

SORPTION AND THERMODYNAMIC PROPERTIES OF OLD AND NEW *PINUS SYLVESTRIS* WOOD

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ABSTRACT

The 35° and 50°C isotherms of juvenile *Pinus sylvestris* L. wood from recently cut trees were compared with those of juvenile wood of the same species previously forming part of an 18th century wooden building in order to determine the thermodynamic properties of the two types of wood through the isotherms. The isotherms were plotted using the gravimetric method of saturated salts in the water activity range of 0.11 to 0.97 for the 35°C isotherm and 0.11 to 0.96 for the 50°C isotherm. The sorption curves were fitted using the GAB method, and the isosteric heat of sorption was obtained by means of the integration method of the Clausius-Clapeyron equation. In both types of wood, the net isosteric heat decreases as the moisture content of the specimen increases, and the maximum values of isosteric heat in the new wood are greater than in the old wood, both in adsorption and desorption. This indicates that the bond energy in the new wood is greater than in the old wood.

Keywords: Thermodynamics, isosteric heat, isotherms, sorption, juvenile wood.

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INTRODUCTION

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 particular importance given that hygroscopicity is a very important property that has a direct effect on the dimensional stability of wood. Wood that has been in use for some time shows different hygroscopic behavior from that of recently cut wood of the same species. Old wood, for instance, has higher equilibrium moisture contents (M_{emc}) than new wood, both in adsorption and in desorption; the hysteresis coefficients are higher than in new wood, indicating a decrease in the free energy in the hysteresis cycle; and the proportion of amorphous zones increases in comparison with recently cut wood (Esteban et al. 2006).

Plotting the sorption isotherms of wood enables its hygroscopic behavior to be known, but it is also very useful for studying the thermodynamic properties of wood (Zhang and Peralta 1999; Aviara et al. 2004). While the bonding of water vapor to the -OH groups in the cell wall is an exothermic process, the loss of the water vapor is endothermic. The adsorption and desorption heat generated are measurements of the energy required to break the intermolecular forces between the water vapor and the substrate (Al-Muhtaseb et al. 2004).

The isosteric heat of sorption is in fact an indicator of the total number of hydroxyl groups that are accessible to water (Avramidis 1997), but it is also an indicator of the state of the water absorbed by the substrate (McMinn and Magee 2003) and it measures the bond strength between the water molecules and the substrate (Avramidis 1997; Quirijns et al. 2005). Knowledge of the isosteric heat of sorption and of the sorption isotherms provides a very important method for characterizing a material and studying its interaction with gaseous systems (Wadsö 1997).

The aim of this study was to establish the sorption isotherms of wood at 35° and 50°C in specimens of recently cut and old *Pinus sylvestris* L. wood, both from the same forest, and to use the isotherms to determine the thermody-

namic properties through net isosteric heat of sorption and total heat of wetting.

MATERIALS AND METHODS

The specimens of old wood (Valsaín pine (*Pinus sylvestris* L.)) were obtained from the renovation work carried out on the Casa del Gobernador (Governor's House) in Aranjuez, Madrid, Spain. The original house, dating from the end of the 18th century, was the work of the architect Juan de Villanueva. The wood was never subjected to aggressive exposure. Fungus was removed from two of the rafters studied in order to avoid modifications in the hemicellulose content.

Eight rafters were studied. From each rafter discs were cut, and from these a radial slice was obtained using a radial saw. A slicer was used to obtain the final test pieces from the radial slices.

Since the hygroscopic response of mature and juvenile wood is significantly different (Helińska-Raczowska and Fabisiak 1999; Bao et al. 2001; Bhat et al. 2001), the wood age was determined using a method developed by Macaya (2002) for *Pinus sylvestris* L., which relates the juvenile-mature cambial age to the number of rays/mm².

$$\text{ray density} = \frac{59.541 - 0.969 \cdot \text{age}}{1 - 88.476 \cdot \text{age}} \quad (1)$$

This model determined that the wood samples taken from the rafters were from rings with an age of 25–30 yr. Other studies on the same species define it as mature at this age (Mutz et al. 2004). 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 specimens were considered to be juvenile 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 95% confidence level, the juvenile-mature cambial age did not occur (Macaya 2002).

The new wood was obtained from 6 trees felled during scheduled cutting (120 yr) of *Pinus sylvestris* L. in the Valsaín Forest in Segovia, Spain. The first or basal log was selected from each of the trees and the central radial board was cut from each log at a sawmill. The wood was air-dried to a moisture content of 35% and then cut with a radial saw to obtain test pieces from the zone of the radial board between rings 25 and 30. The old and new wood test specimens were 15 mm long, 10 mm wide, and 1 mm thick. In both cases there were 15 test specimens for each moisture equilibrium point, divided over 3 flasks holding 5 specimens each. Prior studies using Fourier transform infrared spectroscopy (FTIR) showed that the chemical composition of the old and new wood was similar (García 2004). The COST Action E8 saturated salts method was used to plot the 35° and 50°C isotherms (Themelin et al. 1997). The thermostatic baths were verified using microcrystalline cellulose and the corresponding comparison protocols (Community Bureau of Reference 1989; Jowitt and Wagstaffe 1989). Ten equilibrium points were obtained for each isotherm, corresponding to the ten salts shown in Table 1.

For the plotting of the desorption isotherm of the old wood, the first step consisted of immersing the test specimens in water for 3 d to saturate them. When this was achieved, the specimens were removed in order to eliminate excess water and then placed in the specimen flasks of each

salt, where they remained until equilibrium was reached for all the salts; that is, when the results of two consecutive weighings taken 24 h apart showed a difference of no more than 0.1%. This process took 2 mo, after which the test specimens were weighed to obtain the weight and then placed in a desiccator with phosphorous pentoxide in order to reach the anhydrous state. The M_{emc} were then calculated by means of the following equation:

$$M_{\text{emc}}(\%) = \frac{W_e - W_0}{W_0} \cdot 100 \quad (2)$$

where

W_e = equilibrium weight

W_0 = anhydrous weight

For new wood, the test specimens, still with the moisture contents above the fiber saturation point (M_{fsp}), were placed directly in the specimen holders, after which the same procedure was followed as for the old wood.

Once the desorption process had finished, all the test specimens were dried in phosphorous pentoxide for 40 d until anhydrous weight was reached, after which the adsorption isotherms were plotted following the same criteria as for desorption. This process took 30 d.

The Guggenheim, Anderson, and Boer-Dent (GAB) model was used to plot the isotherms.

TABLE 1. Equilibrium moisture content (M_{emc}) for 35° and 50°C isotherms in old and new *Pinus sylvestris* wood.

Equilibrium moisture content (M_{emc}) for 35° and 50°C isotherms										
Salt	35°C					50°C				
	a_w	Adsorption $M_{\text{emc-a}}$ (%)		Desorption $M_{\text{emc-d}}$ (%)		a_w	Adsorption $M_{\text{emc-a}}$ (%)		Desorption $M_{\text{emc-d}}$ (%)	
		New wood	Old wood	New wood	Old wood		New wood	Old wood	New wood	Old wood
LiCl	0.1117	1.51*	2.41*	1.90 ^{n.s.}	2.25 ^{n.s.}	0.1105	1.30*	2.11*	1.50 ^{n.s.}	2.16 ^{n.s.}
CH ₃ COOK	0.2137	2.89*	3.35*	3.52 ^{n.s.}	3.87 ^{n.s.}	0.2006	2.33*	3.18*	2.61*	3.17*
MgCl ₂	0.3200	3.21*	4.79*	4.03*	5.51*	0.3054	2.96*	4.61*	3.59*	5.01*
K ₂ CO ₃	0.4255	4.29*	5.71*	5.29*	6.34*	0.4091	3.84*	5.47*	4.37*	5.89*
Mg(NO ₃) ₂	0.4972	4.84*	6.92*	6.04*	7.96*	0.4544	4.23*	5.85*	5.14*	6.28*
SrCl ₂	0.6608	6.42*	9.61*	8.20*	10.93*	0.5746	5.32*	8.04*	6.48*	8.76*
NaCl	0.7511	7.98*	11.13*	9.96*	12.55*	0.7484	6.91*	10.52*	8.56*	11.44*
KCl	0.8295	9.52*	13.22*	11.80*	15.10*	0.8120	8.53*	11.93*	10.88*	13.15*
BaCl ₂	0.8940	12.74 ^{n.s.}	15.84 ^{n.s.}	14.96*	18.13*	0.8823	11.17*	15.07*	13.73 ^{n.s.}	16.35 ^{n.s.}
K ₂ SO ₄	0.9671	16.18*	22.56*	18.19*	26.45*	0.9582	14.64*	21.29*	17.07*	23.29*

a_w : water activity. $M_{\text{emc-a}}$: Equilibrium moisture content in adsorption. $M_{\text{emc-d}}$: Equilibrium moisture content in desorption. *: significant. n.s.: not significant.

This model is particularly appropriate for RH greater than 90% (Violaz and Rovedo 1999).

$$M = \frac{KC_g a_w}{(1 - Ka_w)(1 - Ka_w + C_g Ka_w)} M_m \quad (3)$$

where:

$$M = M_{emc}$$

$$M_m = \text{monolayer saturation moisture content}$$

$$C_g = \text{Guggenheim constant}$$

$$K = \text{constant}$$

$$a_w = \text{RH or water activity on a scale of zero to one}$$

The fit was regarded as valid if the regression coefficient $R > 0.990$ and the root mean square error (RMSE) $< 4\%$ (Violaz and Rovedo 1999; Bacour and Daudin 2000; Esteban et al. 2004, 2006).

The thermostatic baths had forced circulation, a range of 20–99°C, and a precision of 0.1°C. The balance had a range of 0–100 g and a precision of 0.0001 g.

The specimens were obtained between rings 25 and 30 to enable the degrees of crystallization of the old and the new wood to be compared (Wang and Chio 1990).

In order to make an individual comparison of the sorption curve points, the t-test was used. In the case of the hysteresis coefficient, as the conditions of normality were not met, the Kruskal-Wallis test was used, in addition to the non-parametric version of the ANOVA test, which compares the medians of two or more samples (MathWorks Inc. 2002). The statistical calculations, the fitting of the sorption isotherms and the calculations of the net isosteric heats and the total heat of wetting were done using the MATLAB 6.5.0 Release 13 program for a 95% significance level.

The thermodynamic parameters obtained through the isotherms were net isosteric heat of sorption and total heat of wetting.

The total isosteric heat of sorption is obtained by means of the Avramidis (1997) equation, which relates the three types of energy participating in the sorption process:

$$Q_s = q_s + \Delta H_{vap} \quad (4)$$

where:

Q_s = total isosteric heat of sorption: Energy released when water is absorbed by the sorption points in the cell walls, or energy required to evaporate water from its bound water phase.

ΔH_{vap} = latent vaporization heat (constant): Energy released when the water vapor condenses, or energy required to evaporate water from its liquid phase.

q_s = net isosteric heat of sorption: Differential energy, differential enthalpy, or energy released when the liquid water molecules are absorbed. Also defined as the amount of energy above the latent vaporization heat of the water associated with the sorption process (McMinn and Magee 2003; Moreira et al. 2005).

For the calculation of the net isosteric heat of sorption, the integration method of the Clausius-Clapeyron equation was used (Skaar 1988; Kiranoudis et al. 1993; Peralta et al. 1997), as the results do not show significant differences in relation to the graphic method (Mulet et al. 2002; Chen 2006).

$$q_s = -R \cdot \frac{d(\ln(a_w))}{d(1/T)} \quad (5)$$

where:

$$q_s = \text{net isosteric heat of sorption}$$

$$a_w = \text{water activity}$$

$$T = \text{absolute temperature}$$

$$R = \text{universal gas constant}$$

This method requires at least two isotherms at close temperatures (Skaar 1988; Peralta et al. 1997; Arslan and Toğrul 2006; Chen 2006) and considers that q_s is independent of the temperature (Kiranoudis et al. 1993; Vazquez et al. 1999; Kaya and Kahyaoglu 2007; Chen 2006; Arslan and Toğrul 2006). This presupposes that the sorption process is reversible, which is not entirely true due to the phenomenon of hysteresis. However, there is experimental evidence indicating that cellulosic materials exposed to successive cycles of adsorption and desorption undergo a reduction in the hysteresis cycle

which means that the sorption process can be considered reversible (Peralta et al. 1997).

The heat involved in the sorption process from the M_{fsp} to oven-drying, known as total heat of wetting (Siau 1995), was obtained by integrating the net isosteric heat curve (Avramidis 1997).

$$W_0 = \int_0^{M_{fsp}} q_s \cdot dm \quad (6)$$

where:

W_0 = total heat of wetting

q_s = net isosteric heat of sorption

RESULTS AND DISCUSSION

Table 1 shows the M_{emc} for the 35° and 50°C isotherms in the old and new wood. The t-test shows that the values are significantly different with a 95% probability for the two temperatures.

The eight isotherms show fits to a type II ($C > 2$) sigmoid (Labuza 1984; Singh and Singh 1996). In addition, the regression coefficients $R > 0.990$ and the RMSE $< 4\%$ (Fig.1).

Tables 3 and 4 show the points from which multilayer sorption begins to predominate. These points were obtained by using the minimum of the derivative of the M_{emc} in relation to the RH (Avramidis 1997).

In the 35°C adsorption isotherm of the new wood, the monolayer saturation moisture content in adsorption M_m is $3.33 \pm 0.25\%$; therefore, the maximum amount of water taken up by the specimen via monolayer sorption is 3.33%, as this value represents the total monolayer water sorption capacity. On the other hand, the point of inflection of the isotherm corresponds to a moisture content of 3.23% and occurs at 30.0% RH. This indicates that from 30 to 100% RH the water taken up by the specimen via monolayer sorption is minimal, at only 0.10% of the total. For the same isotherm in the old wood, multilayer sorption begins to predominate over monolayer sorption (point of inflection) from 30.8% RH and the water taken up via monolayer sorption is 0.17%.

In comparing the adsorption findings of the two isotherms, it can be seen that there is a con-

siderable difference in the monolayer saturation moisture content, which is 1.42% higher in the old wood, although the RH percentages corresponding to the points of inflection are practically the same (30.8 and 30.0%, respectively).

For the 35°C desorption isotherm of the new wood, the point of inflection occurs at 31.3% RH. From 31.3% the water taken up via monolayer sorption is only 0.25%. For the old wood the point of inflection occurs at 30.5% RH. From 30.5% the water taken up via monolayer sorption is 0.83%.

As in adsorption, the desorption isotherm of the old wood shows a higher monolayer saturation moisture content than the new wood (1.46%), and the point of inflection is located at around 30% RH (30.5% and 31.3%, respectively).

The same behavior is observed in the 50°C isotherm. The old wood shows higher monolayer saturation moisture contents M_m than the new wood: 1.34% in adsorption and 1.61% in desorption. Similarly, the point of inflection is located at around 30% RH.

As expected, the M_{emc} of the 50°C isotherms, in both adsorption and desorption, are lower than in the 35°C isotherms (Table 1). This is because the increase in temperature on the wood provides the water molecules joined to the substratum with enough energy to break their bonds (McMinn and Magee 2003; Lahsasni et al. 2004; Yazdani et al. 2006).

Therefore, regardless of the isotherm followed or the age of the wood, the point of inflection from which multilayer sorption begins to predominate over monolayer sorption remains at around 30% RH.

On applying the mean test at the significance level of 95%, it was seen that the hysteresis coefficient M_{emc-a}/M_{emc-d} of the old wood is greater than that of the new wood (Table 2). When compared point by point, it can be seen that all the coefficients confirm this except for the point of the K_2SO_4 salt in the 35°C isotherm, which shows a lower hysteresis coefficient in the old vs new wood. However, in the same way as the M_{emc} of the isotherm closest to the anhydrous state are normally eliminated, as the en-

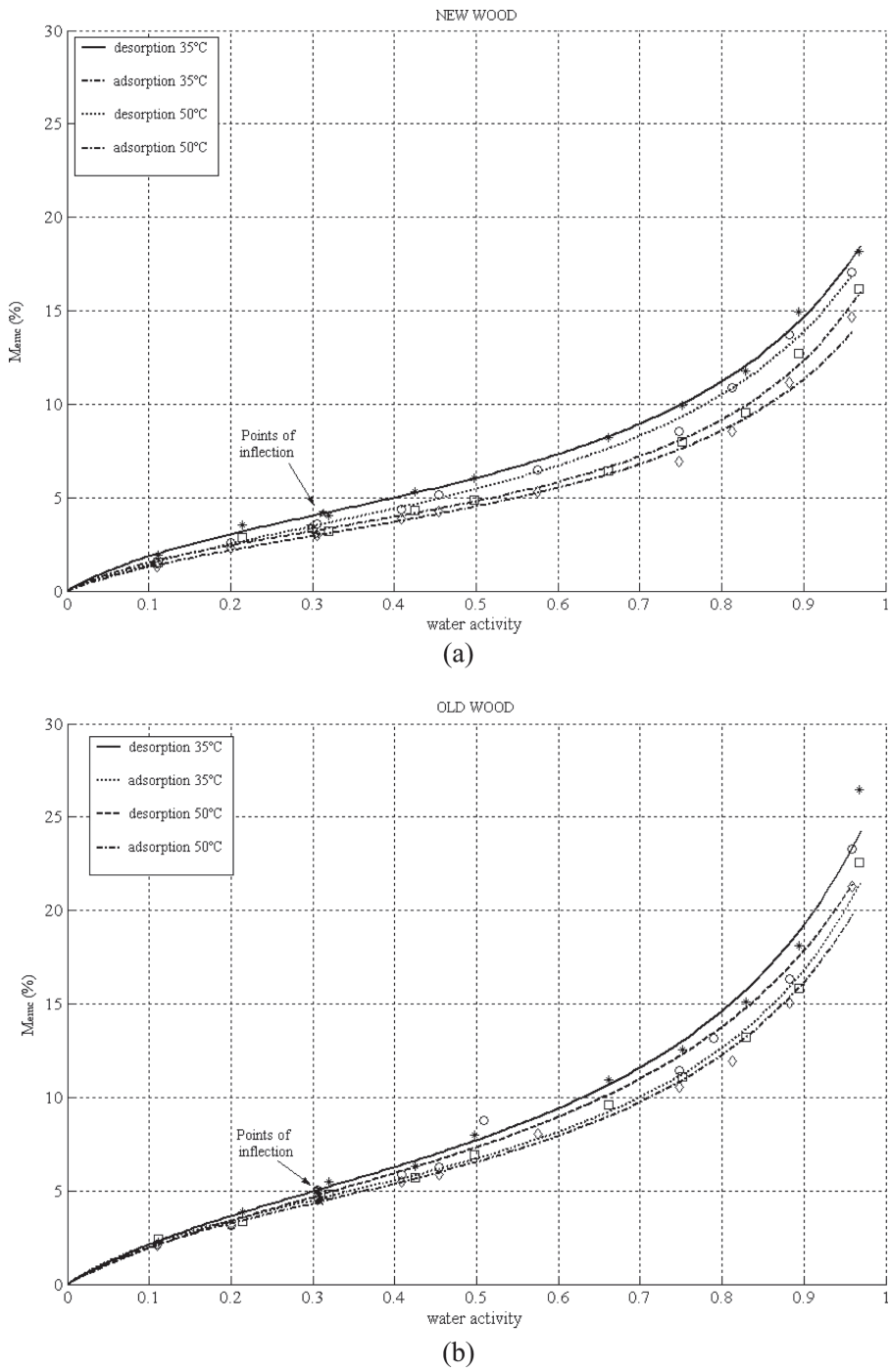


FIG. 1. Sorption isotherms of (a) new wood and (b) old wood at 35° and 50°C.

tropy peaks may have an influence at low RH (Kadita et al. 1961; Yasuda et al. 1995), it is also advisable to remove the points closest to the M_{fsp} because of the difficulties involved in obtaining these points.

Disregarding the points corresponding to the LiCl and K_2SO_4 salts, the mean of the hysteresis coefficient in the 35°C isotherm is 0.88 in the old wood and 0.81 in the new wood. These mean coefficient values are higher in the 50°C isotherm, at 0.93 and 0.83 respectively. The fact that the hysteresis coefficients of the old wood are higher than those of the new wood in both isotherms means that a decrease has occurred in the free energy of the hysteresis cycle (Siau 1995) and, as a consequence of this, the old

wood is more hygroscopically stable than the new wood (Esteban et al. 2005; 2006).

In terms of the thermodynamic characterization, the findings for the net isosteric heat concur with those obtained by other authors (Table 5) (Tsami 1991; Kaymak-Ertekin and Sultanoğlu 2001; McMinn and Magee 2003; Al-Muhtaseb et al. 2004; Moreira et al. 2005; Yazdani et al. 2006). The net isosteric heat values in the interval of the curve where the water molecules and the substrate show maximum interaction are higher in desorption than in adsorption for a given M_{emc} (Fig. 2). This indicates, on the one hand, that the bond energy is greater in desorption than in adsorption, possibly due to the number of bonds lost in the hysteresis cycle (Moreira et al. 2005), and, on the other hand, that the energy required in the desorption process is greater than that required in the adsorption process (Kaymak-Ertekin and Sultanoğlu 2001; Lahsasni et al. 2004), which is most likely due to the higher presence of active polar groups on the surface of the wood during desorption (Tsami 1991).

In the old wood the maximum heat of wetting in desorption was 128.18 J/mol (Fig. 2) as opposed to 106.55 J/mol in adsorption. In the new wood, the maximum values for net isosteric heat are notably higher than in the old wood, both in adsorption and desorption. This means that the bond energy of the new wood is greater than in

TABLE 2. *Hysteresis coefficients.*

35°C Isotherm		50°C Isotherm	
M_{emc-a}/M_{emc-d}		M_{emc-a}/M_{emc-d}	
New wood	Old wood	New wood	Old wood
0.79	1.07	0.87	0.98
0.82	0.87	0.89	1.00
0.80	0.87	0.82	0.92
0.81	0.90	0.88	0.93
0.80	0.87	0.82	0.93
0.78	0.88	0.82	0.92
0.80	0.89	0.81	0.92
0.81	0.88	0.78	0.91
0.85	0.87	0.81	0.92
0.89	0.85	0.86	0.91

M_{emc-a} : Equilibrium moisture content in adsorption. M_{emc-d} : Equilibrium moisture content in desorption.

TABLE 3. *Results of the GAB fit for the 35° and 50°C isotherms in new Pinus sylvestris wood.*

Isotherm	35°C			50°C		
Adsorption	$M_m(\%)$	K	C_g	$M_m(\%)$	K	C_g
	3.33 ± 0.25	0.82 ± 0.46	8.03 ± 0.09	3.40 ± 0.20	0.80 ± 0.32	6.11 ± 0.07
	Correlation factor		RMSE(%)	Correlation factor		RMSE(%)
	0.998		0.948	0.997		0.677
	$^{(1)}RH(\%)$		$^{(1)}M_{\text{emc-a}}(\%)$	$^{(1)}RH(\%)$		$^{(1)}M_{\text{emc-a}}(\%)$
	30.0		3.23	30.0		2.98
Desorption	$M_m(\%)$	K	C_g	$M_m(\%)$	K	C_g
	4.40 ± 0.17	0.79 ± 0.26	7.32 ± 0.04	4.23 ± 0.17	0.80 ± 0.23	5.27 ± 0.06
	Correlation factor		RMSE(%)	Correlation factor		RMSE(%)
	0.999		0.483	0.998		0.513
	$^{(1)}RH(\%)$		$^{(1)}M_{\text{emc-d}}(\%)$	$^{(1)}RH(\%)$		$^{(1)}M_{\text{emc-d}}(\%)$
	31.3		4.15	29.8		3.45

TABLE 4. Results of the GAB fit for the 35° and 50°C isotherms in old Pinus sylvestris wood.

Isotherm		35°C			50°C		
Adsorption	$M_m(\%)$	K	C_g	$M_m(\%)$	K	C_g	
	4.75 ± 0.16	0.81 ± 0.24	7.88 ± 0.04	4.74 ± 0.18	0.80 ± 0.26	7.14 ± 0.05	
	Correlation factor		RMSE(%)	Correlation factor		RMSE(%)	
	0.997		0.731	0.994		0.750	
	$^{(1)}\text{RH}(\%)$	$^{(1)}M_{\text{emc-a}}(\%)$		$^{(1)}\text{RH}(\%)$	$^{(1)}M_{\text{emc-a}}(\%)$		
	30.8	4.58		30.9	4.43		
Desorption	$M_m(\%)$	K	C_g	$M_m(\%)$	K	C_g	
	5.86 ± 0.16	0.79 ± 0.19	5.84 ± 0.04	5.84 ± 0.29	0.78 ± 0.32	5.24 ± 0.09	
	Correlation factor		RMSE(%)	Correlation factor		RMSE(%)	
	0.993		0.8831	0.991		1.864	
	$^{(1)}\text{RH}(\%)$	$^{(1)}M_{\text{emc-d}}(\%)$		$^{(1)}\text{RH}(\%)$	$^{(1)}M_{\text{emc-d}}(\%)$		
	30.5	5.03		30.5	4.74		

M_m : monolayer saturation moisture content. K : constant. C_g : Guggenheim constant. RMSE: Root Medium Square Error. $^{(1)}$ Point of inflection of the isotherm. $M_{\text{emc-a}}$: Equilibrium moisture content in adsorption. $M_{\text{emc-d}}$: Equilibrium moisture content in desorption.

TABLE 5. Thermodynamic parameters.

Wood	Adsorption				Desorption			
	M _{fsp} (%)	Net isosteric heat (J/mol)		Total heat of wetting (J/mol dry wood)	M _{fsp} (%)	Net isosteric heat (J/mol)		Total heat of wetting (J/mol dry wood)
		Maximum	Minimum			Maximum	Minimum	
New	18.4	269.16	24.22	1227.0	20.7	350.10	4.58	1800.3
Old	24.5	106.55	11.59	723.5	27.3	128.18	23.84	1243.0

M_{fsp} : Fiber saturation point.

the old wood. Nonetheless, from the M_{fsp} , the two curves are virtually parallel.

The fact that the net isosteric heat of sorption increases as the M_{emc} decreases (Fig. 2) indicates the high interaction energy existing between the water molecules and the substratum at low M_{emc} (Maskan and Göğüs 1997; Moreira et al. 2005). This rapid increase may be due to the existence of highly active polar groups on the surface of the material, which would initially form the monolayer (Tsami 1991; McMinn and Magee 2003; Al-Muhtaseb et al. 2004; Lahsasni et al. 2004; Yazdani et al. 2006), followed by polar groups with lower activation energy (McMinn and Magee 2003).

In contrast to this, the fact that the net isosteric heat of sorption decreases as the M_{emc} increase indicates a decrease in the bond energy between the water and the substratum (Maskan and Göğüs 1997). This behavior has been observed in other hygroscopic materials (Kiranoudis et al. 1993; Kaya and Kahyaoglu 2007), including wood (Skaar 1988; Peralta et al. 1997).

Finally, the total heat of wetting is greater in desorption than in adsorption in the old wood. This was expected, given that the curve for the net isosteric heat in adsorption is lower than in desorption (Fig. 2). This means that the heat involved in the desorption process is greater than in the adsorption process. Similarly, the fact that the total heat of wetting is greater in the new wood than in the old wood means that the heat involved in the new wood is greater than in the old wood and therefore industrial processes such as drying require greater energy in recently cut wood than in old wood for the same M_{emc} intervals.

CONCLUSIONS

- The point of inflection in desorption or adsorption after which multilayer sorption predominates over monolayer sorption remains at around 30% RH, regardless of the isotherm followed or the age of the wood.

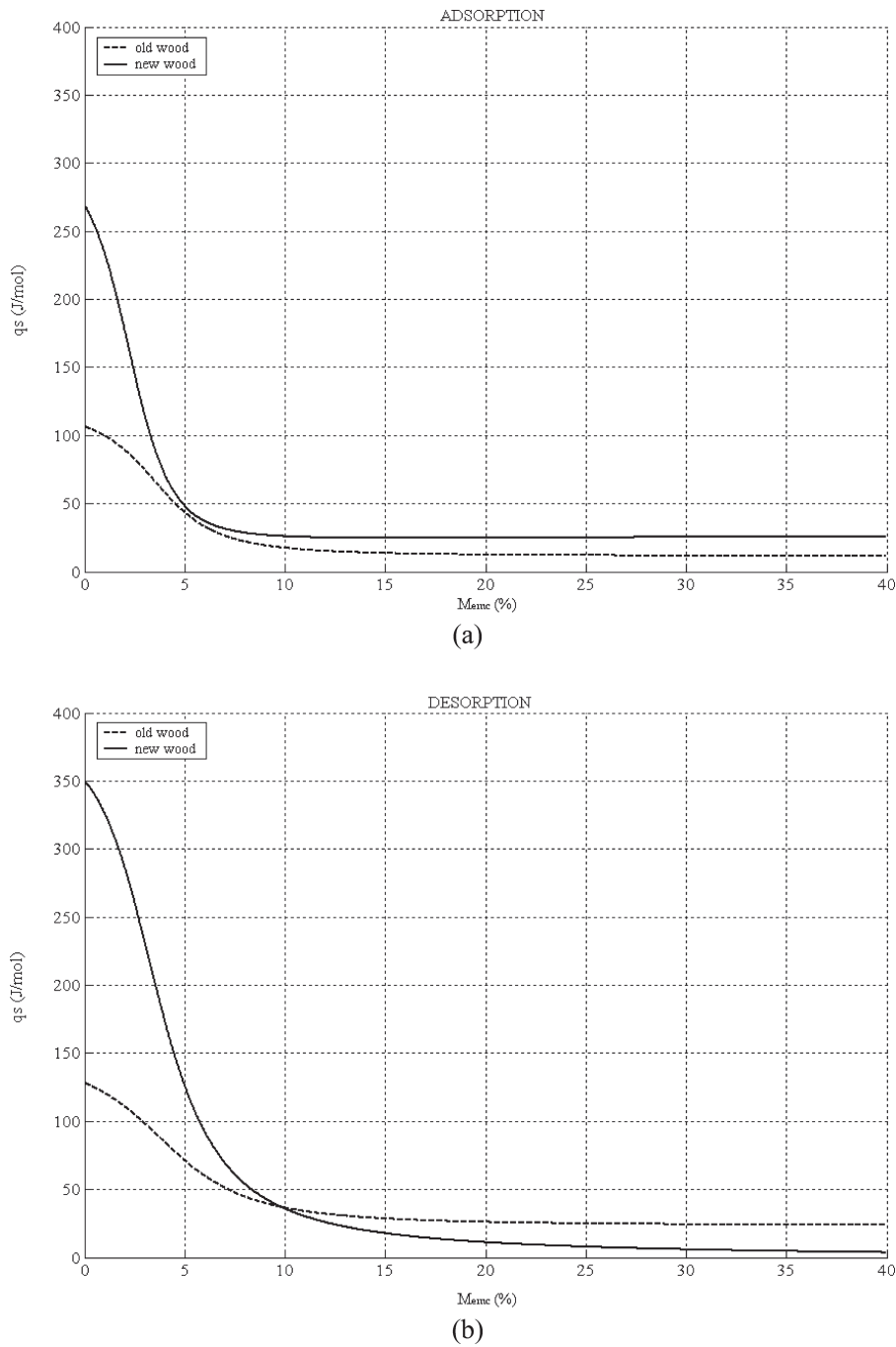


FIG. 2. Comparison of the net isosteric heat of sorption (q_s) in old and new wood during (a) adsorption and (b) desorption.

- The decrease of free energy in the hysteresis cycles means that old wood is more hygroscopically stable than new wood.
- The net isosteric heat decreases as the moisture content of the wood increases.
- The maximum values of net isosteric heat in

new wood are notably higher than in old wood, both in adsorption and desorption, indicating that the bond energy of new wood is greater than in old wood.

- The total heat of wetting is greater in new wood than in old wood, both in adsorption and desorption, indicating that the energy involved in the desorption process is greater in new wood.

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