

Moisture sorption isotherms and thermodynamic properties of Jack pine and palm wood: Comparative study



Sahbi Ouertani^{a,*}, Soufien Azzouz^a, Lamine Hassini^a, Ahmed Koubaa^{b,1}, Ali Belghith^a

^a Laboratoire d'Energétique et des Transferts Thermique et Massique, Département de Physique, Faculté des Sciences de Tunis, Université de Tunis El Manar, Tunis, Tunisia

^b Chaire de recherche du Canada en valorisation, caractérisation et transformation du bois, Université du Québec en Abitibi-Temiscamingue, Rouyn-Noranda, QC, Canada

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ABSTRACT

Currently, the impact of the controlled climate on moisture sorption isotherms of Jack pine and palm wood still remains unclear. The aim of this paper was to determine and compare the moisture sorption isotherms and thermodynamic properties of Jack pine and palm wood. The equilibrium moisture content of wood samples was measured within the range of 5 to 90% relative humidity at 50 °C, 60 °C, 70 °C and 80 °C. For both wood varieties, the equilibrium moisture content decreased with increasing temperature, however the effect of temperature is very remarkable for palm wood. The isosteric heat of desorption, the enthalpy and the entropy decreased with the increase of the moisture content. A good straight line correlated differential enthalpy and entropy, according to the enthalpy–entropy compensation theory. The spreading pressure decreased with increasing temperature at a given water activity, and increased with increasing water activity at a constant temperature. Predictive correlations of the two wood properties, based on experimental methods and physical laws, were established and compared.

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1. Introduction

Jack pine wood (*Pinus banksiana*) is an important wood crop grown extensively in the northern Canada. This wood is frequently used in construction, building and thermal insulation. Canada's forest sector is among the top five contributors to the nation's net trade (Natural Resources Canada, 2014). The palm-tree sector plays a very important role in the socio-economic development of southern Tunisia. This type of wood is used in various fields, particularly in decoration craft and furniture industries (Rhouma, 1996; Ouertani et al., 2011). Otherwise, wood contains large quantities of water and is usually dried to a final moisture content that is close to the equilibrium moisture content under industrial application conditions (Leiker and Aurich, 2003). Controlled, handling, and storage of wood minimize moisture content changes that might occur after drying when physical, chemical and microbiological changes becomes undesirable (Simpson, 1999).

The knowledge of the equilibrium moisture content of wood with its surrounding environment leads to a better prediction

of the drying time, of the optimal storage and usage conditions. Several works have investigated the equilibrium moisture content of wood under controlled temperature and relative humidity (Lartigue, 1987; Ouertani et al., 2011). Indeed, the establishment of empirical and semi-empirical correlations of equilibrium moisture content as function of temperature and relative humidity presents a necessary step to modeling and optimization of the drying process (Pérré and Turner, 1999; Torres et al., 2011). Equilibrium moisture content of a wet solid is defined as the moisture content when water vapor in the pores reaches an equilibrium state with the liquid water attached to the solid (Shivhare et al., 2004). Moisture sorption isotherm is the curve presenting equilibrium moisture content versus water activity (equal to ambient relative humidity) at a fixed temperature (Kaymak-Ertekin and Sultanoglu, 2001; Boudhrioua et al., 2008). Based on Labuza (1968) work, the better understanding of product equilibrium moisture content can lead to improve storage ability at various climatic conditions, to predict drying time (King, 1968) and to design drying apparatus (Young, 1976). The static gravimetric method, using saturated salt solutions to maintain constant relative humidity in enclosed space at a specified and constant temperature, has been recommended to obtain complete sorption data (Lartigue, 1987; Bahloul et al., 2008; Ouertani et al., 2011; Machhour et al., 2012).

Several empirical and semi-empirical mathematical models have been proposed in the literature to describe the relationship

* Corresponding author. Tel.: +216 70860434; fax: +216 70860434.

E-mail addresses: sahbi.ouertani@uqat.ca, ouertani.sahbi@yahoo.fr (S. Ouertani), Ahmed.koubaa@uqat.ca (A. Koubaa).

¹ Tel: +1 819 762 0971x2579; fax: +1 819 797 4727.

between the equilibrium moisture content and relative humidity for biological products at various experimental conditions. These models were used to calculate the thermodynamic properties that could be deduced from experimental data (Brunauer et al., 1938; Oswin, 1946; Dent, 1977; Themelin, 1998; Mrekeb, 2006; Papadopoulos et al., 2005). Previous works demonstrated that there is no a single general equation able to describe the sorption isotherms of all biological products over a wide range of controlled conditions. Therefore, the establishment of a specific moisture sorption isotherm equation relative to a given product and a given range of relative humidity and temperature is necessary (Rodriguez-ramirez et al., 2011; Themelin, 1998).

The isosteric heat of sorption is an important parameter for the design of drying equipments and the optimization of drying and storage processes (Iglesias and Chirifei, 1976; Vishwakarma et al., 2011). Physically, the isosteric heat of desorption measures the energy which is required to break the inter-molecular forces between the bound water and the substratum in the hygroscopic domain. The heat required to remove water molecules in the hygroscopic domain is the sum of the liquid to vapor phase change heat and of the desorption isosteric heat. The isosteric heat of desorption was deduced by fitting experimental desorption data by the Clausius–Clapeyron formula (Tsami, 1991; Boudhrioua et al., 2008; Ouertani et al., 2011; Machhour et al., 2012). The enthalpy–entropy compensation theory has been widely investigated for different physical and chemical processes (Leffler, 1955; Aguerre et al., 1986). This theory states that the enthalpy and the specific reaction entropy are linearly correlated (Madamba et al., 1996).

The aim of this work was to measure the desorption equilibrium isotherms of two wood species at temperature ranging from 50 °C to 80 °C and at relative humidity ranging between 5% and 90% and to determine some fundamentals thermodynamic properties. The experimental equilibrium data were fitted by well-known models in order to choose the best fitting equation for the considered operating conditions. The isosteric heat of desorption at different moisture content was evaluated by the application of Clausius–Clapeyron equation to the best fit desorption model. The differential entropy was calculated using Gibbs–Helmholtz relationship for various equilibrium moisture contents. The free energy and the isokinetic harmonic temperature were calculated according to the enthalpy–entropy compensation theory correlating the enthalpy and the entropy as a linear relationship. For each wood variety, desorption process was defined as a spontaneous or a non-spontaneous one on the basis of the free energy value sign. The comparison between isokinetic temperature and harmonic mean temperature allowed us to check if the desorption process is enthalpy-driven or entropy-controlled. Spreading pressure which represents the surface excess free energy was also evaluated as a function of temperature and moisture content.

2. Material and methods

2.1. Samples preparation

Jack pine lumber pieces were obtained from Tembec's Sawmill in La Sarre, Québec, Canada. Palm wood samples (Deglet nour variety) were obtained from southern Tunisia. To limit wood variability for isotherms data, the samples were sawed from a one freshly felled green tree. In order to focus attention on the processing parameters, the samples were sawed along the longitudinal direction of the fibers; this usually presents much lower properties variations than sawing in the transverse plane (Ouertani et al., 2011). The size of the samples ($1.5 \times 1 \times 0.5 \text{ cm}^3$) (Fig. 1) was small enough to obtain a uniform equilibrium moisture content (Lartigue, 1987).



Fig. 1. Jack pine wood samples used in the experiment.

2.2. Experimental procedure: Static gravimetric method

The equilibrium moisture contents of Jack pine and palm wood at 50, 60, 70 and 80 °C were determined by using static gravimetric method. In this method, diffusion is the only way of mass transfer inside the product. Standard saturated salt solutions were used to maintain constant vapor pressure in closed space. Practically, nine saturated salt solutions (KOH, MgCl, NaBr, NaCl, LiBr, KCl, NaBr and BaCl₂) were prepared by dissolving a necessary quantity of salt in distilled water up to super-saturation which covered water activities range of 0.05 to 0.85. Selected saturated salt solutions and corresponding water activities values are reported in Table 1 (Greenspan, 1977; Labuza et al., 1985; Boudhrioua et al., 2008). Afterward, these solutions were placed inside glass bottles with insulated lid. Wood samples were suspended at the lid of the glass bottle without touching the solution. Finally, glass bottles were placed inside drying oven with controlled temperature.

The thermodynamic equilibrium was considered attained when the mass of the wood sample remained constant after three

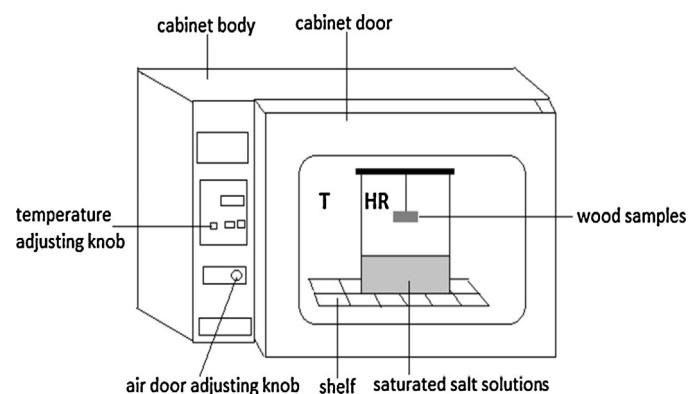


Fig. 2. Experimental apparatus for determination of sorption isotherms (DHG-9053A).

Table 1
Selected saturated salt solutions and corresponding air relative humidity.

Sels	Equations	r	Authors
LiCl	$\ln(a_w) = 500.95/T - 3.85$	0.976	Labuza et al. (1985)
MgCl ₂	$\ln(a_w) = 303.35/T - 2.13$	0.995	
K ₂ CO ₃	$\ln(a_w) = 145/T - 1.3$	0.967	
NaCl	$\ln(a_w) = 228.92/T - 1.04$	0.961	
KCl	$\ln(a_w) = 367.58/T - 1.39$	0.967	
KOH, NaBr			Greenspan (1977)
BaCl ₂			Boudhrioua et al. (2008)

Table 2

Mathematical models used to fit moisture sorption isotherms.

Models names	Models equations	Parameters
GAB (Themelin, 1998)	$X_{eq} = MC_m \times C \times k \times a_w / (1 - K \times a_w)(1 - k \times a_w + C \times K \times a_w)$	X_m, C, K
Oswin (Oswin, 1946)	$X_{eq} = A(a_w/1 - a_w)^B$	A, B
Dent (Dent, 1977)	$X_{eq} = Hr/(A \times Hr^2 + B \times Hr + C)$	A, B, C
Thermodynamic (Mrekeb, 2006)	$\ln(X_{eq}/X_{psf}) = \Phi \times \ln(a_w) \times \exp(a \times a_w)$	X_{psf}, Φ, a
BET (Brunauer et al., 1938)	$X_{eq} = ABa_w / (1 + (A - 1) \times a_w)$	A, B

consecutive measurements at intervals of 24 h. Each sample was weighed on a Toledo balance with a precision of 0.001 g. Wood dry mass was obtained after keeping the samples in a controlled-temperature oven at 103 ± 2 °C until achieving a constant mass. The equilibrium moisture content is given by the following expression:

$$X_{eq} = \frac{M_{eq} - M_d}{M_d} = \frac{M_{H_2O}}{M_d} \quad (1)$$

where X_{eq} is the equilibrium moisture content dry basis, expressed in (kg water/kg DM), M_{eq} is the equilibrium mass and M_d is the dry mass.

The experiments were carried out using a heating oven referenced DHG-9053A ($420 \times 395 \times 350$ mm³) (Fig. 2) with a temperature range of $+10\text{--}250$ °C and temperature fluctuation of ± 1 °C. The temperature was controlled by the drying oven but the relative humidity was controlled by saturated salt solutions.

3. Thermodynamic properties

3.1. Moisture sorption isotherms modeling

The experimental desorption data of Jack pine and palm wood were fitted by five different correlations recommended for hygroscopic products (Themelin, 1998; Navi and Heger, 2005; Mrekeb, 2006; Ouertani et al., 2011). The corresponding mathematical equations are listed in Table 2. These equations have two, three or four parameters. These parameters were calculated by non-linear least square regression analysis, using CurvExpert 1.3 software. The fit goodness of different model was evaluated based on two statistical criteria, namely the correlation coefficient (r) and the standard error (s). The statistical criterions definitions are given in the Appendix.

3.2. Net isosteric heat of desorption

The isosteric heat of desorption was determined by applying Eq. (2), which is derived from the Clausius–Clapeyron equation (Boudhrioua et al., 2008; Ouertani et al., 2011), to data obtained from the best fitting desorption model.

$$\frac{d \ln(a_w)}{d(1/T)|_X} = \frac{Q_{st,n}}{R} = \frac{q_{st} - L_v}{R} \quad (2)$$

Then

$$\ln(a_w) = -\left(\frac{Q_{st,n}}{R}\right)\left(\frac{1}{T}\right) + cte \quad (3)$$

where $Q_{st,n}$ is the net isosteric heat of desorption (J/mol), q_{st} is the total isosteric heat of desorption (J/mol), R is the universal gas constant (8.315 J/mol K), L_v is the latent heat of vaporization (J/mol) and a_w is the water activity.

The net isosteric heat of desorption can be determined from the slope of the graph representing $\ln(a_w)$ versus $(1/T)$ at a given specific equilibrium moisture content. This procedure is repeated for several values of equilibrium moisture content determined by the best fit sorption model. This method allows us to determine the

variation of net isosteric heat ($Q_{st,n}$) with moisture content. Several studies neglected the impact of temperature on isosteric heat (Tsami, 1991). In order to check this behavior, the isosteric heat was determined on the basis of sorption isotherms measured at more than two temperatures.

3.3. Differential entropy

The differential entropy (ΔS) is related to the number of available sorption sites at a specific energy level (Madamba et al., 1996). Entropy defines the degree of order or randomness existing in the water-sorbent system which can help interpreting processes such as dissolution, crystallization and swelling. This parameter can be calculated from the Gibbs–Helmholtz equation as follows (McMinn et al., 2005):

$$\Delta S = \frac{Q_{st,n} - \Delta G}{T} \quad (4)$$

Table 3
Results of fitting of the desorption isotherms of palm wood.

Model names	Temperature (°C)	Model parameters	s	r
GAB	50	$K=0.877$ $X_m=0.0979$ $C_g=8.369$	0.0122	0.997
	60	$K=0.873$ $X_m=0.09599$ $C_g=4.036$	0.0122	0.996
	70	$K=0.849$ $X_m=0.0967$ $C_g=2.766$	0.008	0.998
	50	$A=1.3847$ $B=7.7817$ $C=-7.8938$	0.12	0.997
	60	$A=2.911$ $B=5.382$ $C=-6.935$	0.012	0.996
	70	$A=4.338$ $B=3.209$ $C=-5.725$	0.008	0.998
	50	$X_{psf}=0.687$ $\Phi=1.006$ $a=1.5536$	0.01145	0.997
	60	$X_{psf}=0.635$ $\Phi=1.154$ $a=1.389$	0.011	0.997
	70	$X_{psf}=0.5459$ $\Phi=1.254$ $a=1.2611$	0.00738	0.9984
BET	50	$A=93.752$ $B=0.0551$	0.0457	0.9537
	60	$A=26.941$ $B=0.0525$	0.033	0.97018
	70	$A=19.448$ $B=0.048$	0.026	0.9747
	50	$A=0.1516$ $B=0.508$	0.0129	0.9964
	60	$A=0.128$ $B=0.5644$	0.013	0.9956
	70	$A=0.1116$ $B=0.5818$	0.01	0.996
Oswin	50	$A=0.1516$ $B=0.508$	0.0129	0.9964
	60	$A=0.128$ $B=0.5644$	0.013	0.9956
	70	$A=0.1116$ $B=0.5818$	0.01	0.996

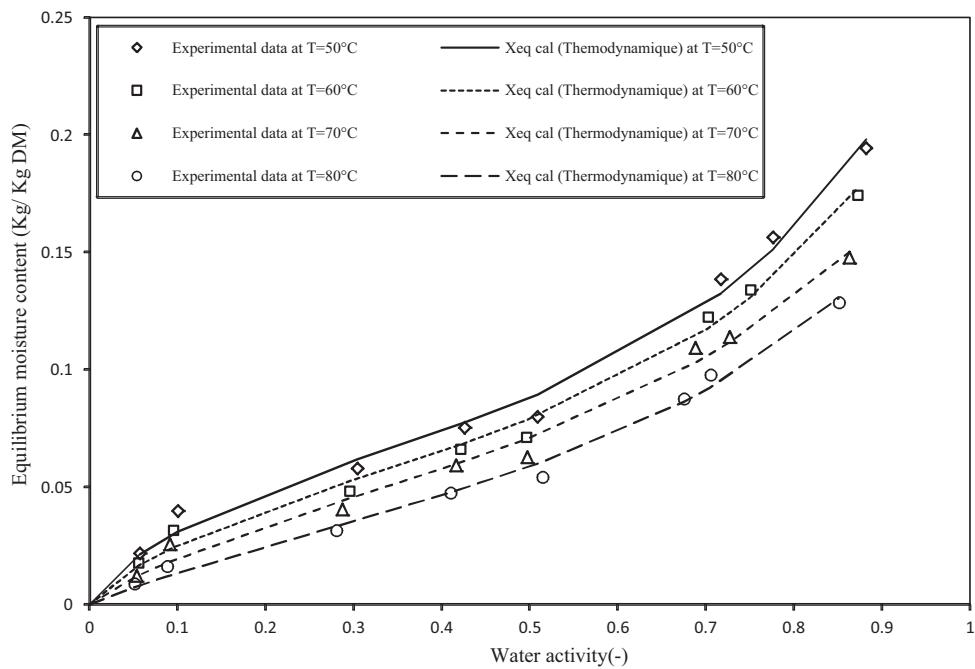


Fig. 3. Influence of temperature on the equilibrium moisture content of Jack pine wood.

where Gibbs free energy (ΔG) is calculated as

$$\Delta G = -RT \ln(a_w) \quad (5)$$

Inserting Eq. (4) into Eq. (5), we can obtain Eq. (6):

$$-\ln(a_w) = \frac{Q_{st,n}}{RT} - \frac{\Delta S}{R} \quad (6)$$

From the plot of $\ln(a_w)$ versus $(1/T)$ for various equilibrium moisture contents, the differential entropy can be determined as the intercept of the linearized experimental curve and the a_w axis.

3.4. Enthalpy–entropy compensation theory

The enthalpy–entropy compensation theory has been widely studied for several physical and chemical processes (Aguerre et al., 1986). According to this theory, there is a linear relationship between enthalpy and entropy for a specific reaction which is given by Eq. (7) (Leffler, 1955):

$$Q_{st,n} = T_\beta \Delta S + \Delta G_\beta \quad (7)$$

The isokinetic temperature (T_β) represents the temperature at which all reactions in the series proceed at the same rate, and ΔG_β is the free energy at the specific temperature (T_β). The sign of ΔG_β indicates whether water sorption is a spontaneous (negative) or a

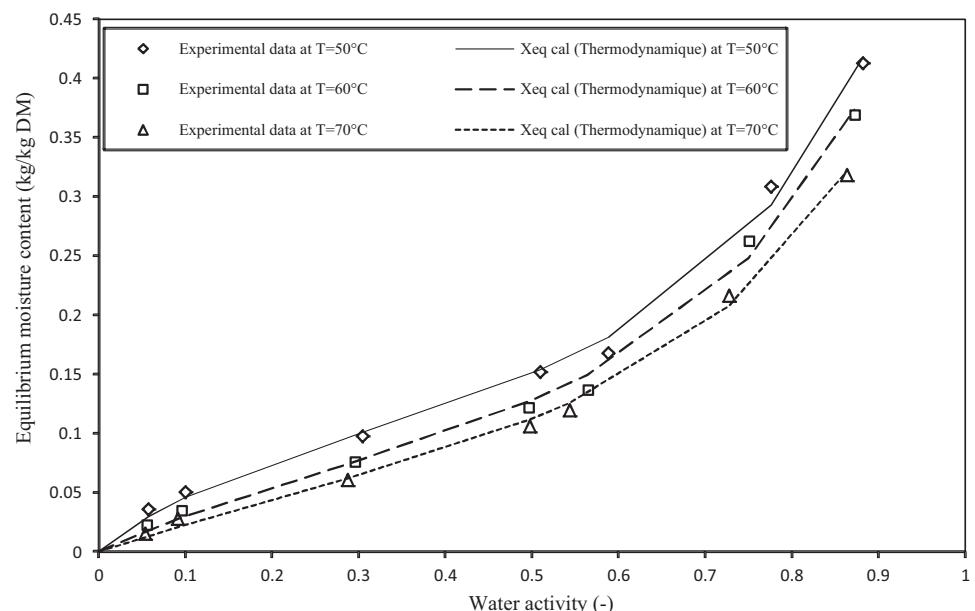


Fig. 4. Influence of temperature on the equilibrium moisture content of palm wood.

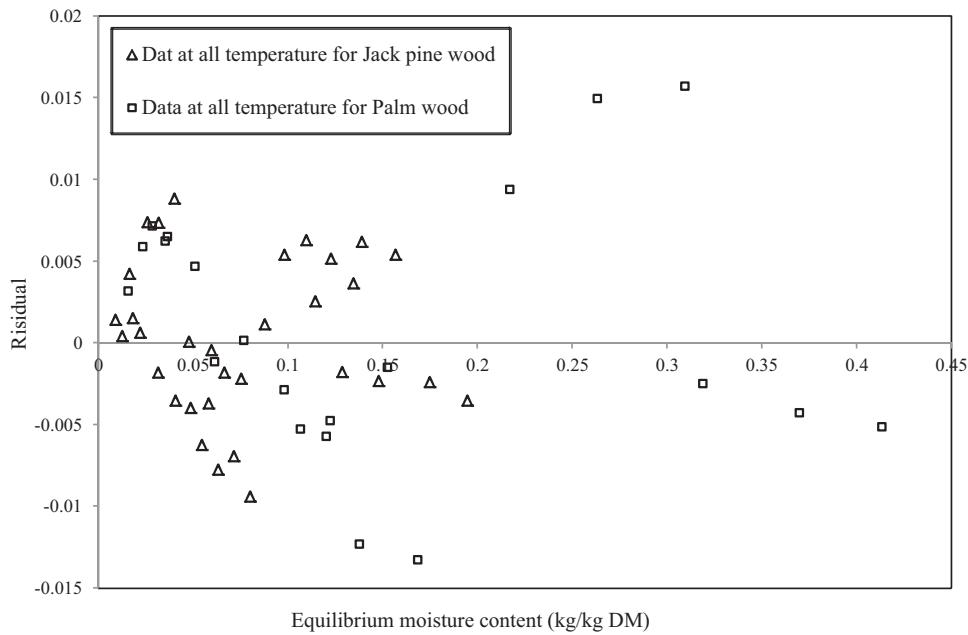


Fig. 5. Residual plot for predicted equilibrium moisture content using thermodynamic model for Jack pine and palm wood.

non-spontaneous process (positive). T_β and ΔG_β were calculated by linear regression from the experimental data using Eq. (7).

In order to check the compensation theory, Krug et al. (1976a, 1976b) proposed Eq. (8) to compare the isokinetic temperature (T_β) with the harmonic mean temperature (T_{hm}):

$$T_{hm} = \frac{n}{\sum_{i=1}^n (1/T)} \quad (8)$$

In compensation enthalpy–entropy theory, the isokinetic temperature (T_β) should be different to the harmonic temperature (T_{hm}). Leffer and Grunwald (1963) assumed that if ($T_\beta > T_{hm}$) the process is enthalpy-driven and if ($T_\beta < T_{hm}$) the process is entropy-controlled.

To model the temperature influence on the sorption isotherms behavior, the enthalpy–entropy compensation theory can be used by rearranging Eqs. (6) and (7) to obtain the following Eq. (9). Parameter (ΔG_β) is neglected for its small contribution in the enthalpy change (Aguerre et al., 1986).

$$-\ln(a_w) = \frac{Q_{st,n}}{R} \left(\frac{1}{T} - \frac{1}{T_\beta} \right) \quad (9)$$

The influence of temperature on moisture equilibrium properties can be considered by rewriting Eq. (9) in the following form:

$$\Psi_T \ln(a_w) = K\Phi(X) \quad (10)$$

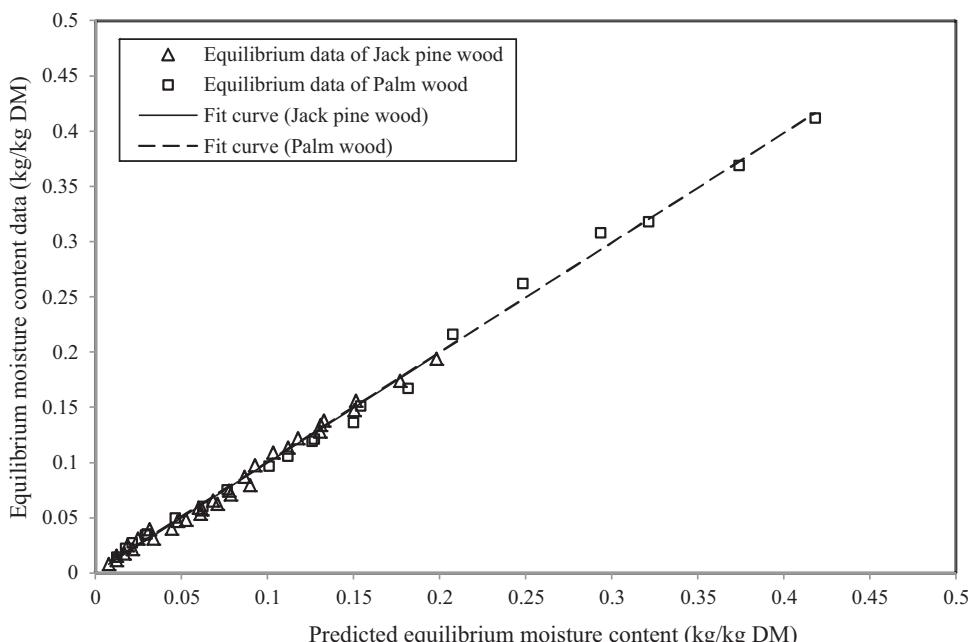


Fig. 6. Correlation between the values predicted by the thermodynamic model and the experimental values of the equilibrium moisture content at all temperatures of Jack pine and palm wood.

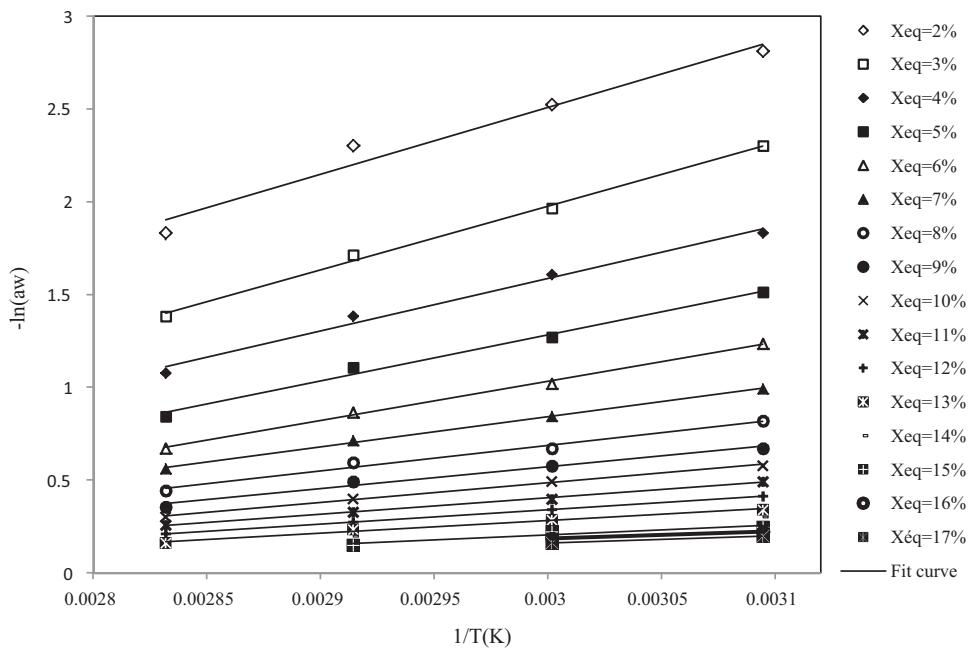


Fig. 7. Desorption isosteric curve of Jack pine wood.

where $\Psi_T = ((1/T) - (1/T_\beta))^{-1}$ is the temperature correction factor. $\Phi(X)$ is an empirical function of the equilibrium moisture content. The equilibrium data can be represented plotting $\ln(\Psi_T \ln(a_w))$ as a function of the equilibrium moisture content. Aguerre et al. (1986) asserted that if this correction factor is adequate, the equilibrium data of a given product, at different temperatures, present the same mathematical form when plotted in accordance with Eq. (11). A power law was proposed in our study:

$$\Psi_T \ln(a_w) = K_1 K_2^X \quad (11)$$

After plotting $\ln(\Psi_T \ln(a_w))$ versus equilibrium moisture content, the constants K_1 and K_2 were calculated by linear regression.

3.5. Spreading pressure

The spreading pressure (π) called ‘surface potential’ is the force applied in the surface plane perpendicularly to each unit length of edge to keep the surface from spreading. It represents the surface excess free energy (Noshad et al., 2012). It was estimated by the following equation:

$$\pi = \frac{K_B T}{A_m} \int_0^{a_w} \frac{\theta}{a_w} da_w \quad (12)$$

To determine spreading pressure, an empirical procedure assumed between moisture content and water activity. The

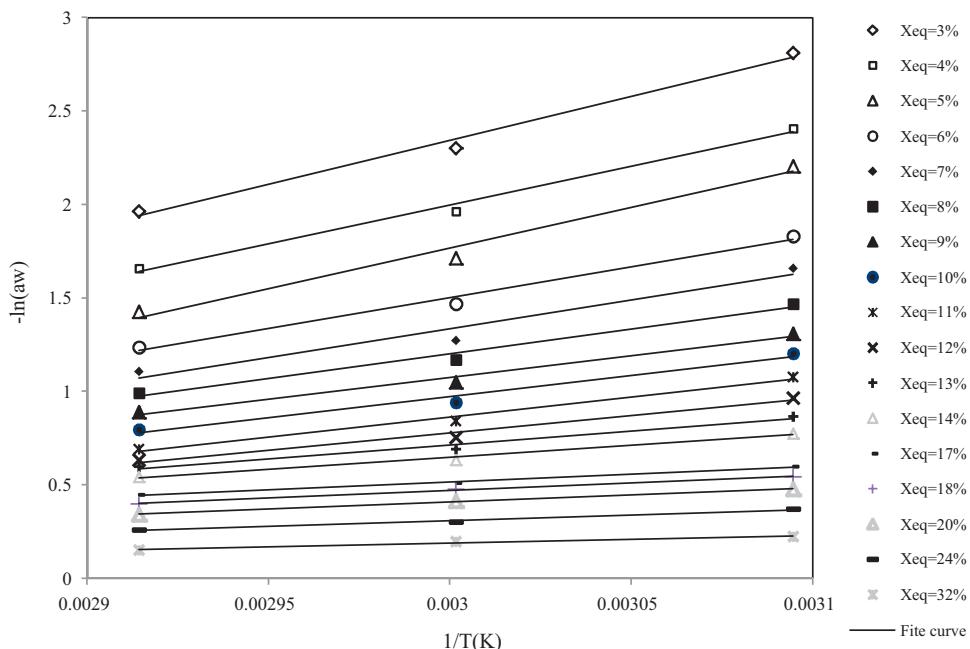


Fig. 8. Desorption isosteric curve of palm wood.

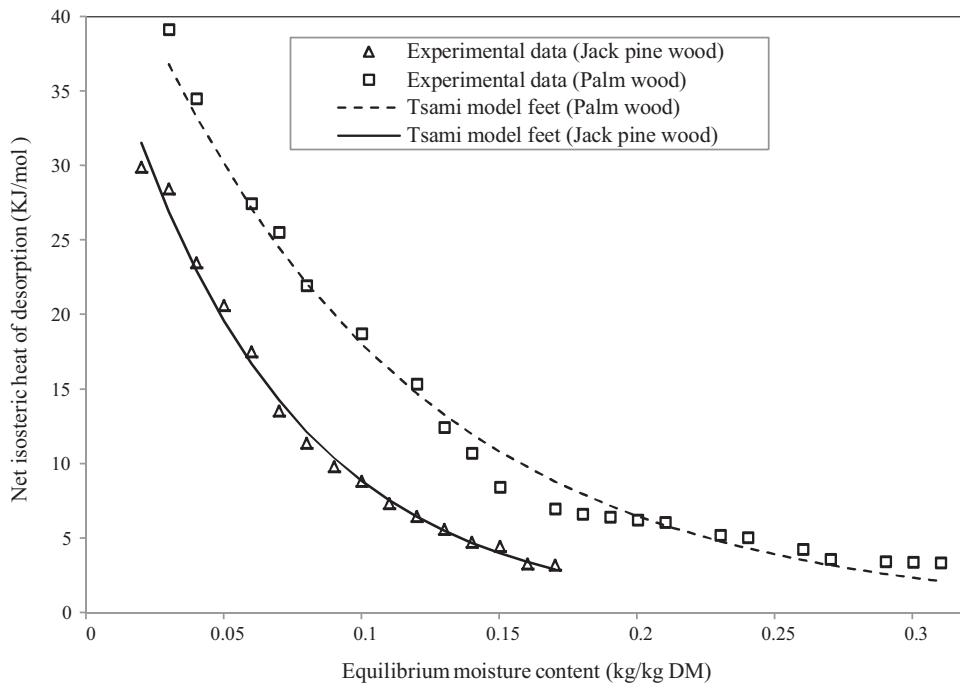


Fig. 9. Net isosteric heat of desorption isotherms of Jack pine and palm wood.

solution proposed by Dent (1977) was used in this study. The final form of spreading pressure in term of surface area per sorption site is reported by (Togrul and Nurhan, 2007; Polatoglu et al., 2011) and given by the following equation:

$$\pi = \frac{K_B T}{A_m} \ln \left[\frac{1 + A - Ba_w}{1 - Ba_w} \right] \quad (13)$$

BET equation was used to calculate the parameters A and B (Tables 3 and 4). This equation has the advantage to describe the monolayer product moisture content, which represents an important parameter to determine the spreading

pressure. π is the spreading pressure (J/m^2), K_B is the Boltzmann constant ($1.38 \times 10^{-23} J/K$), A_m is the area of water molecule ($1.06 \times 10^{-19} m^2$), $\theta = X/X_m$ and T is the absolute temperature (K).

4. Results and discussions

4.1. Equilibrium moisture content

Experimental desorption isotherms of Jack pine and palm wood are shown in Figs. 3 and 4. The desorption isotherms curves have a sigmoid shape of type II for palm wood and type III for Jack

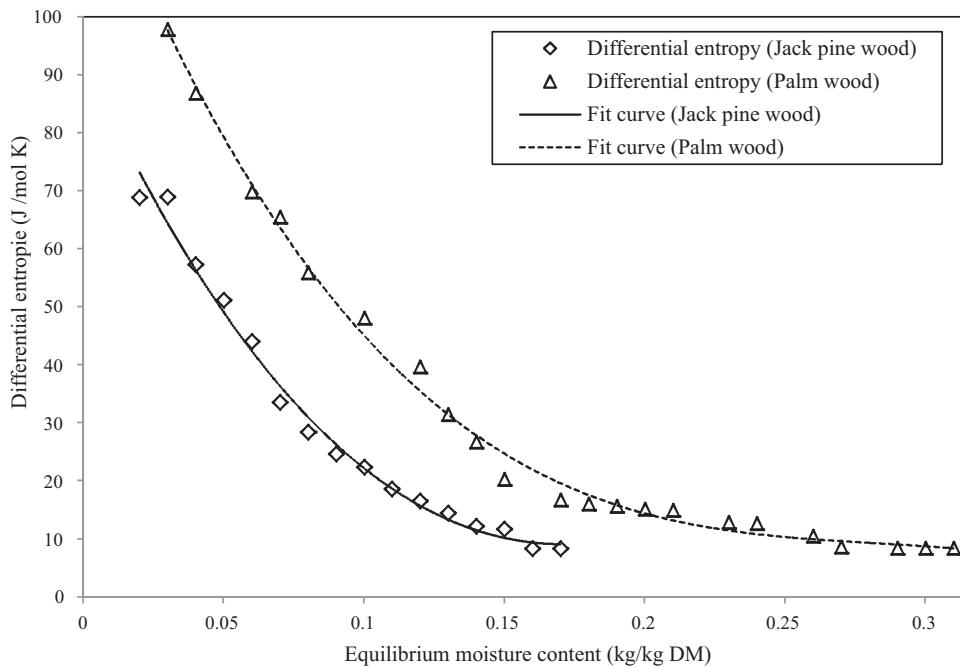


Fig. 10. Differential entropy of Jack pine and palm wood.

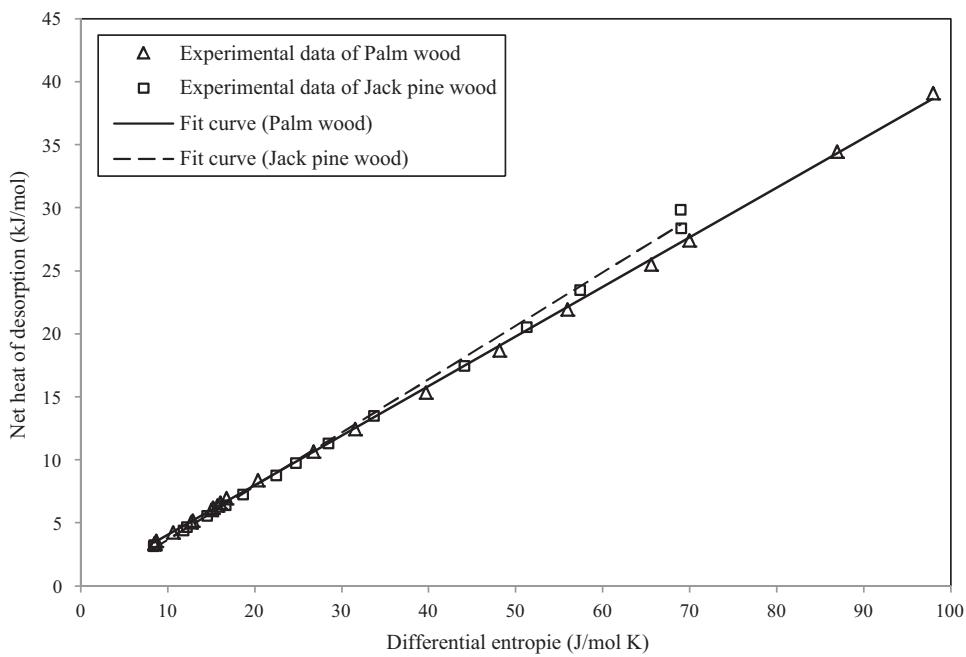


Fig. 11. Plot of enthalpy change against entropy change for water adsorbed by Jack pine and palm wood.

pine wood, according to the BET classification. For a given value of water activity, the equilibrium moisture content decreases with increasing temperature. The increase of temperature promotes the detachment of water molecules from the water binding sites (Ethmane Kane et al., 2008). The difference in the equilibrium moisture content of the two wood varieties can be explained by the difference of internal structures. The sigmoid shape of sorption isotherms is common behavior for many hygroscopic products documented in literature such as Maritime pine (*Pinus pinaster Aiton*) (Lartigue, 1987), Eucalyptus and Angelique (Themelin, 1998), tropical wood (Nkolo Meze'e et al., 2008), beech red spruce and white fir (Khouya and Draoui, 2009) and palm wood (Ouertani et al., 2011).

4.2. Fitting of sorption models to experimental data

The results of the non-linear regression of desorption isotherms of Jack pine and palm wood at various temperatures are shown in Tables 3 and 4, respectively. For all the models tested, the correlation coefficient (r) and standard error (s) are reported as a comparison criterion. The lowest values of standard error and highest values of correlation coefficient explained the best goodness of fit. A residuals plot of the predicted by Thermodynamic model equilibrium moisture content versus water activity is also shown in Figs. 3 and 4. Analysis of the residuals for the thermodynamic model is shown in Fig. 5. The residuals obtained from

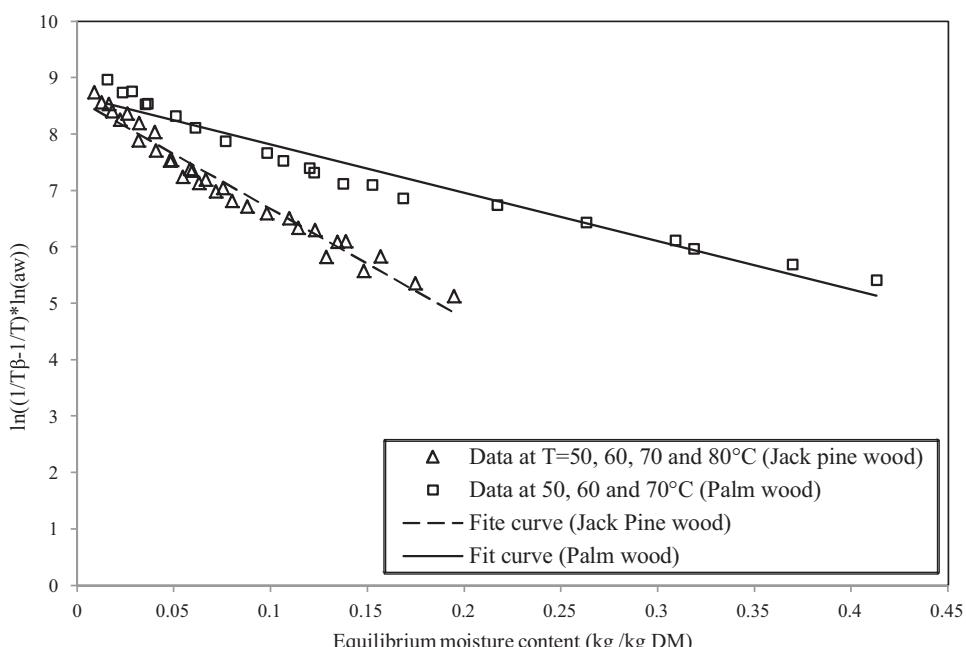


Fig. 12. Equilibrium moisture data of Jack pine and palm wood plotted according to Eq. (11).

Table 4

Results of fitting of the desorption isotherms of Jack pine wood.

Model names	Temperature (°C)	Model parameters	S	r
GAB	50	$K=0.886$ $X_m=0.044$ $C_g=-1.746 \times 10^{11}$	0.016	0.974
	60	$K=0.9$ $X_m=0.0396$ $C_g=2.639 \times 10^{10}$	0.0155	0.9709
	70	$K=0.8998$ $X_m=0.0349$ $C_g=6.754 \times 10^{10}$	0.0164	0.9562
	80	$K=0.7516$ $X_m=0.0547$ $C_g=3.377$ $A=1.6598$ $B=14.588$ $C=-12.9736$	0.0046	0.9956
Dent	50	$A=2.3531$ $B=14.809$ $C=-13.628$	0.0071	0.9950
	60	$A=3.9046$ $B=11.963$ $C=-11.417$	0.0059	0.9957
	70	$A=7.054$ $B=7.848$ $C=-9.952$	0.0063	0.9935
	80	$X_{psf}=0.2855$ $\phi=0.8366$ $a=1.4154$	0.0046	0.9956
Thermodynamic	50	$X_{psf}=0.260$ $\phi=0.8868$ $a=1.3244$	0.0072	0.9948
	60	$X_{psf}=0.2106$ $\phi=0.9252$ $a=1.055$	0.0058	0.9959
	70	$X_{psf}=0.1931$ $\phi=1.0451$ $a=0.9955$	0.0059	0.9943
	80	$A=20.76 \times 10^4$ $B=0.02813$	0.0043	0.9961
BET	50	$A=907.3$ $B=0.02703$	0.0318	0.875
	60	$A=99.6883$ $B=0.0248$	0.02571	0.9
	70	$A=35.425$ $B=0.02277$	0.2311	0.893
	80	$A=0.0873$ $B=0.4174$	0.0163	0.93312
Oswin	50	$A=0.07790$ $B=0.4397$	0.0081	0.9922
	60	$A=0.0688$ $B=0.443$	0.0067	0.9934
	70	$A=0.057$ $B=0.9903$	0.0078	0.9883
	80		0.0062	0.9903

experimental and predicted equilibrium moisture content are negligible. The results revealed that the Thermodynamic model provided better fit than Dent, GAB, Oswin and BET model. A plot of predicted versus measured equilibrium moisture content for the Thermodynamic model is shown in Fig. 6.

4.3. Isosteric heat of desorption and differential entropy

The desorption isosters curves for palm and Jack pine wood are shown in Figs. 7 and 8. The net isosteric heat of desorption for Jack pine and palm wood versus moisture content obtained by applying Clausius–Clapeyron equation is shown in Fig. 9. As seen in Fig. 9, the net isosteric heat of desorption increases continuously with decreasing moisture content for two wood species. The

Table 5

Characteristic parameters for enthalpy–entropy relationship.

Material	T_β (K)	ΔG_β (J/mol)	r
Jack pine wood	424	-552.9	0.99
Palm wood	393.2	157.26	0.998

importance of the net isosteric heat of desorption at low moisture content is an indication of strong water–surface interactions in the product (Tsami, 1991; Polatoglu et al., 2011). Similar behavior has been observed for various biological products such as palm wood (Ouertani et al., 2011), Olive leaves (Bahoul et al., 2008) and *Mentha pulegium* and *Mentha rotundifolia* (Ethmane Kane et al., 2008). The variation of the net isosteric heat of desorption with moisture content was fitted by an exponential function:

$$Q_{st\ pred} = 43.32 \times \exp\left(\frac{-X_{eq}}{0.063}\right) \quad (\text{Jack pine wood}) \quad (r = 1)$$

$$Q_{st\ pred} = 50 \times \exp\left(\frac{-X_{eq}}{0.098}\right) \quad (\text{palm wood}) \quad (r = 0.98)$$

Similar results were reported by Nkolo Meze'e et al. (2008) for tropical wood and Ouertani et al. (2011) for palm wood (Besser variety). For a given moisture content, the heat required to evaporate the water in the hygroscopic region was found to be higher for palm wood than for Jack pine wood.

Fig. 10 shows the differential entropy for Jack pine and palm wood versus equilibrium moisture content. It can be seen that the differential entropy increases with decreasing equilibrium moisture content. The entropy data display a strong dependence on equilibrium moisture content. The variation of desorption differential entropy (ΔS) with moisture content for the two wood species was best fitted by a three-degree polynomial function as follows:

$$\Delta S = 92.911 - 1060X_{eq} + 3804.9X_{eq}^2 - 2763.93X_{eq}^3 \quad (\text{Jack pine wood}) \quad r = 0.994$$

$$\Delta S = 131.1 - 1238.02X_{eq} + 4284X_{eq}^2 - 2253.47X_{eq}^3 \quad (\text{palm wood}) \quad r = 0.997$$

4.4. Enthalpy–entropy compensation theory

A good straight line related the net desorption isosteric heat and the differential entropy of desorption for the two wood species, at different temperatures (Fig. 11). This behavior confirms the enthalpy–entropy compensation hypothesis (Leffer and Grunwald, 1963). It was assumed that at a specific moisture content, the net isosteric heat and differential entropy of desorption are independent with temperature (Aguerre et al., 1986). The isokinetic temperature (T_β) and the free energy (ΔG_β) were determined by linear regression of Eq. (7). The characteristic parameters (Table 5) for enthalpy–entropy relationship for Jack pine and palm wood are, respectively:

$$Q_{st,n} = -0.5529 + 0.424 \Delta S \quad (\text{Jack pine wood})$$

$$Q_{st,n} = 0.15726 + 0.3932 \Delta S \quad (\text{palm wood})$$

The value of (ΔG_β) was found to be negative (-552.9 J/mol) for Jack pine wood, indicating a spontaneous desorption process, and positive (+157.26 J/mol) for palm wood indicating a non-spontaneous desorption process. The values of isokinetic temperature (T_β) for Jack pine and palm wood were 424 K and 393.2 K,

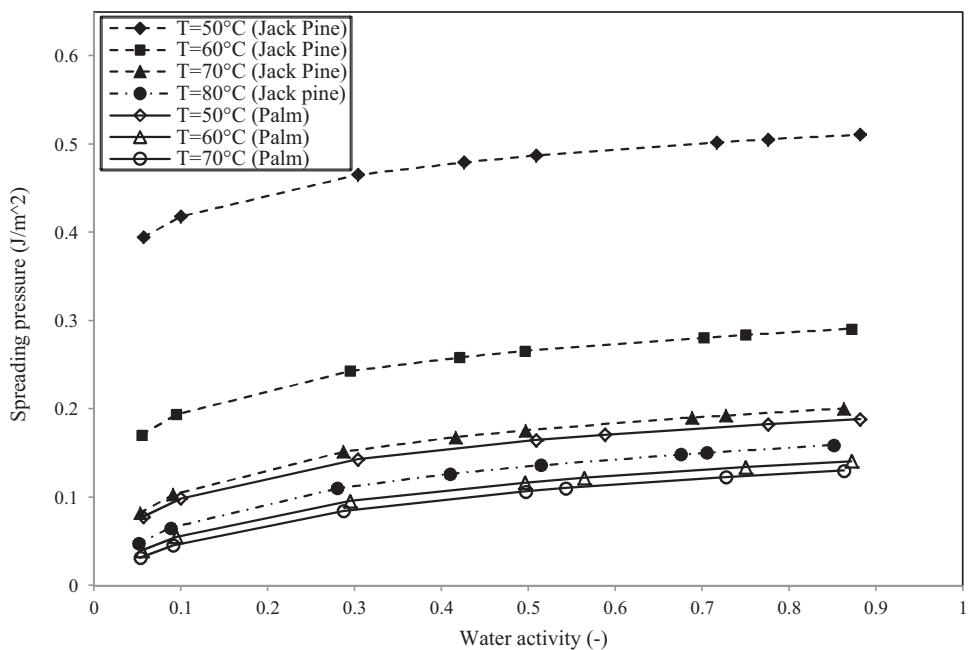


Fig. 13. Spreading pressure desorption isotherms for Jack pine and palm wood at different temperatures.

Table 6
Values of parameters relative to Eq. (11).

Material	K_1 (K)	K_2	r
Jack pine wood	5506.5854	$3.6997510^{(-9)}$	0.981
Palm wood	5859.38542	0.000188691	0.974

respectively. The harmonic temperature (T_{hm}) was found to be $T_{hm} = 337.78\text{ K}$ for Jack pine wood and $T_{hm} = 332.95\text{ K}$ for palm wood. It was observed then that $T_{hm} \neq T_\beta$ for the two varieties of wood.

This difference between harmonic and isokinetic temperature corroborates also the enthalpy–entropy compensation theory (Rawat and Khall, 1996). Similar results were found by Koumoutsakos and Avramidis (1999) for Douglas fir heartwood. Our result shows that (T_β) is higher than (T_{hm}), the desorption process is thus enthalpy-driven (Leffer and Grunwald, 1963).

The compensation theory was used also to model the temperature influence on moisture sorption according to Eqs. (10) and (11). Fig. 12 shows a typical evolution of $\ln((1/T_\beta - 1/T) \ln(a_w))$ with moisture content. A straight line was obtained for the two wood species. This confirms that the temperature effect on moisture sorption follows a power law (Aguerre et al., 1986). The values of parameters K_1 and K_2 were calculated using linear regression and are reported in Table 6.

4.5. Spreading pressure data

Fig. 13 shows the evolution of spreading pressure versus equilibrium moisture content of Jack pine and palm wood at different temperature by applying Eq. (13). Analysis results show that for the two wood varieties the spreading pressure increased with increasing water activity, and decreased with increasing temperature at constant water activity. Similar behavior was reported for various biological products (Polatoglu et al., 2011; McMinn and Magee, 2003).

5. Conclusion

According to our results, the following conclusions can be proposed. For the two wood varieties the increase of temperature enhances the water desorption. At constant temperature, the equilibrium moisture content values increases with increasing water activity. The Thermodynamic model best describes the experimental desorption isotherms for the two wood varieties. The net isosteric heat of desorption, estimated using Clausius–Clapeyron equation, is an exponential function of the moisture content. The differential entropy evaluated on the basis of the Gibbs–Helmholtz relationship, is a third degree polynomial function of moisture content. A linear relationship between differential entropy and enthalpy exists what confirms the enthalpy–entropy compensation theory. According to the value of the free energy for the two varieties, desorption is a spontaneous process. As the isokinetic temperature is greater than the harmonic mean temperature, the desorption process is enthalpy-driven. As concern the spreading pressure, this parameter decreases with an increase in temperature at constant water activity and increases with increasing moisture content at constant temperature. The empirical and semi-empirical correlations established in this work can describe rigorously the hygroscopic behavior of the two considered woods in order to optimize its drying process and in general its industrial processing. This study can be extended to measure the mechanical properties of these wood varieties. The knowledge of mechanical wood behavior is important before its use for building purposes.

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Appendix A.

$$s = \sqrt{\frac{\sum_{i=1}^{n_{\text{exp data}}} (X_{eqi} - X_{eqCali})^2}{n_{\text{exp data}} - n_{\text{param}}}}$$

$$r = \sqrt{1 - \frac{\sum_{i=1}^{n_{\text{exp data}}} (X_{eqi} - X_{eqCali})^2}{\sum_{i=1}^{n+} (\bar{X}_{eq} - X_{eqi})^2}}$$

$$\bar{X}_{eq} = \frac{1}{n_{\text{exp data}}} \sum_{i=1}^{n_{\text{exp data}}} X_{eqi}$$

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