

Comparison of the hygroscopic behaviour of 205-year-old and recently cut juvenile wood from *Pinus sylvestris* L.

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Abstract – The hygroscopic response of the juvenile wood of *Pinus sylvestris* L. from recently cut trees from the Valsáin Forest in Segovia, Spain (new wood) was compared to that of the juvenile wood of the same species used in roof rafters installed at the end of the eighteenth century (old wood), which came from the same forest. The 35 °C isotherms were plotted using the saturated salts method, and the mathematical fit used was the GAB model. The infrared spectrums and the X-ray diffractograms were used in order to study the possible chemical variations and crystallinity indices of the cell wall. The adsorption-desorption loop of the old wood is above the loop of the new wood, although the hysteresis coefficient is higher in the old wood. The peaks corresponding to the -OH groups are similar, although the degree of crystallinity is significantly lower in the old wood. While cellulose crystallinity differs between the old and new wood, and has a major influence on wood hygroscopicity, other modifications in the amorphous components of the cell wall may have contributed to the changes in hygroscopicity between the old and new wood.

hygroscopicity / sorption isotherm / juvenile wood / Fourier transform infrared spectroscopy (FTIR) / X-ray diffraction (XRD)

Résumé – Comparaison du comportement hygroscopique d'un bois juvénile de *Pinus sylvestris* L. âgé de 205 ans avec celui d'un bois juvénile récemment coupé. La réponse hygroscopique du bois juvénile de *Pinus sylvestris* L. provenant d'arbres récemment coupés de la forêt de Valsáin en Segovia, Espagne (bois récent) a été comparée à celle de bois juvénile de la même espèce utilisé comme bois de charpente à la fin du XVIII^e siècle (vieux bois), originaire de la même forêt. Les isothermes de sorption à 35 °C ont été obtenus par la méthode des sels saturés, et l'ajustement mathématique utilisé était le modèle GAB. La spectrographie infrarouge et la diffractométrie par rayons X- ont été utilisées pour étudier d'éventuelles différences de composition chimique et d'indices de cristallinité de la paroi cellulaire. La boucle d'adsorption-désorption du vieux bois est au-dessus de celle du bois récent, tandis que le coefficient d'hystérésis est plus élevé dans le vieux bois. Les pics correspondant aux groupes -OH sont similaires, bien que le degré de cristallinité soit significativement plus bas dans le vieux bois. Bien que ces différences de cristallinité puissent expliquer pour une bonne part le contraste hygroscopique entre bois vieux et actuel, des modifications au niveau des composés amorphes de la paroi peuvent également être invoquées.

hygroscopicité / isotherme de sorption / bois juvénile / spectroscopie infrarouge par transformée de Fourier / diffraction par rayons X

1. INTRODUCTION

Wood is a hygroscopic material because of the presence of -OH groups in the hydrophilic polymers of the cell wall, celluloses and hemicelluloses, which are capable of fixing water molecules by means of hydrogen bonds. However, not all the -OH groups can be reached by the water vapour molecules, because the cellulose molecules form crystalline regions where the -OH groups of the adjacent molecules are in a parallel arrangement [33]. As a result of this process, wood varies its moisture content in relation to the temperature and the relative

humidity of the surrounding air. Plotting the adsorption and desorption isotherms of wood at given temperatures provides information about its hygroscopic behaviour, enabling comparisons to be made between wood of different species and within the same species. Wood hygroscopicity can be modified by physical or chemical means, or by biological degradation. It is reduced by exposure to high temperatures [20], due to a decrease in the hemicellulose content [10]. From the chemical point of view, acylation is a generic process which includes acetylated, butyrylated and hexanoylated wood. All of these chemical processes cause a decrease of the hydroxyl groups in

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the wood, resulting in lower wood hygroscopicity [7, 35]. Finally, the hygroscopic behaviour of wood degraded by fungus depends on the fraction of wood eliminated: if it is hemicellulose, for example, the hygroscopicity decreases, as this is the most hygroscopic component [18]. However, wood also modifies its hygroscopic behaviour naturally with the passage of time, due to the reorientation of the molecules that are likely to participate in the sorption process [31]. This affirmation is related to the degree of crystallinity, as the ability of wood to take up water by sorption decreases as the degree of crystallinity of the material increases [24]. Some studies have been done on the degree of crystallinity and its possible implications in the hygroscopic response [29, 37].

Very few studies have been done on the hygroscopicity of old wood, although from the point of view of reusing materials, such studies are of great importance given that hygroscopicity is an important property which has a direct effect on the dimensional stability of wood. The aim of this study was to compare the hygroscopicity of 205-year-old wood of *Pinus sylvestris* L. with recently cut wood of the same species, both from the same forest, by plotting their 35 °C isotherms, analysing the crystallinity index of the cellulose and using Fourier transform infrared spectroscopy (FTIR).

2. MATERIALS AND METHODS

The samples of old wood were obtained from the renovation work carried out on the Casa del Gobernador (Governor's House) in Aranjuez, Madrid, Spain. The original house was the work of the architect Juan de Villanueva, and dates from the end of the eighteenth century. The samples were taken from the principal roof rafters, which had been taken down at the end of 2000 and held in a storehouse in Madrid.

The old wood used for this study was protected from sunlight at all times, both during its use in the building and subsequent storage. The average annual atmospheric climatic conditions were 14.4 °C and 59% relative humidity while the wood formed part of the building, and 15.1 °C and 56% relative humidity during storage in Madrid. The mixture of straw and mud between the planking and the tiling meant that the rafters did not reach high temperatures and therefore thermal degradation of the wood was avoided. Brown-rot fungi observed at both ends of two of the rafters was removed. Special care was taken not to use old wood with traces of fungi for determining the EMC in order to avoid modifications in the hemicellulose content.

According to the architectural project information, the wood used for the construction of the Casa del Gobernador was Valsáin pine (*Pinus sylvestris* L.). This was verified by means of appropriate microscopic identification.

Slices were obtained from each rafter, and from these a radial slice was obtained using a radial saw, from which the final test pieces were obtained using a slicer. A check was made to ascertain whether the pieces studied were from mature or juvenile wood, as the hygroscopic response of the two types of wood is significantly different [3, 5, 14]. The method developed by Macaya [22] for *Pinus sylvestris* L. was used, which relates the juvenile-mature cambial age to the number of rays/mm². It was determined that all the pieces were of juvenile wood.

$$\text{ray density} = 59.541 - 0.96900 \cdot \text{age} - \frac{4636.8}{1 - 88.476 \cdot \text{age}}$$

The application of this model determined that the age of the pieces of old wood was from 25 to 30 years. Other studies on the same wood presume it to be mature at this age [25]. However, as the cambial age is quite variable between trees of the same forest and between different regions of provenance, particularly in conifers, the old wood samples

were considered to be of juvenile wood in accordance with the specific preliminary study on the forest from which they came, in terms of the number of rays and the length of the tracheids, which enabled it to be established that up to ring 40, with a 5% confidence level, the juvenile-mature cambial age did not occur [22].

The new wood was obtained from six trees felled during scheduled cutting of *Pinus sylvestris* L. in the Valsáin Forest in Segovia, Spain, located in region of origin 10, Sierra de Guadarrama [6]. The first or basal log was selected from each of the six trees and the central radial board was cut out of each log in a sawmill. The wood was immediately air-dried to a moisture content of 35% and then cut with a radial saw to obtain test samples between rings 25 and 30. The old and new wood test samples for sorption tests were 15 mm long (L), 10 mm wide (R) and 1 mm thick (T). In both cases there were fifteen test samples for each moisture equilibrium point, divided into three flasks holding five samples each.

The COST Action E8 saturated salts method was used to plot the 35 °C adsorption-desorption curves. The thermostatic baths were verified by using microcrystalline cellulose in accordance with the Community Bureau of Reference protocol, Certified Reference Materials CRM 302 "Water content of microcrystalline cellulose (MCC) in equilibrium with the atmosphere above specified aqueous saturated SALT solutions at 25 °C". After the humidity content of each of the salts was obtained, the values were compared with the certified value of the Community Bureau of Reference, CRM 302. According to the COST Action E8 protocol and the Community Bureau of Reference, the equipment is regarded as suitable if $\text{Value}_{\text{certified}} - \text{uncertainty}_{\text{CRM302}} \leq \text{Value}_{\text{obtained}} \leq \text{Value}_{\text{certified}} + \text{uncertainty}_{\text{CRM302}}$ [9, 16]. Nine equilibrium points per isotherm were obtained, corresponding to the nine salts shown in Table I. For the plotting of the desorption isotherm of the old wood, the first step consisted of placing the test samples in water for three days in order to saturate them. When this was achieved, the test samples were removed to eliminate excess water and placed in the sample flask of each salt, where they remained until equilibrium was reached in all the salts; that is, when the results of two consecutive weighings taken twenty four hours apart showed a difference of no more than 0.1%. This process took up to 2 months, after which the test samples were weighed in order to obtain the wet weight and then placed in a desiccator with phosphorous pentoxide in order to attain the anhydrous state and calculate the equilibrium moisture contents (EMC) by means of the following equation:

$$\text{EMC}\% = \frac{P_w - P_0}{P_0} \cdot 100$$

P_w : wet weight;

P_0 : anhydrous weight.

In the case of the new wood, the test samples were placed directly in the sample holders, still with the moisture contents above the fibre saturation point, after which the same procedure was followed as for the old wood. Once the desorption process had finished, all the sample pieces were dried in phosphorous pentoxide for 40 days until anhydrous weight was reached, after which the adsorption isotherms were plotted following the same criteria as for desorption. This process took up to 30 days.

The Guggenheim, Anderson and Boer-Dent (GAB) model was used to plot the isotherms. This model is particularly appropriate for obtaining a good fit in studies which include high relative humidities of over 90%, in which adsorption through capillarity and the multi-layer effect play a relevant role [38]. The fit for GAB model corresponds to the equation:

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

where,

X: equilibrium moisture content;

Table I. Equilibrium humidity contents and hysteresis coefficients (C_H) for 35 °C isotherms.

Salt	a_w	Old wood			New wood		
		EMC _d (%)	EMC _a (%)	C_H	EMC _d (%)	EMC _a (%)	C_H
LiCl	0.1117	2.44	2.44	1.00	1.62	1.40	0.86
CH ₃ COOK	0.2137	4.48	3.64	0.81	3.59	2.92	0.81
MgCl ₂	0.3200	6.14	4.97	0.81	4.10	3.27	0.80
K ₂ CO ₃	0.4255	6.96	6.07	0.87	5.38	4.34	0.81
Mg(NO ₃) ₂	0.4972	8.58	7.21	0.84	6.09	4.90	0.80
SrCl ₂	0.6608	11.58	9.87	0.85	8.21	6.55	0.80
NaCl	0.7511	13.15	11.56	0.88	9.96	7.99	0.80
KCl	0.8295	15.68	13.77	0.88	11.60	9.62	0.82
BaCl ₂	0.8940	18.73	16.43	0.88	14.96	13.06	0.87

X_m : moisture content corresponding to complete monolayer coverage of all available sorption sites;

C : constant;

K : Guggenheim constant;

a_w : RH, relative humidity or water activity on a scale of zero to one.

The fit, both in desorption and adsorption, was regarded as valid if the regression coefficient R was greater than 0.990 and the RMS was less than 4% [2, 12, 38]. A hysteresis coefficient was used for comparing the isotherms of the old and the recently cut wood, as the values of this coefficient make it possible to know how much more stable the wood is in relation to the changes of relative humidity which cause the wood to change from a state of adsorption to desorption and vice versa:

$$c_H = \frac{EMC_a}{EMC_d}$$

c_H : hysteresis coefficient;

EMC_a: equilibrium moisture content in adsorption;

EMC_d: equilibrium moisture content in desorption.

All the glass material required was produced using the models specified in the European Community document for obtaining the sorption curves of cellulose [16]. The thermostatic baths used were of the Grant brand, model Y38, with a 38-L capacity, forced circulation, a range of 20–99 °C and a precision of 0.1 °C. The scales used for the weighings were of the Sartorius brand, model Handy H110, with a range of 0–100 g and a precision of 0.0001 g. The oven used to reach the anhydrous weight was of the Heraeus brand, model VT6025, with a range of 0–200 °C and a precision of 0.1 °C.

FTIR was used as a qualitative tool for identifying functional groups because of its high specificity in terms of assigning absorption bands [28]. Any chemical change that may have introduced new bonds, such as carbonyl or carboxyl bonds in the case of an acylation, would be shown in the spectrum by the corresponding absorption band. The qualitative analysis was done from the identification of the functional groups by comparing them with tabulated data (Tab. III).

FTIR is particularly useful for detecting the -OH groups, which are responsible for wood hygroscopicity. There are even a number of studies distinguishing free-OH groups from those involved in inter-molecular and intra-molecular bonds [23]. For the infrared analysis a sample of each of the woods used in the plotting of the sorption curves was prepared, as well as a control sample of pure cellulose. Sawdust was obtained from each of the pieces of wood for this purpose, and the sawdust and the cellulose were dried in an oven at 103 ± 2 °C for 24 h. The reason for using totally anhydrous samples is to remove all the -OH groups belonging to water molecules. The samples were cooled

in a desiccator with silicagel at room temperature. Thirty milligrams was taken from each one and mixed with potassium bromide, and all the material became finely separated dust. This was compressed into a disc in a vacuum press for 5 min. A Perkin-Elmer 1605 FTIR spectrophotometer with a resolution of 4 cm^{-1} was used.

In order to analyse the possible changes in the crystalline fraction of the cellulose, X-ray diffraction was used (XRD Technique) as established by Hermans and Weidinger [15]. By using the diffractograms the crystallinity index $CrI\%$ was calculated [24, 39] as well as the length of the crystallite, L_{hkl} [11]:

$$CrI\% = 100 \cdot \frac{I_{002} - I_{AM}}{I_{002}}$$

$CrI\%$: crystallinity index;

I_{002} : maximum intensity;

I_{AM} : lowest diffraction intensity at $2\theta = 22^\circ$.

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

K : correction factor, $K = [0.9]$;

λ : emitting wavelength. $\lambda = 1.54056 \text{ \AA}$;

$d(2\theta)$: full width at half maximum (in radians) (FWHM).

The samples were obtained between rings 25 and 30, as the degree of cellulose crystallinity does not remain constant throughout the tree but rather increases from the pith to the bark, although from ring 15 it does remain practically constant [39]. The equipment used consisted of a Philips X³Pert diffractometer, whose measuring conditions are 45 Kv tension, 40 mA intensity and 1800 w power. The samples were measured from $2\theta = 5^\circ$ to $2\theta = 90^\circ$, with step size $\Delta\theta = 0.04^\circ$ and a time interval of 1 s on continuous mode. The total time for each diffractogram was 35 min. One degree slits were used in primary and secondary optics and a receiving slit of 0.15 mm.

ANOVA tests were conducted in cases where the normality and homocedasticity hypotheses were met and the Kruskal-Wallis test was used for cases in which either of the two hypotheses was not met. The statistical calculations were done using the MATLAB V.6.5 Release 13 programme for a 95% significance level.

3. RESULTS

The thermostatic baths were shown to be in compliance with the Bureau of Reference Materials CRM 302 requirements.

Table I shows the equilibrium moisture contents and the hysteresis coefficients for old wood and new wood.

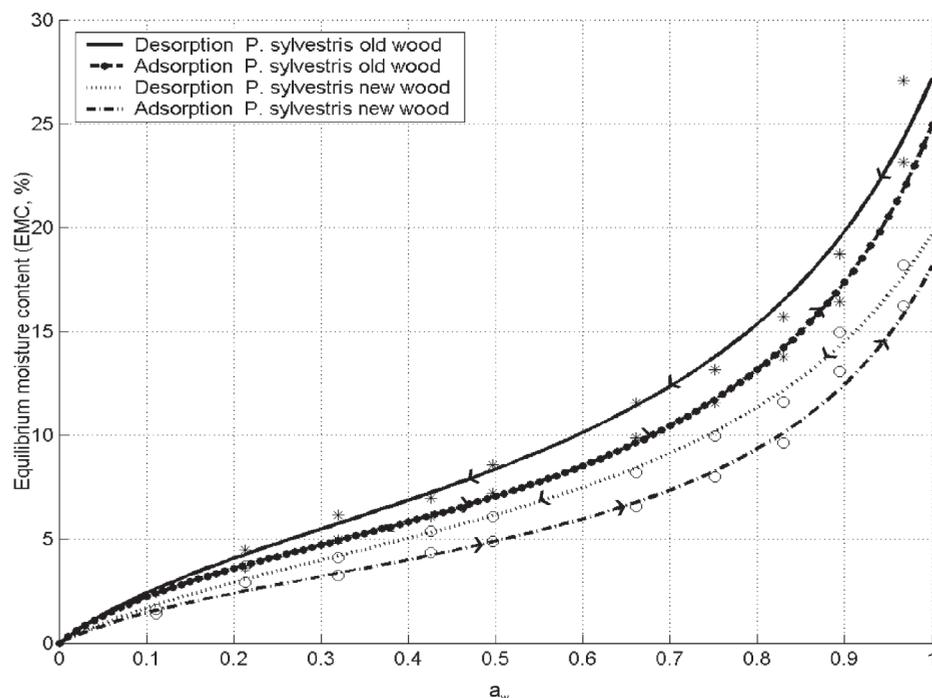


Figure 1. Sorption isotherms at 35 °C.

Table II. Thirty-five degree Celsius isotherm values. RMS: Root Medium Square.

Isotherm	Old wood			New wood		
	X_m	K	C	X_m	K	C
Desorption	6.415 ± 0.191	0.7744 ± 0.223	6.308 ± 0.0473	4.941 ± 0.298	0.7619 ± 0.366	5.53 ± 0.0925
	Correlation coefficient		RMS (%)	Correlation coefficient		RMS (%)
	0.9901		1.125	0.9968		1.803
	RH (%)		EMC _d (%)	RH (%)		EMC _d (%)
	31.6		5.70	31.4		4.12
Adsorption	5.023 ± 0.104	0.8047 ± 0.1507	7.78 ± 0.0246	3.544 ± 0.297	0.8113 ± 0.491	6.727 ± 0.0916
	Correlation coefficient		RMS (%)	Correlation coefficient		RMS (%)
	0.9969		0.420	0.9962		1.491
	RH (%)		EMC _a (%)	RH (%)		EMC _a (%)
	31.0		4.82	30.4		3.23

The four isotherms show appropriate fits for a type II ($C > 2$) curve [21, 34]. They also have regression coefficients higher than 0.990, and the RMS is lower than 4% (Fig. 1).

Table II shows the points after which multilayer sorption begins to prevail. These points were obtained by using the minimum of the derivative of equilibrium moisture content in relation to the relative humidity [1]. In the old wood the monolayer saturation moisture content in desorption X_m , meaning the maximum amount of water taken up by the sample via monolayer sorption, is 6.4%. Furthermore, the point of inflexion of the isotherm corresponds to a moisture content of 5.7% and occurs at 31.6% relative humidity. These findings indicate that

from 31.6% to 100% relative humidity the water taken up by the sample via monolayer sorption is minimal, at only 0.7% of the total. In the case of the new wood, an X_m of 4.9% and an inflexion point of 4.1% occurring at 31.4% relative humidity were obtained. From 31.4% the water taken up via monolayer sorption was 0.8%. If the desorption results of both isotherms are compared, it can be seen that there is a notable difference in the monolayer saturation moisture content, which is higher in the old wood (by 1.5%), although the relative humidity percentage at which multilayer sorption begins to prevail over monolayer sorption is practically the same in both cases (31.6 and 31.4%, respectively).

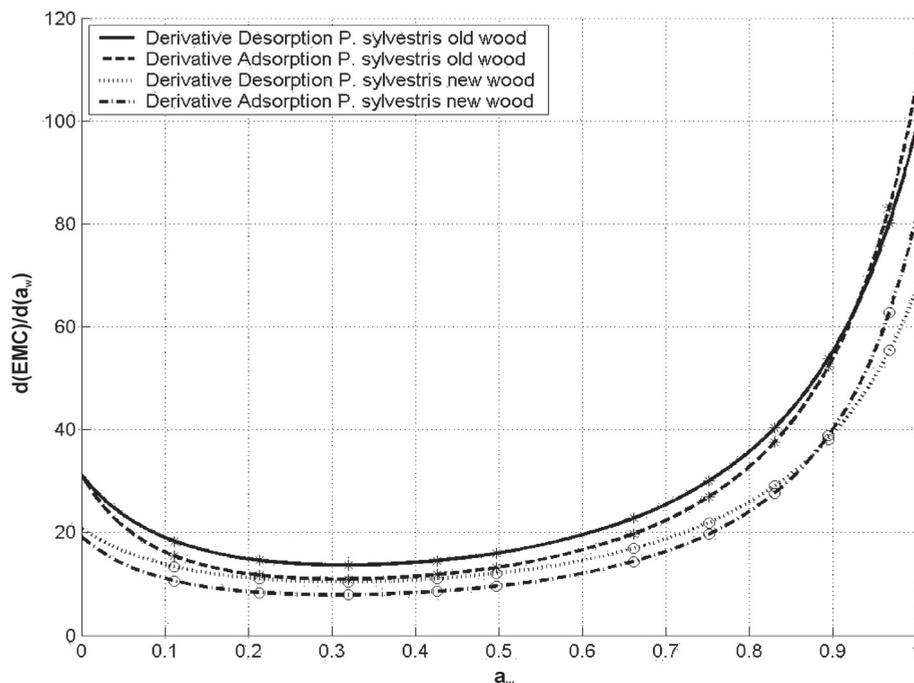


Figure 2. Derivatives of the wood sorption curves at 35 °C.

In the case of old wood in adsorption, the monolayer saturation moisture content is $X_m = 5.0\%$ and the point of inflexion of the sorption curve of the isotherm corresponds to a moisture content of 4.8% and occurs at 31% relative humidity. From 31% the water taken up via monolayer sorption is only 0.2%. For new wood in adsorption, the monolayer saturation moisture content is $X_m = 3.5\%$ and the point of inflexion of the sorption curve of the isotherm corresponds to a moisture content of 3.2% and occurs at 30.4% relative humidity. From 30.4% the water taken up via monolayer sorption is only 0.3%.

Regardless of the age of the wood, the point of inflexion in desorption or adsorption – after which the prevalence of multilayer sorption over monolayer sorption occurs – remains practically constant (Fig. 2). In both groups of isotherms, after the point at which multilayer sorption begins to prevail over monolayer sorption the water taken up via monolayer sorption in the wood is less in the old wood than in the new wood, by around 0.1%, in both desorption and adsorption.

On applying the mean test at the significance level of 0.95, the hysteresis coefficient EMC_d/EMC_a of the old wood is higher than that of the new wood. If they are compared point by point, all the coefficients show values which agree with this affirmation. Despite the fact that at point 11.17% of the LiCl salt the old wood has a higher hysteresis coefficient than in the new wood (1.00 as opposed to 0.86), it was considered that this point should be removed as there was a possibility that entropy peaks may have an influence at low humidities [41]. Kadita et al. [17] speculated that these peaks were due to the fact that the hydroxyl groups in the amorphous region form bonds in the wood when the wood is oven-dried. They consider that when a small number of water molecules are adsorbed in these places, the molecule chains regroup in a different manner. Without

considering the point corresponding to LiCl, the mean of the hysteresis coefficient is 0.85 in old wood and 0.81 in new wood. This means that a decrease in the free energy within the hysteresis cycle has occurred [32] and therefore the old wood is more hygroscopically stable than the new wood.

In relation to the use of FTIR, the cellulose spectrum was examined first (Fig. 3) and it was shown that the cellulose is material with a clear peak of the -OH groups ($3\,342\text{ cm}^{-1}$). This peak is associated with the water linked by hydrogen bonds to the -OH groups of the cellulose and hemicellulose and does not appear at all in the spectrums of the pure water [28]. Another clear peak in the cellulose is that of the carbon-hydrogen links, at $2\,899\text{ cm}^{-1}$, and the deformation peak of this link at $1\,431\text{ cm}^{-1}$. No other peaks typical of wood appear, such as C = O or C-O bonds, or the peak characteristic of lignin at $1\,510\text{ cm}^{-1}$ [4]. From the results shown in Table III, no chemical change can be noted between the spectrums of the old or new wood, which could have a significant influence on the hygroscopicity of the wood. The appearance of carbonyl and carboxyl peaks does not seem to be the result of a change in the wood over time, as these peaks appear in both the old and the new wood. Rather, their origin is due to the numerous bonds of this type which appear in the lignin molecule. Slight variations can be seen in the carbonyl peak, but it is quite a confused zone with two very close peaks where one may hide the other (Fig. 4). Acylations that would have caused a very characteristic peak at $1\,740\text{ cm}^{-1}$ were not detected [4, 7, 8].

The chemical changes that the wood may have undergone and which may have resulted in a variation of the sorption properties should act on the hydroxyl groups, replacing them with other groups or giving rise to bonds between them.

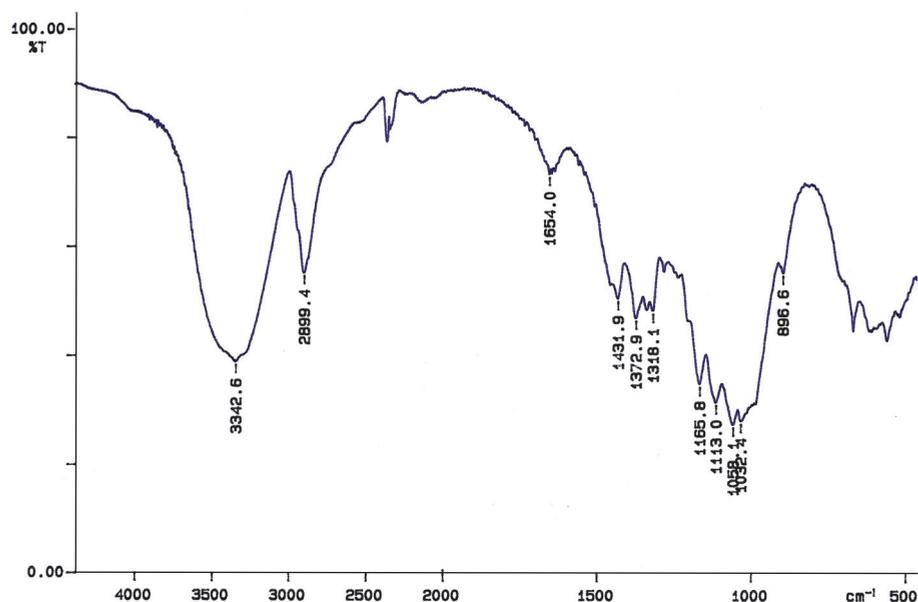


Figure 3. FTIR spectrum of cellulose.

Table III. Main functional groups present in wood and its absorption band. Barker and Owen [4]; Michell and Higgins [23]. Chang and Chang [7]. Functional groups of old wood and new wood.

Functional group	Wavenumber (cm ⁻¹)	Old wood		New wood	
		\bar{x}	σ	\bar{x}	σ
Hydroxyl (–OH)	3400–3500	3382.4	2.9	3360.3	2.0
C-H bond	2890–2930	2912.0	12.8	2912.4	18.2
Carbonyl (C = O) ¹	1730–1750	1720.0	17.4	1708.2	22.0
Lignin ²	1510	1511.0	0.2	1509.7	0.6
Deformation strains CH ₃ , CH ₂ ³	1370	1372.5	0.3	1372.8	1.1
Carboxyl (C–O)	1200	1269.7	0.6	1269.7	1.2
Ester linkages	1030–1170	1099.7	8.3	1117.2	37.9

¹ Vibration of the acetyl and carboxyl groups of the “xylan” ring.

² Vibrations of the benzene ring in the lignin.

³ Deformation in both the cellulose and the hemicellulose.

In relation to the use of X-ray diffraction (XRD Technique), it can be seen that the crystallinity index of the old wood is lower than in the new wood by around 4% (Tab. IV). This was considered a substantial difference, as Mihranyan et al. [24] determined that variations in the crystallinity indices in pure cellulose from 81 to 93% for low relative humidities (11%) modify the EMC by around 1%, while for 75% relative humidities they modify the EMC by 2%.

As the water sorption capacity decreases with the increase in the degree of crystallinity of the material, this means that the old wood must show higher equilibrium moisture contents [24, 40]. The mean length of the cellulose crystal in the old wood is less than in the new wood, which means that the degree of crystallinity of the new wood is greater than in the old wood. The application of a mean test confirms that the data obtained

Table IV. Crystallite length L_{hkl} and crystallinity indices $CrI\%$.

	L_{hkl}		$CrI\%$	
	\bar{x}	s	\bar{x}	s
New wood	246.61	3.15	92.89	6.94
Old wood	225.83	2.71	88.77	4.49

is significantly different, with a probability of 95%. It can therefore be stated that the old wood presents a higher equilibrium moisture content than the new wood because it has a crystallinity index lower than the new wood.

The use of high temperatures causes changes in the wood hygroscopicity which cause physical and chemical changes in

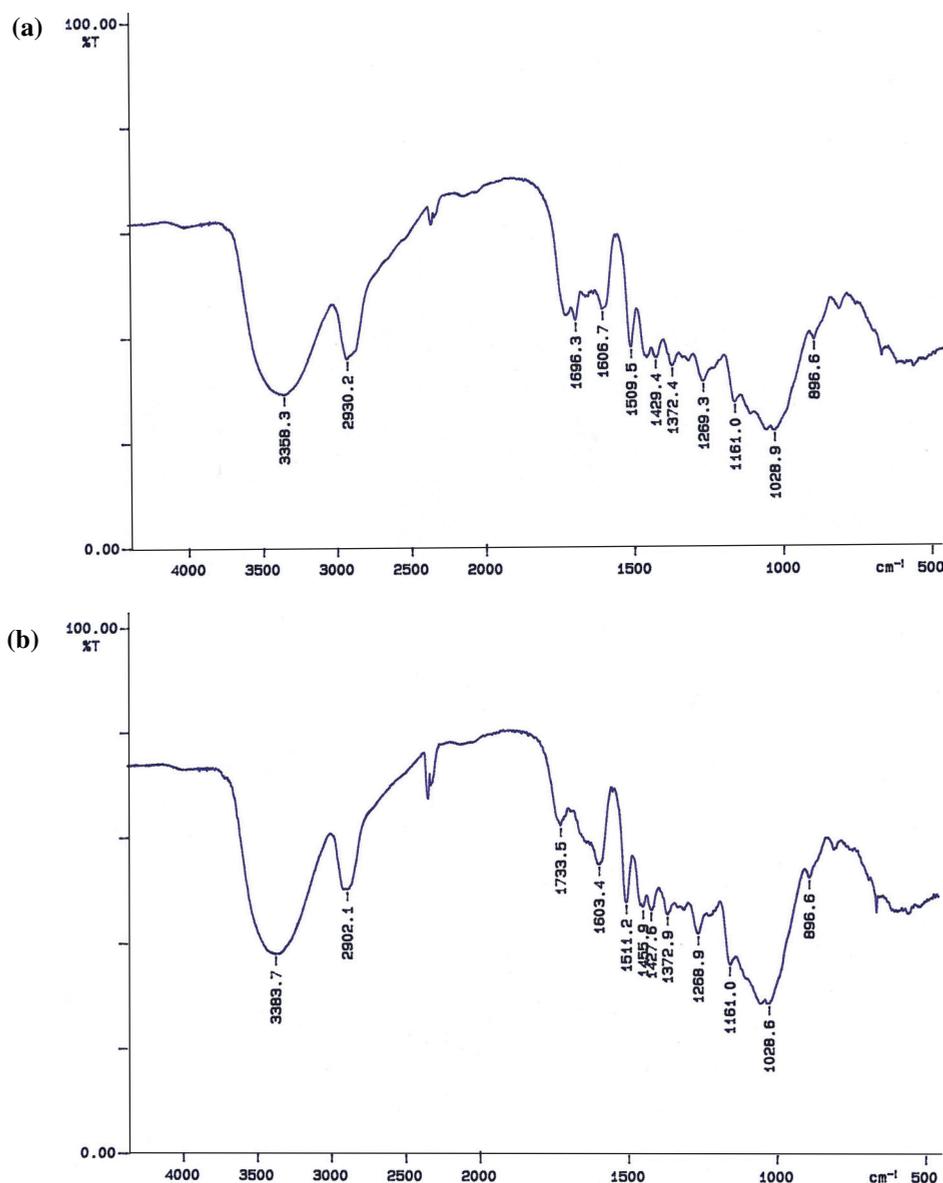


Figure 4. (a) FTIR spectrum of new wood, (b) FTIR spectrum of old wood.

the wood that are different from natural ageing. In fact, the reduction of hygroscopicity in wood subjected to a high temperature cannot be explained by recrystallisation of the cellulose, but fundamentally by chemical changes in the amorphous substances [26]. Therefore, the changes that wood undergoes through natural ageing are not necessarily similar to ageing through artificial processes [13]. Although cellulose is the determining component of the cell wall for water sorption [19], other variations in the amorphous components of the wood (hemicelluloses and lignin) and volatile components may have contributed both to the lower crystallisation coefficient of the old wood and to an increase in its hygroscopicity. In terms of

the volatile components such as polyphenols, a high concentration of these contributes to low wood hygroscopicity [36], while the influence of the alcohol-benzene extractives has an uncertain influence on the hygroscopicity [40]. Perhaps a natural depolymerisation of the hemicelluloses, similar to that produced by high temperatures [27], and the appearance of new regions of accessible OH groups similar to those produced artificially by chemical reaction with organosilicon compounds [30] contribute to the increase in the hygroscopicity of the old wood after centuries of natural ageing.

In relation to the crystallinity index, one factor that directly contributes to the decrease it undergoes is the increase of lignin.

Passialis [29] showed that in wood submerged for thousands of years the lignin content increases up to 3.6 times in comparison with new wood. Although the wood in the present study was not submerged, natural ageing may have caused changes in the chemical composition by decreasing the fraction of carbohydrate composites in favour of the lignin content. Future studies with samples whose ageing process is known will enable these theories to be confirmed.

4. CONCLUSIONS

The old wood presents higher equilibrium moisture content than the new wood, both in adsorption and desorption.

The old wood presents higher hysteresis coefficients than the new wood. This means that a decrease in the free energy within the hysteresis cycle has occurred, and therefore the old wood is more hygroscopically stable than the new wood.

Regardless of the age of the wood, the point of inflexion in desorption or adsorption, after which multilayer sorption prevails over monolayer sorption, remains practically constant, at 30–32% relative humidity.

The total amount of water taken up by monolayer sorption in the old wood is greater than in the new wood, although from the point at which multilayer sorption prevails over monolayer sorption (30–32% RH) less water is taken up via monolayer sorption in the old wood than in the new wood: around 0.1% in both desorption and adsorption.

The old wood and the new wood present similar infrared spectrums, and the hygroscopic differences of the two types of wood cannot be attributed to a chemical change in the cell wall.

The passage of time causes a decrease in the cellulose crystallinity index in the wood, which means that the proportion of amorphous zones increases.

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