Thermodynamic properties of the water sorption isotherms of wood of limba
(*Terminalia superba* Engl. & Diels), obeche (*Triplochiton scleroxylon* K. Schum.), radiata pine (*Pinus radiata* D. Don) and chestnut (*Castanea sativa* Mill.)

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ABSTRACT

The sorption isotherms of limba (*Terminalia superba* Engl. & Diels), obeche (*Triplochiton scleroxylon* K. Schum.), radiata pine (*Pinus radiata* D. Don) and chestnut (*Castanea sativa* Mill.), were plotted at 15 °C, 35 °C and 50 °C. The curves were fitted using the Guggenheim-Anderson-de Boer (GAB) model. The thermodynamic properties (net isosteric heat of sorption, total heat of wetting, differential entropy and spreading pressure) were determined from the isotherms to define the energy associated with the sorption processes. Net isosteric heat of sorption was obtained using the Clausius-Clapeyron equation and showed a negative relation with moisture content. Differential entropy showed the same behaviour. These two parameters were higher in desorption than in adsorption. Total heat of wetting was also higher in desorption than in adsorption and higher in chestnut than in the other species. The enthalpy-entropy theory was validated as there was a good linear fit between net isosteric heat of sorption and differential entropy, and the isokinetic temperatures were different from the harmonic mean temperature. Using the enthalpy-entropy theory, it was possible to conclude that the adsorption and desorption processes were enthalpy driven and spontaneous. Spreading pressure increased as water activity increased. The variation of spreading pressure with temperature depends on the species type.

**Key words:** differential entropy, enthalpy-entropy theory, equilibrium moisture content (*EMC*), net isosteric heat, spreading pressure, total heat of wetting.
1. INTRODUCTION

Wood is a hygroscopic material that tends towards a state of equilibrium with its surroundings (Esteban et al., 2004). Wood is one of the renewable resources most commonly used by humanity since ancient times. Knowledge of the physical and mechanical properties of wood is necessary to optimise industrial processes and obtain increasingly better wood-based materials to satisfy market demands.

Today the 4,033 million hectares occupied by forests around the world produce 1,837 Mm$^3$ industrial round wood, and 1,863 Mm$^3$ is used as fuel (FAO, 2015; FAOSTAT, 2014). The use of wood in various sectors (construction, furniture, biomass, etc.) not only has socioeconomic repercussions, creating 13.7 million jobs and providing an average value of 1% to global GDP (FAO, 2011), but also mitigates the effects of climate change by fixing carbon.

Forest plantations as source crops to supply wood for primary processing industries (sawn timber and boards) and cellulose pulp industries occupy 289 million hectares, accounting for approximately 7% of total forest area (FAO, 2015).

Although a significant part of the timber produced and processed is used directly without the need to control its moisture content, such as when it is used for fuel, the use of wood in other products e.g. industrialised carpentry (wooden doors, windows and floors), heavy or light construction timber, laminated glued timber, plywood, particleboard, fibre board, OSB (oriented strand board) and solid wood panels, requires drying technology at some stage of the manufacturing process.

Because wood has a hygroscopic nature and therefore constantly exchanges water vapour with its surroundings, it is a material which, during industrial processing and end use, must undergo the corresponding moisture content controls to ensure it is used correctly.
The relation between the equilibrium moisture content (EMC) of wood and the relative humidity (RH) of the air for a constant temperature is represented by a sigmoid curve known as the sorption isotherm (Avramidis, 1997; Skaar, 1988). The literature includes many models through which these isotherms can be determined (Van den Berg and Bruin, 1981). This isotherm makes it possible to know the moisture content of wood for a given relative humidity and temperature. Various models have been used to represent the sorption isotherm, and although they can be fitted very well to the data obtained, they typically have errors from the thermodynamic point of view (Simpson, 1980). However, whenever a model is developed, it always involves some simplification of the sorption process. The Langmuir sorption model, developed in 1916, is the simplest and earliest (Atkins, 1999). It starts from the premise that adsorption cannot occur beyond a monolayer and once the monolayer is completed, sorption ceases. The BET model (Brunauer, Emmett and Teller) extended the Langmuir monolayer model to the phenomena of multilayer adsorption and capillary condensation (Brunauer et al., 1938). The GAB-Dent model, derived from the BET multilayer model, considers that the second and following layers are thermodynamically identical but distinct from liquid water. It is a more general model than the BET and the Langmuir model, and the sorption sigmoids fit much better using the experimental data obtained for lignocellulosic products (Avramidis, 1997). The Hailwood-Horrobin model (Hailwood and Horrobin, 1946), very similar to the GAB-Dent model, also fits well to a sigmoid curve for water sorption isotherms in wood (Skaar, 1972; Siau, 1995). The Henderson model is one of the few to include temperature as a variable and is widely used because it is more easily linearised than others, such as the GAB model (Avramidis, 1989). Although these and other models can lead to different conclusions, Among these, the Guggenheim-Anderson-de Boer model is widely used in the study of the hygroscopic
behaviour of wood (Bratasz et al., 2012; Esteban et al., 2008, 2010; Hartley, 2000; Kelsey, 1957; Lam et al., 2012; Lesar et al., 2009; Olek et al., 2013; Themelin et al., 1997; Todoruk and Hartley, 2011). For many years the saturated salt method has been the most commonly used method for obtaining the moisture content in various materials. Although use of the dynamic vapour sorption (DVS) instrument is becoming more widespread (Himmel and Mai, 2015; Popescu et al., 2014), the saturated salt method continues to be used (Ouertani et al., 2014; Simon et al., 2015).

Several authors have determined the sorption behaviour of different types of wood (Esteban et al., 2009; Glass and Zelinka, 2010; Hoffmeyer et al., 2011), in some cases distinguishing between sapwood and heartwood (Rautkari et al., 2014; Song et al., 2014; Telkki et al., 2013), and juvenile and mature wood (Esteban et al., 2015; Neimsuwan et al., 2008; Simon et al., 2015). The hygroscopic properties of chemically modified wood (Himmel and Mai, 2015; Popescu et al., 2014; Soltani et al., 2013) and thermally modified wood (Pearson et al., 2013; Rautkari et al., 2014; Rautkari and Hill, 2014) have been obtained and the difference in the hygroscopic response of old and recent wood has been studied (Esteban et al., 2006, 2010; Popescu and Hill, 2013).

The hygroscopic properties of wood have been widely studied because of their influence on the physical and mechanical properties of this material (Glass and Zelinka, 2010; Rautkari et al., 2014; Skaar, 1988). However, few studies have addressed the thermodynamic properties of enthalpy and entropy in the sorption process. Determining these properties is becoming increasingly important because it allows the sorption mechanism to be fully understood (Avramidis, 1992) and, from an economic point of view, it optimises industrial processes, such as drying (Meze'e et al., 2008). Freshly cut wood contains a large quantity of water. Drying is required to stabilise the dimensions and shape of wooden components, improve mechanical strength and protect the wood.
from biological attack by reducing the moisture content to the desired value (EMC 8% to 15%).

The thermodynamic properties include net isosteric heat of sorption, total heat of wetting, differential entropy and spreading pressure.

Net isosteric heat of sorption ($q_s$) provides a measure of the strength of intermolecular attraction between the sorption sites and the water molecules (McMinn and Magee, 2003; Togrul and Arslan, 2007; Wang and Brennan, 1991). Determining this parameter is essential for understanding the sorption mechanism (Xiao and Tong, 2013). Total heat of wetting ($W_0$) is the heat involved in the sorption process from fibre saturation point (FSP) to oven drying (Siau, 1995). Differential entropy ($\Delta S$) is associated with the number of sorption sites with a given level of energy (Lago et al., 2013; Madamba et al., 1996; Togrul and Arslan, 2007; Xiao and Tong, 2013). This parameter is used to obtain information about energy balance during industrial processing (Spada et al., 2013). The enthalpy-entropy compensation theory or isokinetic relationship is used to evaluate physical phenomena, such as sorption reactions (McMinn and Magee, 2003). This theory has been widely applied in various materials, including potato (McMinn and Magee, 2003), starch materials (McMinn et al., 2005), walnut kernels (Togrul and Arslan, 2007), pearl millet grain (Goneli et al., 2010), potato and sweet potato (Lago et al., 2013), quince (Noshad et al., 2013), Parana pine (Araucaria angustifolia (Bertol.) Kuntze) seeds (Spada et al., 2013) and prickly pear seeds (Hassini et al., 2015). Avramidis (1992) used it to study Western white pine (Pinus monticola Douglas ex D. Don) wood. Koumoutsakos and Avramidis (1999) studied the enthalpy-entropy compensation theory in Western hemlock (Tsuga heterophylla Sarg.), Douglas fir (Pseudotsuga menziesii (Mirb.) Franco), Western red cedar (Thuja plicata Donn ex D. Don), Sitka spruce (Picea sitchensis (Bong.) Carrière) and lodgepole pine (Pinus contorta Douglas), and determined that the
adsorption and desorption processes were enthalpy driven. It was also determined in studies of bubinga (Guibourtia tessmanii (Harms) J. Léonard and Guibourtia pellegriniana J.Léonard) (Meze'e et al., 2008). The results of Ouertani et al. (2014) in Jack pine (Pinus banksiana Lamb.) and palm “wood” were similar to the findings of Koumoutsakos and Avramidis (1999). Spreading pressure (ϕ) represents the surface excess free energy and is an indicator of the increase in surface tension in the free sorption sites due to adsorption of molecules (Fasina et al., 1999). From a practical point of view, spreading pressure makes it possible to know the hydrostatic pressure necessary to prevent swelling during the change from one relative humidity to another RH = 100% (Willems, 2014).

The objective of this study was to determine the thermodynamic properties of the wood of limba (Terminalia superba Engl. & Diels), obeche (Triplochiton scleroxylon K. Schum.), radiata pine (Pinus radiata D. Don) and chestnut (Castanea sativa Mill.), timbers commonly used in industry, through their sorption isotherms at 15 ºC, 35 ºC and 50 ºC.

2. MATERIALS AND METHODS

2.1. Moisture sorption isotherms measurement

The experiments were conducted on wood of limba (Terminalia superba), obeche (Triplochiton scleroxylon), radiata pine (Pinus radiata) and chestnut (Castanea sativa). The samples of limba and obeche were obtained at a sawmill (Fernandez et al., 2014) from green wood and identified under the microscope after preparation of slides using the traditional methods of softening, cutting and staining. The radiata pine samples were
from trees felled in the municipality of Zeanuri, province of Biscay (Spain), and the chestnut samples were from Teverga, in the province of Asturias. The dimensions of the test pieces were 15 mm long, 10 mm wide and 1 mm thick.

The 15 °C, 35 °C and 50 °C isotherms were plotted following the saturated salt method of COST Action E8 (Themelin et al., 1997), using 10 equilibrium points corresponding to 10 different salts (LiCl, CH₃COOK, MgCl₂, K₂CO₃, Mg(NO₃)₂, SrCl₂, NaCl, KCl, BaCl₂, K₂SO₄).

Fig. 1. Samples and equipment used in the experiment. A) Thermostatic baths with saturated salts; B) Flasks for holding the wood samples; salt saturated at the bottom; C) Flask with wood samples during weighing on a balance.

The test pieces were submerged in water to ensure saturation of the cell wall and then 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 24h interval. After this, the wet weight of the samples was obtained and the test pieces were placed in a desiccator with phosphorous pentoxide until they reached anhydrous state and the EMC could be calculated:

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

where \(W_w\) is the wet mass (g) and \(W_0\) is the anhydrous mass (g).

The adsorption isotherms were then obtained using the same criteria as for desorption. The Guggenheim-Anderson-de Boer (GAB) model was used to fit the isotherms. This model is appropriate when high RH values are included (Arevalo-Pinedo et al., 2004; Jannot et al., 2006):
\[ X = \frac{K \cdot C_g \cdot a_W}{(1 - K \cdot a_W)(1 - K \cdot a_W + C_g \cdot K \cdot a_W)} \cdot X_m \]  

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 RH or water activity on a scale of zero to one (dimensionless).

The isotherm fits were considered acceptable when the correlation coefficient (\( R \)) was greater than 0.990 and the root mean square error (\( RMSE \)) was less than 4% (Esteban et al., 2010, 2015; Viollaz and Rovedo, 1999). These parameters were calculated using equations:

\[ R = 1 - \frac{\sum_{i=1}^{n} (m_i - m_{pi})^2}{\sum_{i=1}^{n} (m_i - m_{mi})^2} \]  

\[ RMSE \% = 100 \cdot \sqrt{\frac{\sum_{i=1}^{n} (m_i - m_{pi})^2}{n}} \]  

where \( m_i \) is the experimental value, \( m_{pi} \) is the predicated value, \( m_{mi} \) is the average of experimental values and \( n \) is the number of observations.

2.2. Determination of net isosteric heat of sorption and total heat of wetting

Net isosteric heat was determined from the sorption isotherms using the Clausius-Clapeyron equation (Peralta et al., 1997; Tsami, 1991):

\[ q_s = -R \cdot \frac{d(\ln(a_w))}{d\left(\frac{1}{T}\right)} \]  

where \( q_s \) is the net isosteric heat of sorption (J/mol), \( a_w \) is the water activity (dimensionless), \( T \) is the absolute temperature (K) and \( R \) is the universal gas constant (J/(mol K)).
Assuming that net isosteric heat is invariable with temperature for a given EMC, the integration of the Clausius-Clapeyron equation is expressed as (Nourhene et al., 2008; Ouertani et al., 2011, 2014; Wang and Brennan, 1991):

\[ \ln(a_W) = -\frac{q_s}{R \cdot T} + cte \]  

(6)

Net isosteric heat was calculated from the slope of the line represented by \( \ln(a_w) \) versus \( 1/T \). This procedure was repeated for various EMC.

Total heat of wetting was calculated using the integration of the net isosteric heat curve from 8.7% to 20.8% EMC (Avramidis, 1997).

\[ W_0 = \int_0^{m_f} q_s \cdot dm \]  

(7)

where \( W_0 \) is the total heat of wetting (J/mol dry wood), \( q_s \) is the net isosteric heat of sorption (J/mol) and \( m_f \) is the FSP moisture content (%).

2.3. Determination of differential entropy

The differential entropy of water adsorption and desorption for each EMC was determined using the Gibbs-Helmholtz equation (Meze'e et al., 2008):

\[ \Delta S = \frac{q_s - \Delta G}{T} \]  

(8)

where \( \Delta G \) is the Gibbs free energy (kJ/mol) and it is calculated with the Van’t Hoff equation (Avramidis, 1992):

\[ \Delta G = -R \cdot T \cdot \ln(a_W) \]  

(9)

By combining Eq. (8) and Eq. (9), the relation between net isosteric heat and differential entropy is described by Eq. (10) (Aguerre et al., 1986; Everett, 1950):
\[
\ln(a_W) = -\frac{q_s}{R \cdot T} + \frac{\Delta S}{R}
\] (10)

Differential entropy was obtained from the intersection of the linearised curve and the \(ln(a_w)\) axis. This equation assumes that \(q_s\) and \(\Delta S\) are invariable with temperature or constant in the range of temperatures considered (Aguerre et al., 1986).

2.4. Enthalpy-entropy compensation theory

The enthalpy-entropy compensation theory, or isokinetic theory, provides a linear relation between enthalpy and entropy (Leffler and Grunwald, 1963):

\[
q_s = T_\beta \cdot \Delta S + \Delta G_\beta
\] (11)

where \(T_\beta\) is the isokinetic temperature (K) and \(\Delta G_\beta\) is the Gibbs free energy at \(T_\beta\) (kJ/mol). \(T_\beta\) and \(\Delta G_\beta\) were calculated from the linear regression of the experimental data using Eq. (11). The parameter \(T_\beta\) represents the temperature at which all the reactions in the series proceed at the same rate (Goneli et al., 2010; Noshad et al., 2013). The sign \(\Delta G_\beta\) makes it possible to determine whether the sorption of water molecules is a spontaneous process \((\Delta G<0)\) or a non-spontaneous process \((\Delta G>0)\) (Apostolopoulos and Gilbert, 1990).

To corroborate the existence of the compensation theory, Krug et al. (1976a, 1976b) proposed conducting a test to compare the isokinetic temperature with the harmonic mean temperature \((T_{hm})\):

\[
T_{hm} = \frac{n}{\sum_{i=1}^{n}(1/T_i)}
\] (12)

where \(n\) is the total number of isotherms used.
According to Krug et al. (1976a, 1976b), the enthalpy-entropy theory exists only if $T_β \neq T_{hm}$. Leffler and Grunwald (1963) determined that if $T_β > T_{hm}$, the process is enthalpy driven, and if $T_β < T_{hm}$, it is entropy controlled.

### 2.5. Spreading pressure

Spreading pressure was calculated from equation:

$$\phi = \frac{K_B \cdot T}{A_m} \int_0^{a_w} \frac{\theta}{a_w} d a_w$$  \hspace{1cm} (13)

where $\phi$ is the spreading pressure (J/m$^2$), $K_B$ is the Boltzmann constant (1.38 x 10$^{-23}$ J/K), $A_m$ is the surface area of a water molecule (1.06 x 10$^{-19}$ m$^2$), and $\theta$ is the ratio of moisture content ($X$) and monolayer saturation moisture content ($X_m$).

The value of the integral for $a_w = 0$ is indeterminate. Therefore $a_w = 0.05$ was taken as the lower limit of Eq. (13).

After replacing the GAB equation in Eq. (13) and integrating, spreading pressure was determined by the equation:

$$\phi = \frac{K_B \cdot T}{A_m} \cdot \ln \left[ 1 + \frac{C_g \cdot K \cdot a_w - K \cdot a_w}{1 - K \cdot a_w} \right]$$  \hspace{1cm} (14)

### 3. RESULTS AND DISCUSSION

#### 3.1. Moisture sorption isotherms

Table 1 shows the EMC values in adsorption and desorption for the wood of limba, obeche, radiata pine and chestnut at 15 °C, 35 °C and 50 °C. The data for limba and obeche are available in Fernandez et al. (2014). The fitted isotherms are type II ($C_g > 2$)
characteristic of wood (Avramidis, 1997; Simpson, 1980; Skaar, 1988). In all cases the fits are valid, as the values of $R$ are greater than 0.990 and the $RMSE$ values are less than 4% (Table 2). A dependence between sorption capacity and temperature can be seen. For a constant $a_w$, $EMC$ decreases as the temperature increases. This decrease in $EMC$ is due to the bonds in the sorption sites breaking down because of activation of the water molecules to higher energy levels as the temperature increases (Al-Muhtaseb et al., 2004; McMinn and Magee, 2003).

Fig. 1. Influence of temperature on the equilibrium moisture content of a) limba ($Terminalia superba$); b) obeche ($Triplochiton scleroxylon$); c) radiata pine ($Pinus radiata$); d) chestnut ($Castanea sativa$). a) adsorption limba; b) desorption limba; c) adsorption obeche; d) desorption obeche; e) adsorption radiata pine; f) desorption radiata pine; g) adsorption chestnut; h) desorption chestnut.

The existence of differences between the hygroscopic response of the four species studied is due to their chemical composition and internal structure. However, recent studies point to the coexistence of other possible mechanisms that also influence sorption (Rautkari et al., 2013).

3.2. Net isosteric heat of sorption and total heat of wetting

Net isosteric heat of sorption shows a strong dependence with moisture content (Fig. 2), as it decreases as $EMC$ increases. The maximum net isosteric heat of sorption for low $EMC$ indicates that the bond between the water molecules and the wood occurs first of
all in the more active sorption sites, generating strong interactions. When these sites are occupied, sorption occurs in the less active sites and the interactions are weaker (McMinn and Magee, 2003). This behaviour concurs with the findings for other species, both softwoods and hardwoods (Esteban et al., 2010, 2015; Fernandez et al., 2014; Hill et al., 2010; Ouertani et al., 2011, 2014; Tagne et al., 2011).

Fig. 2. Net isosteric heat of isotherms as a function of equilibrium moisture content for a) limba (*Terminalia superba*); b) obeche (*Triplochiton scleroxylon*); c) radiata pine (*Pinus radiata*); d) chestnut (*Castanea sativa*). The net isosteric heat of sorption values are higher in desorption than in adsorption for all the species. This may be due to the higher number of sorption sites on the surface of the material and greater bond energy during the desorption process (Tsami, 1991). As a result, total heat of wetting is also higher in desorption than in adsorption (Table 3, Fig. 2). It is also higher in the chestnut wood and lower in the radiata pine wood, indicating that the energy involved in the former is greater than in the other species, probably because of the presence of a higher number of active sites per unit of volume in the chestnut wood. As a result, the energy cost required in the chestnut wood to change its moisture content during the drying process is higher than in the other species studied.

3.3. **Differential entropy**

In Figure 3 it can be seen that differential entropy also depends on the moisture content, as it increases as *EMC* decreases. This behaviour can be attributed to an increase in the
order of the sorbed molecules as they are attracted by the sorption sites in the wood, mainly at low moisture content (Koumoutsakos and Avramidis, 1999; Skaar, 1988). Similar results were obtained by McMinn and Magee (2003) in potato, Goneli et al. (2010) in pearl millet grain, Goneli et al. (2013) in coffee fruits, pulped and green coffee, Ouertani et al. (2014) in Jack pine and palm “wood” and Hassini et al. (2015) in prickly pear seeds.

Fig. 3. Differential entropy of isotherms as a function of equilibrium moisture content for a) limba (Terminalia superba); b) obeche (Triplochiton scleroxylon); c) radiata pine (Pinus radiata); d) chestnut (Castanea sativa). a) limba; b) obeche; c) radiata pine; d) chestnut.

Figure 3 also shows that the differential entropy values in the desorption process are higher than in the sorption process. The differential entropy of a material is proportional to the number of sorption sites available for a specific energy level (Madamba et al., 1996); in this case, it indicates the state of mobility of the water molecules in the wood. The results obtained in this study indicate that the water molecules had greater mobility during desorption than in adsorption (Goneli et al., 2010). The desorption process presents higher values of differential entropy than the adsorption process. This can be explained by the greater mobility of the water molecules during desorption (Goneli et al., 2010).

3.4. Enthalpy-entropy compensation Theory
Figure 4 shows the linear relations between net isosteric heat of sorption and differential entropy for the four species. The relations are considered acceptable because they have determination coefficients higher than 0.988 (Table 4). This result validates the existence of the enthalpy-entropy compensation theory.

**Fig. 4.** Net isosteric heat as a function of differential entropy for a) limba (*Terminalia superba*); b) obeche (*Triplochiton scleroxylon*); c) radiata pine (*Pinus radiata*); d) chestnut (*Castanea sativa*). a) limba; b) obeche; c) radiata pine; d) chestnut.

To corroborate the existence of the compensation theory, the isokinetic temperature was compared with the harmonic temperature in each species (Krug et al., 1976a, 1976b). The value of $T_{hm}$ (305.6 K) differed from the values of $T_\beta$ (Table 4). This confirms the presence of the enthalpy-entropy compensation theory in the wood of limba, obeche, radiata pine and chestnut. As the isokinetic temperature values are higher than the harmonic temperature value ($T_\beta \geq T_{hm}$), the sorption processes can be considered enthalpy driven (Leffler and Grunwald, 1963). This result concurs with the findings of Koumoutsakos and Avramidis (1999) in the wood of Western hemlock (*Tsuga heterophylla*), Douglas fir (*Pseudotsuga menziesii*), Western red cedar (*Thuja plicata*), Sitka spruce (*Picea sitchensis*) and lodgepole pine (*Pinus contorta*), and the findings of Ouertani et al. (2014) in Jack pine (*Pinus banksiana*) and palm “wood”.

Gibbs free energy at $T_\beta (\Delta G)_{\beta}$ takes negative values in both adsorption and desorption for all the samples studied (Table 4). This indicates that the sorption processes are spontaneous. Koumoutsakos and Avramidis (1999) found the same behaviour in Douglas fir (*Pseudotsuga menziesii*) wood. Gibbs free energy with negative values was
determined by McMinn et al. (2005) in starch materials and Goneli et al. (2010) in pearl millet grain.

3.5. Spreading pressure

The spreading pressure of limba, obeche, radiata pine and chestnut is shown in Figure 5. The results show that spreading pressure grows as water activity increases. Spreading pressure has been used as the driving force responsible for diffusion in porous solids (Skaar and Babiak, 1982). High spreading pressure values indicate high affinity of water molecules to active sites (Torres et al., 2012).

However, unlike the behaviour of the isotherms, the spreading pressure value does not vary with temperature in the limba, obeche and radiata pine wood. Similar results were found by Arslan and Togrul (2005) in macaroni, Kaya and Kahyaoglu (2005) in pestil and Kaya and Kahyaoglu (2006) in dehulled sesame seed and dehulled-roasted sesame seed. In contrast, in the chestnut wood the spreading pressure values decrease as temperature decreases. The same behaviour was observed by Lago et al. (2013) in potato flakes and sweet potato flakes. While these materials have different hygroscopic behaviour to wood, in which other mechanisms come into play, the comparison enables analogies and differences with other materials to be established, helping to give a better understanding of the thermodynamic mechanisms of wood.

Fig. 5. Spreading pressures isotherms at different temperatures of a) adsorption limba (Terminalia superba); b) desorption limba (Terminalia superba); c) adsorption obeche (Triplochiton scleroxylon); d) desorption obeche (Triplochiton scleroxylon); e)
adsorption radiata pine \((\textit{Pinus radiata})\); f) desorption radiata pine \((\textit{Pinus radiata})\); g) adsorption chestnut \((\textit{Castanea sativa})\); h) desorption chestnut \((\textit{Castanea sativa})\).

4. CONCLUSIONS

The GAB model adequately describes the sorption isotherms of limba, obeche, radiata pine and chestnut at 15 °C, 35 °C and 50 °C. The decrease in temperature results in an increase in \(\text{EMC}\), for a constant \(a_w\).

Thermodynamic analysis shows that net isosteric heat of sorption and differential entropy decrease as \(\text{EMC}\) increases. These parameters are higher in desorption than in adsorption.

The amount of energy involved in the desorption process is greater than in adsorption. Total heat of wetting is higher in the chestnut wood and lower in the radiata pine wood.

The relation between net isosteric heat of sorption and differential entropy confirms the enthalpy-entropy compensation theory.

The adsorption and desorption processes of these species were found to be enthalpy driven, as the isokinetic temperatures are higher than the harmonic mean temperature \((T_\beta \geq T_{hm})\). The Gibbs free energy values are negative \((\Delta G_\beta<0)\), indicating that the sorption processes are spontaneous.

Spreading pressure increases as water activity increases. The effect of temperature on the spreading pressure values differs with the species, probably because of the structure and chemical composition of the specific wood.

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Table 1 Equilibrium moisture contents of radiata pine (*Pinus radiata*) and chestnut (*Castanea sativa*) for 15 °C, 35 °C and 50 °C isotherms. Data for limba (*Terminalia superba*) and obeche (*Triplochiton scleroxylon*) are available in Fernandez et al. (2014). (Tª: temperature; a_w: RH or water activity on a scale of zero to one; EMC_a: Equilibrium moisture content in adsorption; EMC_d: Equilibrium moisture content in desorption)

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<tr>
<th>Tª</th>
<th>a_w</th>
<th>EMC_a (%)</th>
<th>EMC_d (%)</th>
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<tr>
<td></td>
<td></td>
<td>Radiata pine</td>
<td>Chestnut</td>
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<tr>
<td>15 °C</td>
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<td>4.06</td>
<td>3.69</td>
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<td></td>
<td>0.2340</td>
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Table 2 Results of the GAB fit of radiata pine (*Pinus radiata*) and chestnut (*Castanea sativa*). Data for limba (*Terminalia superba*) and obeche (*Triplochiton scleroxylon*) are available in Fernandez et al. (2014). (*X*<sub>m</sub>: Monolayer saturation moisture content (%); *C*<sub>g</sub>: Guggenheim constant; **K**: Constant; **R**: Correlation coefficient; **RMSE**: Root Medium Square Error)

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<th>Desorption</th>
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<td>Radiata pine</td>
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<td><strong>K</strong></td>
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<td>0.76±0.14</td>
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<td><strong>R</strong></td>
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<td>0.998</td>
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<td><strong>RMSE</strong></td>
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<td>0.28</td>
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<tr>
<td>Chestnut</td>
<td><em>X</em>&lt;sub&gt;m&lt;/sub&gt;</td>
<td>7.83±0.24</td>
<td>6.97±0.15</td>
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<tr>
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<td><em>C</em>&lt;sub&gt;g&lt;/sub&gt;</td>
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<td><strong>K</strong></td>
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<td><strong>R</strong></td>
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<td></td>
<td><strong>RMSE</strong></td>
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Table 3 Total heat of wetting values (kJ/mol dry wood).

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<td>Obeche</td>
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<td>Chestnut</td>
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<td>64.91</td>
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</table>

Table 4 Results of the enthalpy-entropy theory. ($T_\beta$: isokinetic temperature; $\Delta G_\beta$: Gibbs free energy at $T_\beta$; $r^2$: determination coefficient)

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<tr>
<th>Material</th>
<th>Adsorption</th>
<th>Desorption</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_\beta$ (K)</td>
<td>$\Delta G_\beta$ (kJ/mol)</td>
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<tr>
<td>Limba</td>
<td>639.6</td>
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<tr>
<td>Obeche</td>
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<tr>
<td>Radiata pine</td>
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<tr>
<td>Chestnut</td>
<td>576.2</td>
<td>-1.55</td>
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Figure captions

Fig. 1. Influence of temperature on the equilibrium moisture content of a) limba (*Terminalia superba*); b) obeche (*Triplochiton scleroxylon*); c) radiata pine (*Pinus radiata*); d) chestnut (*Castanea sativa*). a) adsorption limba; b) desorption limba; c) adsorption obeche; d) desorption obeche; e) adsorption radiata pine; f) desorption radiata pine; g) adsorption chestnut; h) desorption chestnut.

Fig. 2. Net isosteric heat of isotherms as a function of equilibrium moisture content for a) limba (*Terminalia superba*); b) obeche (*Triplochiton scleroxylon*); c) radiata pine (*Pinus radiata*); d) chestnut (*Castanea sativa*). a) limba; b) obeche; c) radiata pine; d) chestnut.

Fig. 3. Differential entropy of isotherms as a function of equilibrium moisture content for a) limba (*Terminalia superba*); b) obeche (*Triplochiton scleroxylon*); c) radiata pine (*Pinus radiata*); d) chestnut (*Castanea sativa*). a) limba; b) obeche; c) radiata pine; d) chestnut.

Fig. 4. Net isosteric heat as a function of differential entropy for a) limba (*Terminalia superba*); b) obeche (*Triplochiton scleroxylon*); c) radiata pine (*Pinus radiata*); d) chestnut (*Castanea sativa*). a) limba; b) obeche; c) radiata pine; d) chestnut.

Fig. 5. Spreading pressures isotherms at different temperatures of a) adsorption limba (*Terminalia superba*); b) desorption limba (*Terminalia superba*); c) adsorption obeche (*Triplochiton scleroxylon*); d) desorption obeche (*Triplochiton scleroxylon*); e) adsorption radiata pine (*Pinus radiata*); f) desorption radiata pine (*Pinus radiata*); g) adsorption chestnut (*Castanea sativa*); h) desorption chestnut (*Castanea sativa*).