted from a section at the upper part of the tree can be considered to contain only mature wood.

The samples of juvenile and mature recent wood were taken from a pine tree known as “Pino de Pílancones”, on Gran Canaria (Genova and Santana 2006). Both samples were taken from a radial section: the juvenile sample from the zone between rings 9–16 and the mature wood from rings 40–60.

The recommendations of COST Action E8 saturated salt method (Themelin et al. 1997) were used to obtain the 35 and 50 °C sorption isotherms. The test pieces of juvenile, mature and buried wood measured $10 \times 10 \times 1 \text{ mm}^3$.

The isotherms were plotted from 10 equilibrium points corresponding to 10 different salts (Table 1). Samples were submerged in water to ensure saturation of the cell wall. After this, the desorption isotherms were plotted. The samples were considered to have reached equilibrium in each salt when the weight difference was no more than 0.1% when they were weighed in a 24-h interval. It took two months to obtain the desorption isotherms. After this process, the wet weight of the samples was determined. The samples were then placed in a desiccator with phosphorous pentoxide for 40 days and dried to anhydrous state, and the EMC were calculated.

The adsorption isotherms were then plotted using the same criteria as for desorption. This process took 1 month.

Table 1 Water activity on a scale from zero to one (a_w) for 35 and 50 °C isotherms

Salt	a_w for 35 °C isotherm	a_w for 50 °C isotherm
LiCl	0.1117	0.1105
CH ₃ COOK	0.2137	0.2006
MgCl ₂	0.3200	0.3054
K ₂ CO ₃	0.4255	0.4091
Mg(NO ₃) ₂	0.4972	0.4544
SrCl ₂	0.6608	0.5746
NaCl	0.7511	0.7484
KCl	0.8295	0.8120
BaCl ₂	0.8940	0.8823
K ₂ SO ₄	0.9671	0.9582

The Guggenheim–Anderson–de Boer (GAB) model was used, as it is appropriate for obtaining the fit of the sorption isotherm for all relative humidity (RH) values (Arevalo-Pinedo et al. 2004; Jannot et al. 2006):

$$X = \frac{K \cdot C_g \cdot a_w}{(1 - K \cdot a_w)(1 - K \cdot a_w + C_g \cdot K \cdot a_w)} \cdot X_m \quad (1)$$

where X is the *EMC* (%), X_m is the monolayer saturation moisture content (%), C_g is the Guggenheim constant (dimensionless), K is the constant (dimensionless), and a_w is the water activity on a scale of zero to one (dimensionless).

The isotherm fits were considered valid when the correlation coefficient (R) was higher than 0.990 and the root mean square error (RMSE) was lower than 4% (Viollaz and Rovedo 1999; Esteban et al. 2008a, 2009).

The three types of wood—recently felled juvenile and mature wood and wood buried by ash (buried wood)—were analysed chemically. The ethanol extractives were determined following the standard procedure published by National Renewable Energy Laboratory NREL/TP-510-42619 (Sluiter et al. 2005). Lignin and sugar contents were analysed by two-step hydrolysis, applying NREL Laboratory Analytical Procedure NREL/TP-510-42618 (Sluiter et al. 2011). Sugar content was quantified by high-performance liquid chromatography in an Agilent Technologies 1260 HPLC fitted with an Agilent Hi-Plex Pb column and an RI detector system. Separation was conducted at 70 °C with a flow of 0.6 ml min⁻¹ using water as the mobile phase. Two replicates of each sample were measured, and the mean was calculated.

The cellulose and hemicellulose contents, both hexoses and pentoses, were obtained from the amount of sugars determined (Easty and Malcolm 1982; Vaaler et al. 2005; Jones et al. 2006):

$$\text{Cel (\%)} = \text{Glu} - \left(\frac{1}{3} \cdot \text{Man} \right) \quad (2)$$

$$\text{Hexosan (\%)} = (\text{Gal} + \text{Glu} + \text{Man}) - \text{Cel} \quad (3)$$

$$\text{Pentosan (\%)} = \text{Ara} + \text{Xyl} \quad (4)$$

$$\text{Hem (\%)} = \text{Hexosan} + \text{Pentosan} \quad (5)$$

where the contents (in %) are Cel: cellulose, Glu: glucan, Man: mannan, Gal: galactan, Ara: arabinan, Xyl: xylan and Hem: hemicellulose.

A 95% confidence interval was determined for each compound of the samples.

Infrared spectroscopy (FTIR) was used to identify the functional groups. 3 mg sample of dry sawdust was taken from each wood and mixed with 250 mg potassium bromide to produce a disc for analysis. Data were obtained after 128 scans using a Nicolet spectrophotometer, model Magna-IR 750 Series II, with a precision of 4 cm^{-1} .

X-ray diffraction was applied to determine the crystalline fraction of the cellulose. The diffractometer used was a Philips X'Pert model (45 kV, 40 mA, 1800 W). The diffractograms were used to calculate the crystallinity index, CrI% (Mihrianyan et al. 2004; Huo et al. 2013), and the crystallite length, L_{hkl} (Jahan and Mun 2005; Lionetto et al. 2012):

$$\text{CrI\%} = 100 \cdot \frac{I_{002} - I_{AM}}{I_{002}} \quad (6)$$

where CrI% is the crystallinity index, I_{002} is the overall intensity of the peak at 2θ about 22° (counts), and I_{AM} is the intensity of the base line at 2θ about 18° (counts).

$$L_{hkl} = \frac{K \cdot \lambda}{d(2\theta) \cdot \cos \theta} \quad (7)$$

where L_{hkl} is the crystallite length ($\text{\AA}$), K is the correction factor ($K = 0.9$ (dimensionless)), λ is the emitting wavelength ($\lambda = 1.54056 \text{ \AA}$) and $d(2\theta)$ is the full width at half maximum (in radians) (FWHM).

To compare the CrI% and L_{hkl} data, a 95% confidence interval was defined for each sample.

The number of theoretical $-\text{OH}$ groups in moles per gram of dry wood was calculated using the equation developed by Rowell (1980) (Hill and Jones 1996, 1999; Chang and Chang 2002; Hill 2006; Hill et al. 2009, 2010; Rautkari et al. 2013):

$$\frac{3A}{162} + \frac{3B}{162} + \frac{2C}{132} + \frac{D}{180} \quad (8)$$

where the contents (in %) are A : cellulose, B : hexosan hemicellulose, C : pentosan hemicellulose and D : lignin.

Assuming that the $-\text{OH}$ groups in the crystalline portion of the cellulose are inaccessible, the accessible $-\text{OH}$ content was estimated by correcting the hydroxyl group content of the cellulose with the crystallinity index (Hill and Jones 1999; Hill 2006; Hill et al. 2009, 2010; Rautkari et al. 2013).

Total isosteric heat of sorption was calculated using the equation (Avramidis 1997):

$$Q_s = q_s + \Delta H_{\text{vap}} \quad (9)$$

where Q_s is the total isosteric heat of sorption (J mol^{-1}), ΔH_{vap} is the latent vaporisation heat (constant) (J mol^{-1}), and q_s is the net isosteric heat of sorption (J mol^{-1}).

Net isosteric heat of sorption was calculated using the integration method of the Clausius–Clapeyron equation (Peralta et al. 1997):

$$q_s = -R \cdot \frac{d(\ln(a_w))}{d(\frac{1}{T})} \quad (10)$$

where q_s is the net isosteric heat of sorption (J mol^{-1}), a_w is the water activity (dimensionless), T is the absolute temperature (K), and R is the universal gas constant (J mol K^{-1}).

Total heat of wetting is the heat involved in the sorption process from fibre saturation point (FSP) to oven drying (Siau 1995). This value was calculated using the integration of the net isosteric heat curve (Avramidis 1997):

$$W_0 = \int_0^{m_f} q_s \cdot dm \quad (11)$$

where W_0 is the total heat of wetting (J mol^{-1} dry wood), q_s is the net isosteric heat of sorption (J mol^{-1}), and m_f is the FSP moisture content (%).

Results and discussion

The EMC values of the juvenile, mature and buried wood are shown in Fig. 1. In all cases the isotherms describe a type II sigmoid (Olek et al. 2013) characteristic of cellulosic materials (Avramidis 1997; Zaihan et al. 2011; Englund et al. 2013). The isotherm fits with the GAB model were considered valid, as they show R values greater than 0.990 and RMSE values less than 4% for all cases. Table 2 shows the parameters of the model.

Figure 1 shows the relation between the sorption behaviour of the juvenile wood compared to the mature wood and between these two woods and the buried wood. The first comparison indicates a relation between growth ring location and hygroscopic behaviour. This was corroborated by authors who studied different species, both softwoods and hardwoods (Zobel et al. 1968; Lenth and Kamke 2001; Militz et al. 2003; Majka and Olek 2008; Neimsuwan et al. 2008; Esteban et al. 2015; Simon et al. 2015). In this study, the EMC values of the mature wood are higher than those of the juvenile wood for each temperature (Fig. 1), concurring with Zobel et al. (1968), Militz et al. (2003), Neimsuwan et al. (2008), Esteban et al. (2015) and Simon et al. (2015). The differences between the EMC values obtained can be explained by the chemical composition of the cell wall. Hemicellulose is the cell wall compound that contributes the highest number of sorption sites to the

Fig. 1 35 and 50 °C sorption isotherms of juvenile, mature and buried wood of *Pinus canariensis*

process, followed by cellulose and lignin (Christensen and Kelsey 1959). The juvenile wood has less hemicellulose and cellulose content than the mature wood (Table 3), which would explain why the juvenile wood EMC values are lower. The greatest difference between the two compositions is the extractives content (Table 3). This is also responsible for the lower EMC (Wangaard and Granados 1967; Choong and Achmadi 1991; Hernandez 2007), because extractives are deposited in the matrix and the mesopores, preventing water from entering the sorption sites (Song et al. 2014).

At both temperatures, the sorption isotherms of the buried wood are below the isotherms of the recent wood, in adsorption and desorption (Fig. 1). This result does not concur with observations made on old wood of *P. sylvestris* and *T. cordata*

Table 2 Results of the GAB fit for the 35 and 50 °C isotherms

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35 °C isotherm			50 °C isotherm	
Juvenile				
Adsorption	X_m (%)	RH (%) ^a	X_m (%)	RH (%) ^a
	3.91 ± 0.22	32.30	3.88 ± 0.44	32.10
	EMC _a (%) ^a	EMC _f (%)	EMC _a (%) ^a	EMC _f (%)
	3.35	0.56	3.05	0.83
Desorption	X_m (%)	RH (%) ^a	X_m (%)	RH (%) ^a
	4.58 ± 0.23	33.50	4.54 ± 0.37	32.70
	EMC _d (%) ^a	EMC _f (%)	EMC _d (%) ^a	EMC _f (%)
	3.84	0.74	3.38	1.16
Mature				
Adsorption	X_m (%)	RH (%) ^a	X_m (%)	RH (%) ^a
	4.16 ± 0.16	31.90	4.03 ± 0.38	32.00
	EMC _a (%) ^a	EMC _f (%)	EMC _a (%) ^a	EMC _f (%)
	3.63	0.53	3.36	0.67
Desorption	X_m (%)	RH (%) ^a	X_m (%)	RH (%) ^a
	4.86 ± 0.14	32.40	4.49 ± 0.29	32.10
	EMC _d (%) ^a	EMC _f (%)	EMC _d (%) ^a	EMC _f (%)
	4.13	0.73	3.65	0.84
Buried				
Adsorption	X_m (%)	RH (%) ^a	X_m (%)	RH (%) ^a
	3.63 ± 0.30	33.40	3.34 ± 0.37	32.40
	EMC _a (%) ^a	EMC _f (%)	EMC _a (%) ^a	EMC _f (%)
	2.86	0.77	2.47	0.87
Desorption	X_m (%)	RH (%) ^a	X_m (%)	RH (%) ^a
	4.38 ± 0.13	34.40	4.01 ± 0.35	34.00
	EMC _d (%) ^a	EMC _f (%)	EMC _d (%) ^a	EMC _f (%)
	3.31	1.07	2.88	1.13

X_m monolayer saturation moisture content, RH relative humidity, EMC_a equilibrium moisture content in adsorption, EMC_d equilibrium moisture content in desorption, EMC_f water taken up via monolayer sorption after the point of inflexion

^a Point of inflexion of the isotherm

(Esteban et al. 2006, 2008a; Popescu and Hill 2013) or buried wood of *P. sylvestris* and *Quercus* spp. (Esteban et al. 2009, 2010). Using the description made by Nogales and Schmincke (1969), it cannot be confirmed whether the falling pyroclastic ash that buried the tree carbonised any part of it. However, other studies of the same volcanic event (Mangas et al. 2002) reported the presence of carbonised wood in the area, which was used to date the eruption. For the samples to have been carbonised, the temperature would have had to reach at least 280 °C. Although the sample obtained from the upper part of the tree shows no sign of carbonisation, it is likely that when the wood was buried under the pyroclastic ash, it was subjected to this (or an even higher) temperature due to the lack of oxygen after burial. Therefore, the low EMC content obtained in the wood buried under ash compared to recently felled wood or the EMC obtained in other samples of buried wood (Esteban et al. 2009, 2010) shows the influence of the high temperatures, with an effect similar to the findings in some studies of thermally treated wood (Stamm and

Table 3 Chemical composition of juvenile, mature and buried wood

	Juvenile				Mature				Buried			
	$\bar{x}$	σ	X_1	X_2	$\bar{x}$	σ	X_1	X_2	$\bar{x}$	σ	X_1	X_2
Glucan (%)	28.61	0.03	28.57	28.65	31.36	0.41	30.78	31.93	21.75	0.29	21.35	22.15
Xylan (%)	1.99	0.07	1.89	2.09	1.41	0.01	1.40	1.42	1.76	0.02	1.73	1.79
Galactan (%)	0.81	0.06	0.73	0.89	1.31	0.06	1.23	1.39	0.75	0.06	0.67	0.83
Arabinan (%)	0.06	0.08	0.00	0.17	0.14	0.02	0.11	0.17	0.11	0.01	0.10	0.12
Mannan (%)	8.62	0.08	8.51	8.73	9.53	0.01	9.52	9.54	6.59	0.16	6.37	6.81
Total sugar (%)	40.09	0.10	39.95	40.23	43.75	0.49	43.08	44.42	30.96	0.41	30.39	31.53
Cellulose (%)	25.74	0.06	25.66	25.82	28.18	0.42	27.60	28.76	19.55	0.24	19.23	19.87
Hemicellulose (%)	14.35	0.15	14.14	14.56	15.57	0.07	15.47	15.67	11.41	0.18	11.16	11.66
Hexosan (%)	12.30	0.16	12.08	12.52	14.02	0.05	13.95	14.09	9.54	0.15	9.33	9.75
Pentosan (%)	2.05	0.01	2.04	2.06	1.55	0.02	1.53	1.57	1.87	0.03	1.83	1.91
Lignin (%)	22.15	0.16	21.92	22.38	21.95	0.05	21.88	22.02	20.64	0.37	20.12	21.16
Extractives (%)	29.37	0.94	28.07	30.67	24.39	1.09	22.88	25.90	43.76	0.22	43.46	44.06

X_1 lower limit confidence interval at 95% probability, X_2 upper limit confidence interval at 95% probability

Hansen 1937; Hill 2006; Murata et al. 2013; Olek et al. 2013; Rautkari et al. 2013, 2014; Willems et al. 2013). Studies on temperatures of pyroclastic materials reported that it is usual for temperatures to reach 200–300 °C (Voight and Davis 2000; Freundt 2003; Gurioli et al. 2012; Major et al. 2013).

The values of the minimum of the derivative of the EMC in relation to the RH correspond to the points where multilayer sorption starts to predominate over monolayer sorption (Fig. 2). The saturation moisture content of the monolayer (X_m) reaches higher values in the mature wood and lower values in the buried wood, in both desorption and adsorption and at the two temperatures (Table 2). This behaviour described between the recent wood and the buried old wood is similar to

Fig. 2 Derivatives of the 35 and 50 °C sorption isotherms of juvenile, mature and buried wood of *Pinus canariensis*

that observed in an earlier study (Esteban et al. 2010). Moreover, the multilayer prevails over the monolayer at around 30% RH. This result was obtained in earlier studies of other species (Esteban et al. 2009, 2010; Fernandez et al. 2014), indicating that this value is independent of species, tree age, position of the wood in the tree and type of exposure.

The FSP values are particularly low (Table 4), due to the high extractives content (Table 3). Unlike other softwoods, Canary Island pine wood has subsidiary tissue around the resin canals, with a high proportion of axial parenchyma (Esteban et al. 2005) and carbohydrates due to the ability of the species to accumulate large amounts of reserve starch (Climent et al. 1998, 2002), probably developed as a response to extreme situations (fire, drought, etc.) (Climent et al. 1998).

The chemical composition of the juvenile, mature and buried wood of *P. canariensis* is shown in Table 3. Significant differences are observed between the compositions of the three types of wood. The mature wood has higher sugar content than the juvenile and the buried wood. As a result, the cellulose and hemicellulose contents are higher in the mature wood than in the buried wood (8.63 and 4.16%, respectively) and in the juvenile wood (2.44 and 1.22%). The higher cellulose content in the mature wood than in the juvenile wood agrees with the findings of earlier studies (Larson 1966; Fengel and Wegener 1983; Tsoumis 1991; Yokoyama et al. 2002; Illic et al. 2003; Bertaud and Holmbom 2004; Balakshin et al. 2005; Rowell 2005; Peura et al. 2008; Simon et al. 2015). In addition, Iiyama et al. (1988) studied the behaviour of the chemical compounds in old woods that had been buried and concluded that the sugar content decreased considerably. This may be due to the intense attack by fungi and bacteria on old woods, which primarily causes hemicellulose degradation (Blanchette 2000; Singh 2012). However, in the wood buried in ash, the influence of attack by fungi or bacteria as hemicellulose degrading agents probably had less influence than high temperatures, which cause degradation in the cell wall polysaccharides, particularly the hemicellulose (Hill 2006; Olek et al. 2013; Rautkari et al. 2014). The lignin content is higher in the juvenile wood than in the buried wood, by 1.51% (Table 3), because lignin changes chemically over time and its structure increasingly differs from its original state (Fengel 1991). However, the most significant changes occur in the extractives content, which is higher in the buried wood than in the mature wood and the juvenile wood (by 19.37 and 14.39%, respectively). This behaviour is similar to that observed in other aged wood, and it can be generally stated that ageing of wood causes an increase in

Table 4 Thermodynamic parameters

	FSP (%)	Total heat of wetting (kJ mol ⁻¹ dry wood)	FSP (%)	Total heat of wetting (kJ mol ⁻¹ dry wood)
Juvenile	14.73	0.58	15.00	0.74
Mature	16.69	0.61	17.86	0.87
Buried	11.09	0.56	11.83	0.72

extractives content (Fengel 1991). This high extractives content in the xylem of Canary Island pine explains the durability of the resinous heartwood of this species in the typical balconies of buildings on the islands, some dating from the 17th century.

The FTIR spectra of the three types of wood have the same characteristic peaks. No chemical changes were detected between them. In studies by Esteban et al. (2008b, 2010), differences were observed between the functional groups in aged wood of *P. sylvestris* L. and *Quercus* spp. compared to recently felled wood of the same species.

The crystallinity indices and crystallite lengths of the juvenile, mature and buried wood show no significant differences (Table 5), indicating that there are no variations throughout the radial direction or as a result of the wood being buried. Andersson et al. (2003) determined that in *Picea abies* the crystallinity index and crystallite length increased slightly close to the pith and remained practically constant after the tenth growth ring. Andersson et al. (2004) obtained similar results for the crystallinity index in *P. abies* and *P. sylvestris*. In relation to buried wood, an earlier study comparing buried and recently felled wood found variations in both the crystallinity index and the crystallite length (Esteban et al. 2010). The non-significant differences observed in this study may be due to the different burial conditions, as the wood was subjected to high temperatures that could also have caused variations in the crystallinity (Hill 2006).

Table 6 shows the values corresponding to the number of theoretical –OH groups in the wood and the estimated content of accessible –OH groups taking into account the crystallinity index of the sample. The mature wood has higher –OH content, both in the number of theoretical hydroxyl groups and the number of accessible –OH groups, followed by the juvenile wood and the buried wood. This result was expected, as the sugar content is higher in the mature wood and the hemicellulose and the cellulose are the compounds that provide a higher number of –OH groups to the wood (Hill et al. 2010). This would explain the hygroscopic behaviour experienced by each type of wood (Fig. 1). However, experimental techniques such as hydrogen–deuterium exchange (Hill et al. 2009) are required to determine the number of accessible –OH groups more accurately.

Table 5 Crystallite length L_{hkl} and crystallinity index CrI%

	L_{hkl} (Å)				CrI%			
	$\bar{x}$	σ	X_1	X_2	$\bar{x}$	σ	X_1	X_2
Juvenile	102.18	39.44	57.54	146.81	40.07	6.69	32.49	47.46
Mature	74.53	10.75	62.37	86.70	36.75	3.05	33.30	40.20
Buried	110.35	31.89	74.26	146.44	44.34	7.92	35.28	53.31

X_1 lower limit confidence interval at 95% probability, X_2 upper limit confidence interval at 95% probability

Table 6 Estimate of –OH concentration

	Number of theoretical –OH (mmol g ^{–1})	Estimated number of accessible –OH groups (crystallinity of cellulose considered) (mmol g ^{–1})
Juvenile	8.58	6.67
Mature	9.27	7.35
Buried	6.82	5.21

The study of the thermodynamic properties showed that the net isosteric heat of sorption is higher in desorption than in adsorption for the three types of wood when the EMC are below the FSP (Fig. 3). This behaviour occurs because more energy is required in the desorption process than in adsorption (Siau 1995; Avramidis 1997). The same result was obtained in other studies of different species (Esteban et al. 2008a, b, 2009, 2010; Fernandez et al. 2014). Moreover, the isosteric heat decreases as the EMC increases. This trend was observed in other softwoods and hardwoods (Weichert 1963; Avramidis and Dubois 1992; Peralta et al. 1997; Hill et al. 2010) and is caused by a very strong interaction between the water molecules and the substratum at low EMC (Telis et al. 2000), due to the existence of highly polar sites on the surface of the material that are occupied by water molecules forming a monolayer (McMinn and Magee 2003). After saturation of the monolayer (X_m) at around 30% RH and 4–5% EMC (Table 2) in the three types of wood studied (juvenile, mature and buried), the isosteric heat of the process is primarily due to multilayer sorption. Once the most active sites are occupied, the molecules bond to the less active sites, resulting in lower heats of sorption (Li et al. 2011).

Total heat of wetting is higher in desorption than in adsorption for the three types of wood (Table 4). This was expected, given that the net isosteric heat curve in adsorption is below the curve in desorption, which means that more energy is involved in the desorption process. Similarly, the higher total heat of wetting in the mature wood than in the juvenile wood, and the higher value in the juvenile wood than in the buried wood, means that the energy involved in the mature wood is greater than in the other two woods, with the lowest value occurring in the buried wood. In addition, Avramidis (1997) identified a proportional relation between total heat of wetting and the total number of –OH groups accessible to water. As a result, the mature wood has a higher number of accessible hydroxyl groups. This concurs with the results obtained using the equation developed by Rowell (1980) (Table 6).

Conclusion

The EMC of the mature wood are higher than those of the juvenile wood, which in turn are higher than those of the buried wood, for both temperatures studied, due to their chemical composition. The mature wood has higher cellulose and hemicellulose contents and lower extractives content than the juvenile wood and the buried wood. The most significant change occurs in the extractives content, which is

Fig. 3 Comparison of the net isosteric heat of sorption of juvenile, mature and buried wood of *Pinus canariensis*

greater in the buried wood, resulting in a better response of this wood to adverse conditions.

Like thermally modified wood, the wood buried in volcanic ash experienced polysaccharide degradation, resulting in lower EMC than in the recent wood.

The points of inflexion where multilayer sorption predominates over monolayer sorption are at around 30% for the three types of wood.

The number of accessible sorption groups is higher in the mature wood than in the juvenile wood and the buried wood.

The amount of energy involved in the desorption process is greater than in adsorption. Total heat of wetting is higher in the mature wood than in the juvenile wood and the buried wood.

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