

Sorption and thermodynamic properties of cork from the 35°C and 50°C isotherms

Francisco GARCÍA FERNÁNDEZ¹
Paloma DE PALACIOS¹
Luis G. ESTEBAN¹
Alberto GARCÍA-IRUELA¹
José R. GONZÁLEZ-ADRADOS²
José Vicente LÓPEZ ÁLVAREZ¹

¹ Universidad Politécnica de Madrid
Escuela Técnica Superior de Ingenieros de Montes
Departamento de Ingeniería Forestal
Ciudad Universitaria s/n
28040 Madrid
Spain

² Instituto Nacional de Investigación
y Tecnología Agraria y Alimentaria.
Centro de Investigación Forestal
Departamento de Productos Forestales
Ctra. Coruña Km 7.5
28040 Madrid
Spain



Photograph 1.
Quercus suber L. woodland.
Photograph L. G. Esteban.

F. GARCÍA FERNÁNDEZ, P. DE PALACIOS,
L. G. ESTEBAN, A. GARCÍA-IRUELA, J. R.
GONZÁLEZ-ADRADOS,
J. V. LÓPEZ ÁLVAREZ

RÉSUMÉ

SORPTION ET PROPRIÉTÉS THERMODYNAMIQUES DU LIÈGE POUR LES ISOTHERMES DE 35 °C ET 50 °C

Les caractéristiques du liège font de lui un élément irremplaçable dans le domaine de l'industrie bouchonnière de bouteilles de vin et de champagne de grande qualité. Les études portant sur les relations eau-liège sont peu nombreuses, particulièrement en ce qui concerne le comportement thermodynamique du liège. Dans cette étude, l'hygroscopicité et les propriétés thermodynamiques sur deux échantillons de liège de la même qualité, l'un extrait en 1968 et l'autre en 2006, ont été étudiées afin de déterminer les possibles différences de comportement au fur et à mesure que le temps passe. Pour ce faire, les isothermes de sorption de 35 °C et de 50 °C ont été construites suivant la méthode des solutions de sels saturées, en ajustant les valeurs conformément à la méthode GAB. Des coefficients d'hystérésis ont été utilisés dans la comparaison des isothermes, des spectres d'infrarouge dans l'étude des possibles modifications chimiques de la paroi cellulaire et la méthode d'intégration de l'équation de Clausius-Clapeyron dans la détermination des paramètres thermodynamiques. Aucune différence significative n'a été observée entre les teneurs en humidité d'équilibre obtenues pour les deux lièges ; par contre, les pourcentages de saturation de la monocouche sont significativement inférieurs dans le plus vieux des lièges. Pour les deux types de liège, tout comme pour le bois, les valeurs des points d'inflexion où la physisorption commence à dominer sur la chimisorption sont très similaires, environ 31-35 % d'humidité relative (RH). En ce qui concerne les propriétés thermodynamiques, les courbes de chaleur isostérique nette sont similaires à celles qui sont obtenues pour le bois, et l'énergie de liaison du liège extrait en 2006 est inférieure à celle du liège extrait en 1968.

Mots-clés : liège, désorption, hygroscopicité, isotherme, chaleur isostérique, sorption, thermodynamique.

ABSTRACT

SORPTION AND THERMODYNAMIC PROPERTIES FROM CORK AT THE 35°C AND 50°C ISOTHERMS

Because of its characteristics, cork currently has no substitute in the bottle stopper industry for high quality wines and champagnes. Few studies have been conducted on water-cork interactions, and especially on the thermodynamic behaviour of cork. The hygroscopic and thermodynamic properties of two cork samples of the same quality, harvested in 1968 and 2006, were studied to determine any differences in behaviour over time. The 35°C and 50°C isotherms were plotted following the saturated salts method and fitted using the GAB model. The isotherms were compared by means of hysteresis coefficients. The infrared spectra were recorded to analyse chemical changes in the cell wall, and the thermodynamic parameters were determined using the integration method based on the Clausius-Clapeyron equation. No significant differences were observed between the equilibrium moisture content obtained in the two samples, although the monolayer saturation moisture content was significantly lower in the older cork. In both types of cork, as also occurs with wood, the points of inflexion where multilayer sorption begins to predominate over monolayer sorption occurred at very similar values, at around 31-35% relative humidity (RH). In terms of thermodynamic properties, the net isosteric heat curves were similar to those obtained for wood, and the bond energy in the recently harvested cork was lower than in the older cork.

Keywords: cork, desorption, hygroscopicity, isotherm, isosteric heat, sorption, thermodynamics.

RESUMEN

SORCIÓN Y PROPIEDADES TERMODINÁMICAS DE CORCHO A TRAVÉS DE LAS ISOTERMAS ISOTERMAS DE 35°C Y 50°C

El corcho presenta unas características que lo hacen insustituible, por el momento, para la industria taponera de vinos y champán de alta calidad. En la actualidad existen escasos estudios sobre las relaciones agua-corcho y en especial sobre su comportamiento termodinámico. En este trabajo se han estudiado la higroscopicidad y propiedades termodinámicas de dos muestras de corcho de la misma calidad, extraídas en 1968 y 2006, para determinar las posibles diferencias de comportamiento con el paso del tiempo. Para ello, se han construido las isothermas de sorción de 35°C y 50°C siguiendo el método de sales saturadas, ajustándolas según el método GAB. Se han utilizado los coeficientes de histéresis para la comparación de las isothermas, los espectros de infrarrojos para estudiar las posibles modificaciones químicas de la pared celular y el método de integración de la ecuación de Clausius-Clapeyron para la determinación de los parámetros termodinámicos. No se han observado diferencias significativas entre los contenidos de humedad de equilibrio obtenidos en ambos tipos de corcho, pero los contenidos de saturación de la monocapa son significativamente menores en el corcho más antiguo. En ambos tipos de corcho, al igual que ocurre en la madera, los puntos de inflexión donde comienza a dominar la fisisorción sobre la quimisorción se sitúan en valores muy similares, en torno al 31-35% de humedad relativa (RH). En cuanto a las propiedades termodinámicas, las curvas de calor isostérico neto son similares a las obtenidas en madera y la energía de enlace en el corcho extraído más recientemente es menor que en el corcho más antiguo.

Palabras clave: corcho, desorción, higroscopicidad, isoterma, calor isostérico, absorción, termodinámica.

Introduction

World area of extent of *Quercus suber* L. is around 2.3 million hectares (FAO, 2002) and world cork production is approximately 340,000 tonnes a year (t/yr). The main cork producers are Portugal, with 135,000 t a year, and Spain, with 110,000 t/yr (IPROCOR, 2004) (photo 1). The first (or virgin) cork, used for agglomerates, is harvested when the breast height circumference of the cork oak is greater than 60 cm. This circumference is reached when the tree is approximately 25 years old, although it varies depending on the quality of the growing site. After the first harvest, trees are debarked every nine years, yielding better quality cork suitable for use in the bottle stopper industry (photo 2). The density, impermeability, compressibility and elasticity of cork harvested in these circumstances make it currently irreplaceable in the bottle stopper industry for high quality wines and champagnes.

Cork is known to have been used for bottle stoppers since Roman times. This use has continued to the present day without interruption. However, cork oak stands have experienced so many changes of fortune that sustainable production has at times been endangered.

In Spain, cork oak woodlands achieved stability with the appearance of the first forest management plans, in the late 19th century. Stands were thinned to provide more light and ventilation for the trunk and to attain superior quality cork. Debarking plans laid down at that time, based on ten-year cycles, have been the backbone of successive reviews conducted since then. In privately owned forests, measures proposed by engineers to reconstruct deteriorated woodlands were adopted. Reforestation of cork oak woodlands has been carried out throughout Spain, not only in places where they previously occurred, but also in areas of Portuguese and holm oak whose natural areas of distribution had been reduced. Although livestock still grazed in these zones, pressure from this source decreased, as most reforested areas were fenced off.

In the 1960s, mass emigration to industrial areas and widespread use of fossil fuels led to depopulation of rural areas and brought an end to charcoal making. The disappearance of this activity ended one threat for the forest, but brought with it new and perhaps even more dangerous threats. The lack of cleaning, pruning and thinning after the decline of charcoal making and the consequent accumulation of combustible plant material led to increased sources of infection for cork oaks and more forest fires.

The current situation of cork oak woodlands can be regarded as stabilised, although problems have arisen due to oak decline disease, a phenomenon closely associated with forest ageing. A century after the first cork oak management plans, these trees are no longer subject to the changes of fortune they experienced over the years and it can now be said that the primary objectives initially laid down have been achieved. Cork oak woodlands are a clear example of sustainable use, where humans have learnt to reconcile biodiversity and the harvesting of cork as a multi-purpose product (UPM, 2011).

Cork and wood cell walls have very similar characteristics, except for the secondary cell wall. In wood, the secondary cell wall comprises mainly cellulose, whereas in cork it is made up of alternate layers of suberin and lignin. The primary wall comprises mostly lignin and provides mechanical stiffness to cork cells. The very thin outer layer of the cell wall consists of cellulose and hemicellulose.



Photograph 2.
Debarking.
Photograph A. San Miguel.



Photograph 3.
Sorption flask with samples.
Photograph F. García Fernández.

Suberin is the main cell wall component in cork, at 39.4% of its dry weight, followed by lignin (23.0%), polysaccharides (19.9%), total extractives (14.2%) and ash (1.2%) (PEREIRA, 2007). As in wood, the physical properties of cork are closely associated with water content (LEQUIN *et al.*, 2010). Although many studies have been made of the hygroscopic behaviour of wood through its isotherms (e.g., KOLLMANN, 1951; SKAAR, 1988; SIAU, 1995; WANG, CHO, 1993; ESTEBAN *et al.*, 2004; 2005), cork-water relations have been little studied, particularly through the sorption-desorption isotherms (GONZÁLEZ-ADRADOS, HARO, 1994; GIL, CORTIÇO, 1998; GONZÁLEZ-ADRADOS *et al.*, 2008; ABDULLA *et al.*, 2009; LEQUIN *et al.*, 2010; DE PALACIOS *et al.*, 2011).

Sorption isotherms have been applied to study how wood hygroscopicity is affected by a range of temperature and relative humidity cycles (ESTEBAN *et al.*, 2005); the passing of time in dry environments (ESTEBAN *et al.*, 2006, 2008a); prolonged immersion for more than 100 years (ESTEBAN *et al.*, 2008b); and burial for 1,170 years (ESTEBAN *et al.*, 2009) and for nearly 6,000 years (ESTEBAN *et al.*, 2010). However, the only known study of this type on cork using the 35°C isotherm is by DE PALACIOS *et al.* (2011).

Even fewer studies exist on the thermodynamic properties of cork obtained through its sorption isotherms. Knowledge of these properties would make it possible to obtain the value of isosteric heat of sorption, which is used as an indicator of the total hydroxyl groups accessible to water, the state of the water absorbed by the substratum, and the bond strength between the water molecules and the substratum (AVRAMIDIS, 1997).

Obtaining the isosteric heat measurement in conjunction with the sorption isotherms is one way to characterise a material and study its interaction with gaseous systems (WADSÖ, 1997). Similarly, adsorption and desorption heat are a measurement of the energy required to break the intermolecular forces between the water vapour and the substratum (KOLLMANN, 1951). Studies of this type would make it possible to know whether the passing of time modifies the hygroscopic response and thermodynamics of cork, particularly when used as wine bottle stoppers.

This study compares the hygroscopicity and thermodynamic properties of cork for use in the bottle stopper industry harvested several years apart (1968 and 2006). The 35°C and 50°C sorption isotherms were plotted and used to obtain the thermodynamic properties of net isosteric heat of sorption and total heat of wetting.

Material and methods

Samples were chosen from two batches of circular cork pieces held in the cork collection of the *Instituto Nacional de Investigación y Tecnología Agraria y Alimentaria* (INIA in Madrid, Spain), and maintained in controlled conditions of relative humidity and temperature. Commonly used to manufacture stoppers for sparkling wine, these pieces have a nominal size of 34 mm (diameter) and 6 mm (height).

The batches were from planks of the same age (nine years), although one lot had been harvested in 1968 and the other in 2006. Both batches had similar density. The pieces chosen were of similar commercial quality (extra, *i. e.*, minimum porosity) and were sliced into strips around 1 mm thick with a cutting blade. The test pieces measured 15 x 10 x 1 mm. A total of 15 test pieces were placed in each salt, divided over three flasks, *i. e.*, five per flask (photo 3). Before the first desorption isotherm was plotted, the test pieces were submerged in water for one month to reach cell wall saturation.

The sorption isotherms were plotted following the COST Action E8¹ saturated salt method (ESTEBAN *et al.*, 2004). The thermostatic baths (photo 4) were verified using microcrystalline cellulose, following the protocol of COST Action E8 (JOWITT, WAGSTAFFE, 1989).

¹ Reinforced by European co-operation, the Cost Action provide new co-operations and research on the fracture mechanical properties of wood and the correlating structural features. The results will be of importance for a better understanding and an optimisation of wood machining processes. Cost Action E8 provided many insights into the mechanical performance of wood, especially at a macroscopic scale. Several phenomena of wood behaviour have been described. However, each of these phenomena also needs to be understood at the cellular and ultra-structural levels to achieve a comprehensive protocol for machining wood. COST Actions that contribute to and enhance value of this Action include E8 Mechanical Performance. The field of this Action consists of basic level material science on the mechanical behaviour of wood, with the objective of demonstrating that wood is a modern engineering material.

The isotherms were plotted using 10 salts, resulting in the corresponding equilibrium points (table I). Test pieces were considered to have reached equilibrium moisture content (EMC) in each salt when they showed a weight difference of no more than 0.1% when weighed in a 24-h interval (photo 5). It took four months to plot the desorption isotherm, after which the wet weight of the samples was obtained. The samples were then dried to anhydrous state in a desiccator with phosphorous pentoxide for 40 days to calculate the EMC using Equation (1):

$$EMC (\%) = \frac{W_w - W_0}{W_0} \cdot 100$$

with W_w : Wet weight (g) and W_0 : Anhydrous weight (g).

The adsorption isotherms were plotted immediately afterwards, using the same criteria as for desorption, in a process lasting 90 days.

The Guggenheim-Anderson-Boer-Dent (GAB) model was used, as it is particularly appropriate when dealing with relative humidities (RH) greater than 90% (VIOLLAZ, ROVEDO, 1999) Equation (2) and is the model best suited to this type of material (LEQUIN *et al.*, 2010):

$$X = \frac{KC_g a_w}{(1 - Ka_w)(1 - Ka_w + C_g Ka_w)} X_m$$

With X: EMC (%); X_m : monolayer saturation moisture content (%); C_g : Guggenheim constant (dimensionless); K: constant (dimensionless); a_w : RH or water activity on a scale of zero to one (dimensionless).

The isotherm fits were considered valid if the correlation coefficient (R) was greater than 0.990 and the root mean square error (RMSE) was less than 4% (ESTEBAN *et al.*, 2004).



Photograph 4.
 Thermostatic baths.
 Photograph F. García Fernández.

The EMC of the recently harvested and the older cork were compared using the hysteresis coefficients (Equation (3)):

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

with C_H : Hysteresis coefficient; EMC_a : EMC in adsorption; EMC_d : EMC in desorption.

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 0-200 g and a precision of 0.0001 g; and the oven had a range of 0-200°C and a precision of 0.1°C.

Table I.
 Equilibrium moisture content (EMC) in adsorption (EMC_a) and desorption (EMC_d) and hysteresis coefficients (C_H) for the 35°C and 50°C isotherms of cork harvested in 1968 and 2006.

Salt	a_w	35°C Isotherm						50°C Isotherm					
		2006		C_H	1968		2006		C_H	1968			
EMC_a (%)	EMC_d (%)	EMC_a (%)	EMC_d (%)		EMC_a (%)	EMC_d (%)	EMC_a (%)	EMC_d (%)		EMC_a (%)	EMC_d (%)	C_H	
LiCl	0.1117	1.33	1.47	0.91	1.31	1.35	0.97	1.11	1.20	0.92	1.11	1.12	0.99
CH ₃ COOK	0.2137	1.96	2.39	0.82	2.56	2.68	0.95	1.84	1.98	0.92	2.10	2.25	0.93
MgCl ₂	0.3200	2.58	2.92	0.88	2.87	3.06	0.94	2.42	2.52	0.96	2.34	2.65	0.88
K ₂ CO ₃	0.4255	3.61	3.92	0.92	3.49	3.65	0.96	3.34	3.43	0.97	2.95	3.16	0.93
Mg(NO ₃) ₂	0.4972	4.33	4.53	0.96	3.72	4.27	0.87	3.61	3.80	0.95	3.33	3.50	0.95
SrCl ₂	0.6608	5.72	6.02	0.95	5.33	5.42	0.98	4.45	4.96	0.90	4.35	4.53	0.96
NaCl	0.7511	6.44	6.74	0.96	6.61	6.72	0.98	5.90	6.20	0.95	6.03	6.04	1.00
KCl	0.8295	7.43	7.90	0.94	7.82	8.29	0.94	6.58	6.76	0.97	6.98	7.21	0.97
BaCl ₂	0.8940	9.35	9.72	0.96	9.14	9.92	0.92	8.11	8.24	0.98	8.24	8.60	0.96
K ₂ SO ₄	0.9671	10.18	10.43	0.98	10.79	11.29	0.96	10.02	10.27	0.98	10.40	11.11	0.94



Photograph 5.
Balance for weighing samples.
Photograph F. García Fernández.

The total isosteric heat of sorption was obtained using Equation (3) (AVRAMIDIS, 1997):

$$Q_s = q_s + \Delta H_{vap}$$

with Q_s : total isosteric heat of sorption (J/mol); ΔH_{vap} : latent vaporisation heat (constant) (J/mol); q_s : net isosteric heat of sorption (J/mol).

The net isosteric heat of sorption was calculated using the integration method of the Clausius-Clapeyron equation (PERALTA *et al.*, 1997) (Equation (4)). Implicit in this method is the assumption that net isosteric heat of sorption is independent of temperature (AVRAMIDIS, 1992; AL-MUHTASEB *et al.*, 2004; CORREA *et al.*, 2010). Equation (4):

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

with q_s : net isosteric heat of sorption (J/mol); a_w : water activity (dimensionless); T : absolute temperature (°K); R : universal gas constant [J/(mol °K)].

The heat involved in the sorption process from the cell wall saturation (CWS) to oven drying (total heat of wetting) (SIAU, 1995) was obtained by integrating the net isosteric heat curve (AVRAMIDIS, 1997) (Equation (5)):

$$W_0 = \int_0^{m_f} q_s \cdot dm$$

with W_0 : total heat of wetting (J/mol dry wood); q_s : net isosteric heat of sorption (J/mol); m_f : CWS moisture content (%).

The data was compared by applying the ANOVA statistical contrast analysis, although in the case of the hysteresis coefficient the Kruskal-Wallis test (the non-parametric version of the ANOVA test) was used, as the conditions of normality were not met.

Results and discussion

Table I shows the EMC of the cork samples harvested in 1968 and 2006 for the 35°C and 50°C isotherms. In all cases the isotherms fitted to a type II sigmoid (ESTEBAN *et al.*, 2004) (figure 1), R was greater than 0.990 and the RMSE was less than 4%.

The values for the minimum of the EMC derivative in relation to the RH, shown in table II, correspond to the points where multilayer sorption begins to predominate over monolayer sorption (AVRAMIDIS, 1997) (figure 2).

As expected, in both the 35°C and the 50°C isotherms the desorption values were above the corresponding adsorption values. Analysis of variance (table III) showed no significant difference between the EMC of the two samples, with a probability of 95%.

Based on earlier studies, it can be stated that the water sorption mechanism in cork appears to be similar to this mechanism in wood, and is divided into three phases: monolayer sorption, multilayer sorption and capillary condensation (ABDULLA *et al.*, 2009). However, some authors (LEQUIN *et al.*, 2010) have questioned the monolayer sorption phase. This does not seem logical, however, as the hydrophilic -OH groups belonging to the small amount of cellulose and hemicellulose, as well as the methoxyl groups mentioned by these authors, have a role in fixing water through hydrogen bonds.

Compared to the results obtained for wood using the same isotherms (35°C and 50°C), the EMC of the two cork samples were lower both in conifers (*Pinus sylvestris* L.) and in hardwoods (*Quercus spp*). The same occurred with the monolayer saturation moisture content (X_m) in wood that had undergone ageing of some kind: in cork the EMC was around 50% of the values obtained for these specie (ESTEBAN *et al.*, 2006; 2008a, 2008b, 2009; 2010). This can be explained by the lower number of hydrophilic groups in the cell wall, as a result of the low percentage of cellulose and hemicellulose, and by the presence of suberin, which is hydrophobic.

The monolayer saturation moisture content (X_m) was significantly lower, for a confidence level of 95%, in the older cork in the two isotherms plotted, indicating that this cork has fewer hydrophilic groups. This may be because some of the groups had been saturated over time.

Much more water was taken up via monolayer sorption above the point of inflexion (EMC_p), where multilayer sorption predominates over monolayer sorption, in the recently harvested cork than in the older cork, both in the 35°C and the 50°C isotherm, to the point that in the 1968 cork the amount can be considered insignificant, particularly in the 35°C isotherm. Therefore, beyond 31-35% RH, water sorption by cork via monolayer sorption is minimal.

Although the water taken up via monolayer sorption was significantly different in the eight isotherms, it is interesting to note that the points of inflexion where multilayer sorption begins to predominate over monolayer sorption remained constant, at around 30% RH (table II) (figure 2). This result is similar to those obtained in other studies on wood following the same isotherms (35°C and 50°C) (ESTEBAN *et al.*, 2006, 2008a, 2008b, 2009), seeming to indicate that the predominance of multilayer sorption over monolayer sorption is from 31 to 35% RH, regardless of how old the cork is.

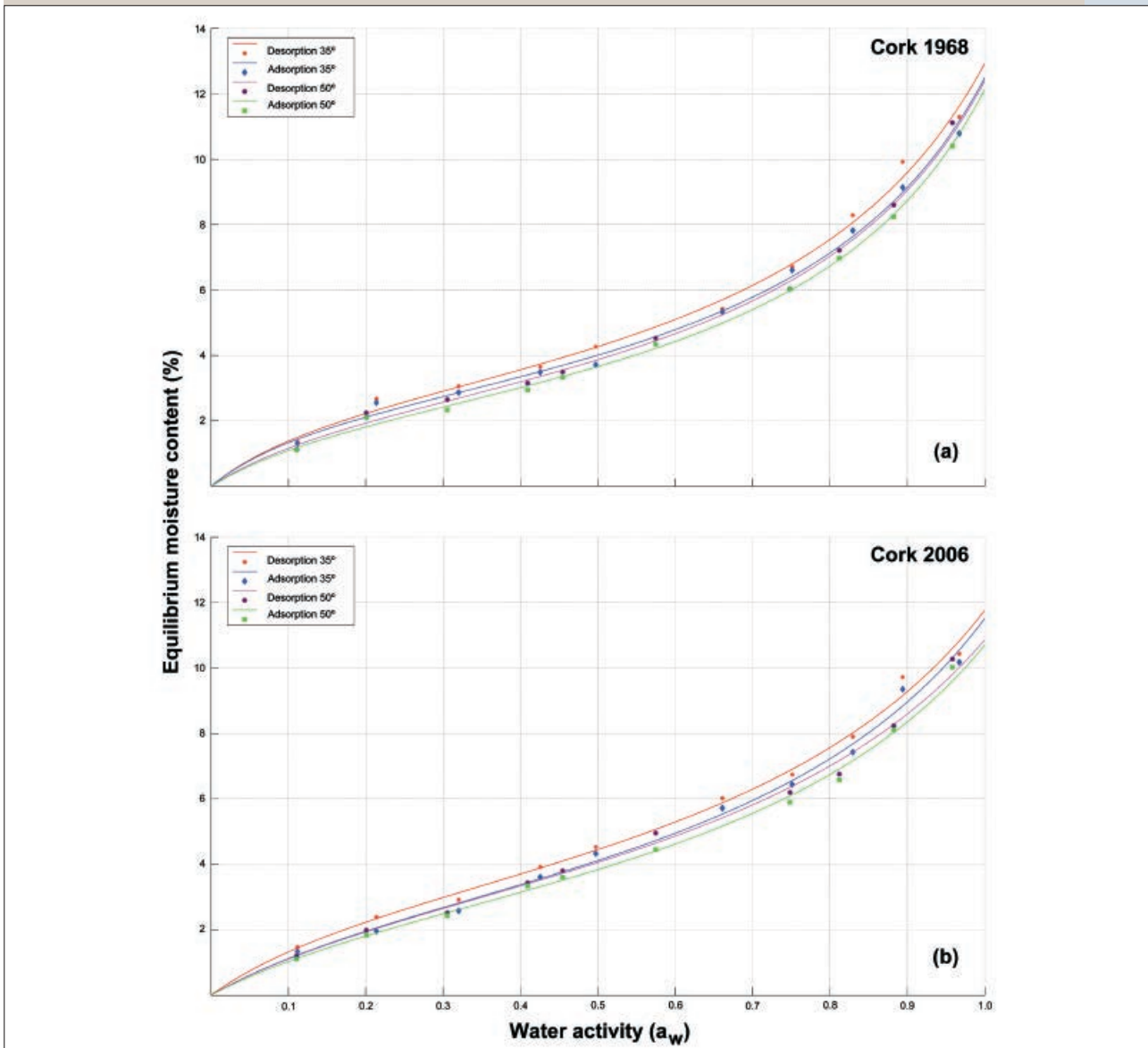


Figure 1.
35°C and 50°C sorption isotherms of cork harvested in (a) 1968 and (b) 2006.

In the hysteresis coefficients obtained in the two isotherms (table I), no significant differences were observed between the two samples, for a confidence level of 95%. Similarly, no clear behaviour pattern was observed to allow the free energy of the hysteresis loop to be related to cork stability. However, in earlier studies on wood (ESTEBAN *et al.*, 2008a), a clear narrowing of the hysteresis loop was revealed. This is a habitual feature of wood subjected to repeated humidity cycles, whether naturally occurring or artificially induced (SKAAR, 1988; ESTEBAN *et al.*, 2005).

A decrease in the isotherm slope of the cork harvested in 1968 was expected. This would have indicated greater stability of the older cork in any given RH interval (SKAAR, 1988; ESTEBAN *et al.*, 2005). However, the derivatives ($dEMC/da_w$)

showed the opposite for both the 35°C and the 50°C isotherms; that is, the isotherm slopes of the older cork showed higher values than in the recently harvested cork, both below 10% RH and above 65% RH, remaining practically the same between these values (figure 2). It could be understood from this that the older cork is less hygroscopically stable, although this cannot be stated with certainty until the physical and chemical changes in cork cell walls caused by the passing of time have been studied in depth.

FTIR spectra applied in earlier studies (DE PALACIOS *et al.*, 2011) showed that both types of cork had the same peaks in the functional groups studied, indicating that the passing of time in more or less stable conditions does not seem to have modified the chemical structure of the cork. More time or

Table II.
Results of the GAB fit for the 35°C and 50°C isotherms of cork harvested in 1968 and 2006.

Isotherm	2006			1968		
	35°C			35°C		
Adsorption	X_m	K	C_g	X_m	K	C_g
	3.51 ± 0.28	0.72 ± 0.40	5.46 ± 0.10	2.90 ± 0.31	0.78 ± 0.64	8.77 ± 0.09
	R	RMSE (%)		R	RMSE (%)	
	0.996	0.920		0.997	0.937	
	(¹)RH (%)	(¹)EMC _a (%)	EMC _f (%)	(¹)RH (%)	(¹)EMC _a (%)	EMC _f (%)
	33.4	2.91	0.60	32.3	2.88	0.02
Desorption	X_m	K	C_g	X_m	K	C_g
	3.68 ± 0.20	0.71 ± 0.30	6.60 ± 0.06	3.16 ± 0.29	0.76 ± 0.56	8.21 ± 0.08
	R	RMSE (%)		R	RMSE (%)	
	0.996	0.433		0.997	0.942	
	(¹)RH (%)	(¹)EMC _d (%)	EMC _f (%)	(¹)RH (%)	(¹)EMC _d (%)	EMC _f (%)
	34.9	3.34	0.34	32.7	3.08	0.08
Isotherm	50°C			50°C		
	Adsorption			Desorption		
Adsorption	X_m	K	C_g	X_m	K	C_g
	3.31 ± 0.19	0.71 ± 0.26	5.28 ± 0.07	2.73 ± 0.29	0.78 ± 0.54	6.88 ± 0.10
	R	RMSE (%)		R	RMSE (%)	
	0.998	0.354		0.999	0.847	
	(¹)RH (%)	(¹)EMC _a (%)	EMC _f (%)	(¹)RH (%)	(¹)EMC _a (%)	EMC _f (%)
	33.3	2.70	0,61	31.6	2.52	0,21
Desorption	X_m	K	C_g	X_m	K	C_g
	3.55 ± 0.24	0.70 ± 0.33	5.44 ± 0.09	2.91 ± 0.32	0.77 ± 0.56	6.96 ± 0.10
	R	RMSE (%)		R	RMSE (%)	
	0.996	0.558		0.998	1.14	
	(¹)RH (%)	(¹)EMC _d (%)	EMC _f (%)	(¹)RH (%)	(¹)EMC _d (%)	EMC _f (%)
	34.2	2.94	0,61	32.0	2.69	0,22

(¹): Point of inflection of the isotherm; X_m : Monolayer saturation moisture content; K: Constant; C_g : Guggenheim constant; R: Correlation coefficient; RMSE: Root Medium Square Error; 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.

much more aggressive conditions may be required for distinct values to be shown in some of the more vulnerable peaks, e. g., hemicellulose, as occurs in wood (FENGEL, 1991; BARDET *et al.*, 2004). This response may be due to the low percentage of polysaccharides in cork cell walls, which can be advantageous when compared to the degradation habitual in wood (DE PALACIOS *et al.*, 2011).

As occurs in wood (ESTEBAN *et al.*, 2009, 2010), the net isosteric heat values in both types of cork are higher in desorption than in adsorption for a given EMC because the energy required in the desorption process is higher than in adsorption (SIAU 1995; AVRAMIDIS, 1997). This is because the bond energy is higher in desorption than in adsorption, probably due to the

number of bonds lost in the hysteresis cycle (KOLLMANN, 1951). In addition, the maximum net isosteric heat values are higher in the older cork than in the recently harvested cork. This means that the bond energy in the recently harvested cork is lower than in the older cork (table IV).

For low EMC the net isosteric heat of sorption increases considerably, indicating the high interaction energy between the water molecules and the substratum in this interval (KOLLMANN, 1951) (figure 3). This rapid increase may be caused by highly active polar groups on the surface of the material (monolayer), followed by polar groups with lower activation energy. In contrast, the decrease in the net isosteric heat of sorption at higher EMC indicates lower bond energy

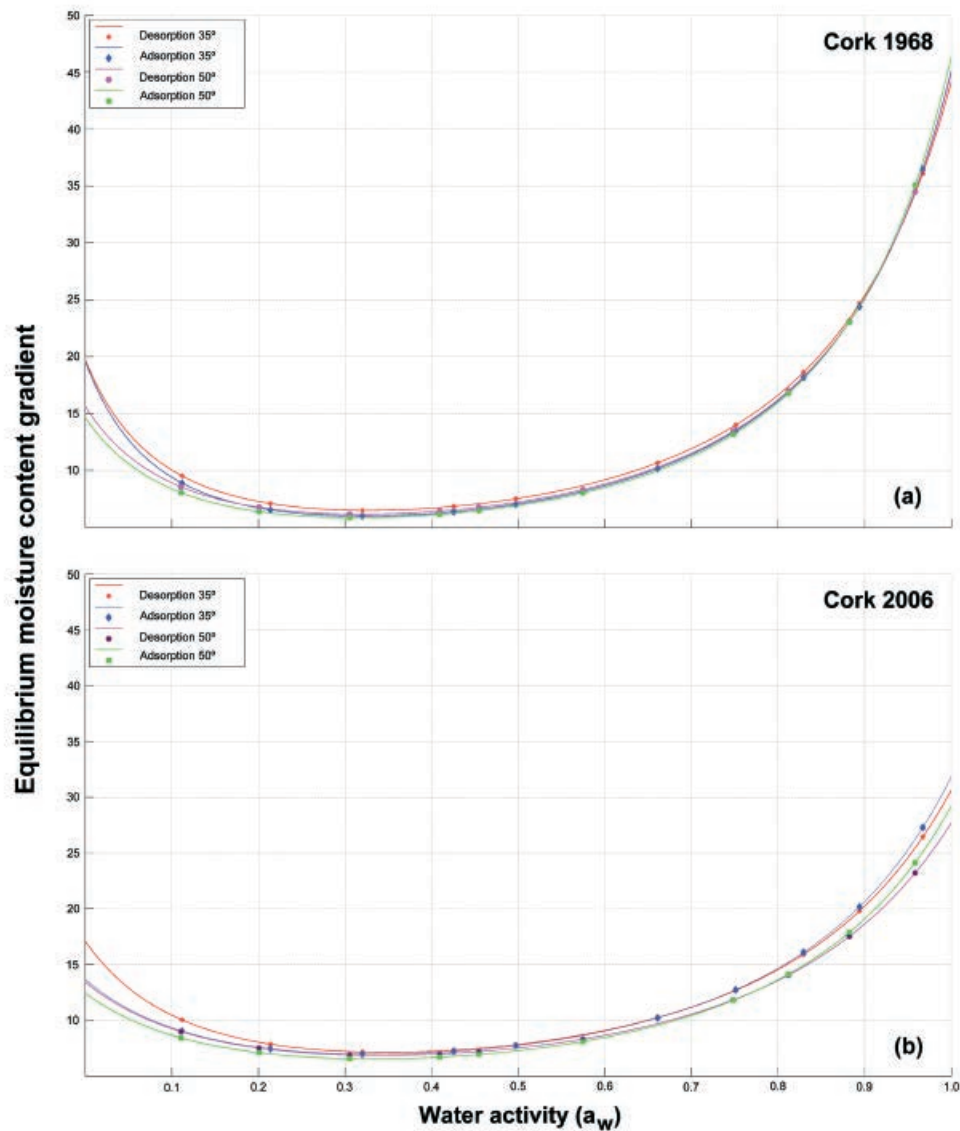


Figure 2. Derivatives of the 35°C and 50°C sorption isotherms of cork harvested in (a) 1968 and (b) 2006.

between the water and the substratum. This behaviour has been observed in other hygroscopic materials, including wood (PERALTA *et al.*, 1997; ESTEBAN *et al.*, 2009, 2010).

As expected, total heat of wetting was greater in desorption than in adsorption, as the net isosteric heat curve in adsorption is lower than in desorption.

Further studies on cork subjected to more aggressive conditions, whether naturally occurring or artificially induced, will increase knowledge of the hygroscopic response of this material and the extent to which its cell wall structure is modified.

Conclusions

The EMC values are not significantly different in any of the isotherms studied, indicating that the passing of time in controlled conditions of RH and temperature did not modify the hygroscopic response of the cork. In both samples, the points of inflexion where multilayer sorption begins to predominate over monolayer sorption are at very similar values, around 31-35% RH. The isotherm slopes are similar from 10% to 65% RH and differences are observed only outside this interval. The amount of water taken up via monolayer sorption above the point of inflexion (EMC_p) is significantly greater in the recently harvested cork than in the older cork.

Table III.
Analysis of variance on the hygroscopic equilibrium points.

Source	Adsorption 35°C					Desorption 35°C				
	SS	df	MS	F	P-value	SS	df	MS	F	P-value
Cork type	0.09	1	0.08	1.56	0.22	0.06	1	0.06	1.9	0.18
a_w	514.53	9	57.17	1,149.03	0	548.25	9	60.92	1,940.84	0
Interaction	2.29	9	0.25	5.1	0	2.29	9	0.25	8.1	0
Error	1.99	40	0.05			1.25	40	0.03		
Total	518.88	59				551.85	59			

Source	Adsorption 50°C					Desorption 50°C				
	SS	df	MS	F	P-value	SS	df	MS	F	P-value
Cork type	0.03	1	0.03	1.54	0.22	0.10	1	0.10	2.66	0.11
a_w	468.94	9	52.10	2,619.43	0	497.86	9	55.32	1,447.37	0
Interaction	0.96	9	0.11	5.35	0	2.18	9	0.24	6.33	0
Error	0.80	40	0.02			1.53	40	0.04		
Total	470.73	59				501.66	59			

SS: Sum of squares due to each source; df: degrees of freedom associated with each source; MS: Mean squares (ratio SS/df); F: F-statistics (ratio of mean squares); P-value: p-value for the null hypothesis.

Table IV.
Thermodynamic parameters.

	CWS (%)	Adsorption		Total heat of wetting (J/mol dry wood)	CWS (%)	Desorption		Total heat of wetting (J/mol dry wood)
		Net isosteric heat (J/mol) Maximum	Minimum			Net isosteric heat (J/mol) Maximum	Minimum	
1968	12.5	225.2	7.1	1,043.9	12.9	279.5	10.9	1,077.6
2006	11.5	96.0	24.8	666.0	11.8	231.1	28.7	1,105.5

More energy is required in the desorption process than in adsorption. Bond energy is lower in the recently harvested cork than in the older cork. The net isosteric heat curves are similar to those obtained in wood, and the isosteric heat values are higher for lower EMC values. Total heat of wetting is higher in desorption than in adsorption.

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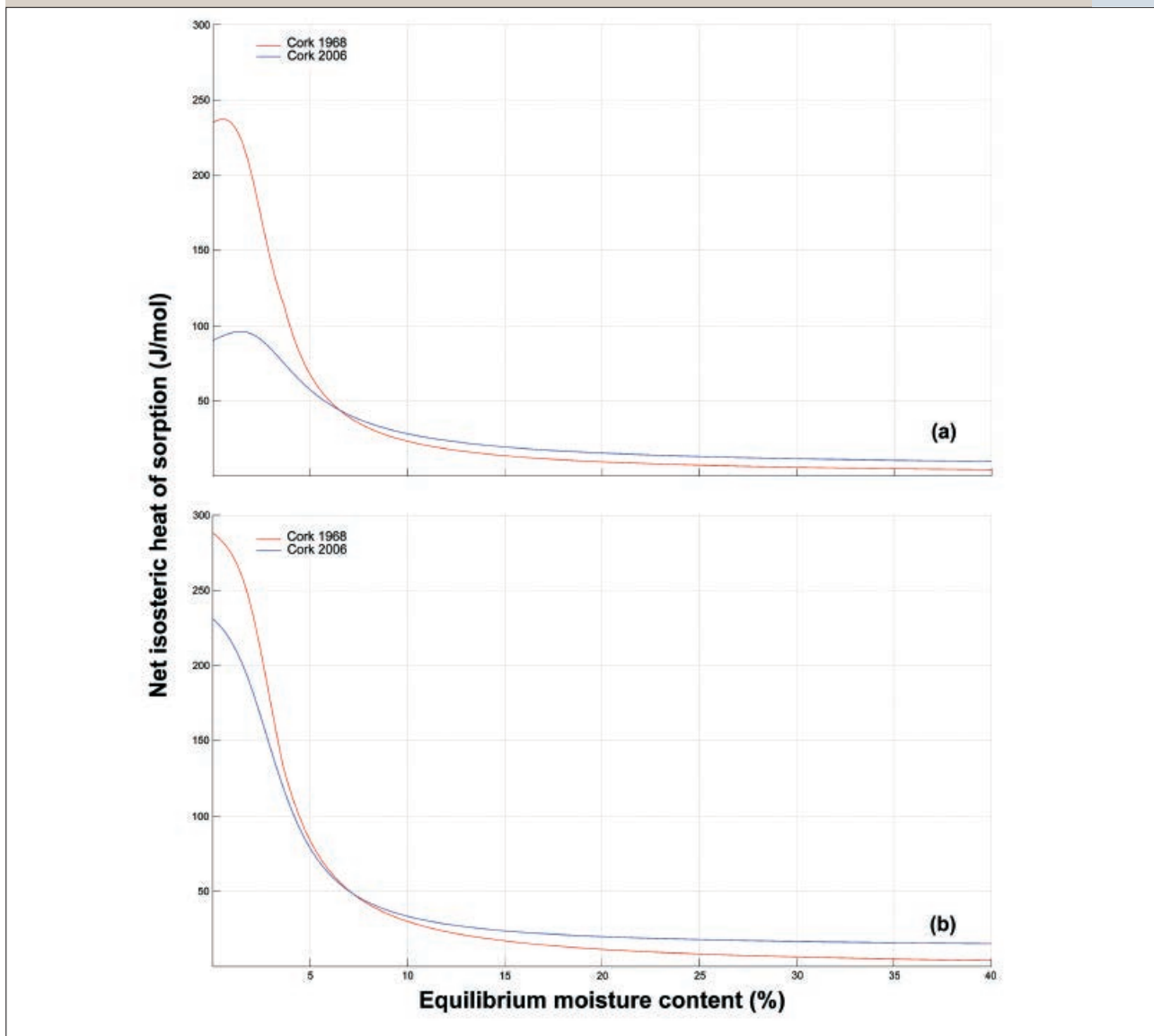


Figure 3. Comparison of the net isosteric heat of sorption (q_s) of cork harvested in 1968 and 2006 during (a) adsorption and (b) desorption.

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