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# Effect of natural cellulosic fibers on the thermodynamic properties of a clay mixture product

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*Abstract - The aim of this work was to study the effect of the natural cellulosic fibers on the essential thermodynamic properties of a clay mixture product. The equilibrium moisture content of clay mixture and clay mixture with natural plant fibers were determined using standard gravimetric method at 60, 70 and 80°C over a range of relative humidity from 5 to 90%. Experimental desorption isotherms of the two products were fitted by five models (GAB, Oswin, Dent, BET and Henderson's) among the most used ones in literature. For both products, the equilibrium moisture content decreased with increasing temperature at constant water activity (ambient relative humidity). However the effect of temperature on the equilibrium moisture content is very remarkable for the clay mixture. The GAB model was found to be the most suitable for clay mixture while the Dent model had the best fit performance for the clay-fibers composite. Based on the thermo dynamical approach, some fundamental properties were evaluated, namely: the isosteric heat of desorption, the enthalpy and the entropy. These functions decreased with the increase of the moisture content. According to the enthalpy-entropy compensation theory, a linear correlation was found between the differential enthalpy and the entropy. Predictive correlations of the clay mixture and the clay-cellulosic fiber composite properties, based on experimental methods and physical laws, were established and compared.*

*Index Terms - clay mixture, natural cellulosic fibers, desorption isotherms, heat of desorption, differential entropy, enthalpy-entropy compensation theory.*

## I. INTRODUCTION

There are several advantages of the addition of natural plant fibers to clay products. These advantages can be social, economic or environmental [1], [2], [3]. Among natural plants fibers, we can cite: seminal hair seeds (cotton, kapok), stems of plants (flax, hemp, jute, ramie), leaf (sisal), trunks (Manila hemp) and envelopes fruit (coconut). In general, the choice of natural fibers is performed according to its physicochemical properties and its availability.

The scientific foundation of natural fibers composites demonstrated that this product is easier to recycle and if their matrix is biodegradable (biopolymer), after grinding are compostable [4],[3]. Despite the composites reinforced with natural fibers are being increasingly developed, their applications are still limited, nevertheless, they will have to play a determinant role in future industries, especially as eco-friendly and/or hybrid materials. The use of natural fibers as composite materials reinforcement has some advantages. In particular, it promotes a local resource in less industrialized countries and enhances the development of materials and technologies taking into account the impacts on the environment [1].

Natural fibers are quality materials that make recycling and naturally on earth for millions of years (renewable and biodegradable materials by crop). In addition, Natural fiber composites open new markets for agricultural products, therefore, there are also the economic and social aspects of planning. Most natural fibers lead to interesting performances (regarding the reinforcing function) of the obtained composites, and they also have a structural role in nature.

In hygroscopic compound materials, in which the equilibrium pressure of water vapour changes with moisture content and temperature, water interacts with, and is in various degrees bound to, other molecules. The degree to which water is bound is described by the water activity. The equilibrium moisture content is defined as being the ratio of water mass over total mass (wet base) of a product when it is submitted to specific condition of temperature and humidity [5].

The equilibrium moisture content and the water activity at given temperature and pressure are related by the sorption isotherm. The better understanding of product equilibrium moisture content can lead to improve storage ability at various climatic conditions, to predict optimum drying process [6] and to design drying apparatus [7].



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Numerous mathematical equations can be found in literature that describe water sorption isotherms of hygroscopic porous materials. Each of the models proposed, empirical, semi-empirical or theoretical, has had some success of a given type material and a given range of water activity [8]. Previous works demonstrated that there is no a single general equation able to describe the sorption isotherms of all hygroscopic 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 [9], [10].

Otherwise, the desorption models were used to calculate some fundamentals thermodynamic properties [11], [10], [12], such as the isosteric heat of desorption and the entropy.

The isosteric heat of desorption is an important parameter for the design of drying equipments and the optimization of drying and storage processes [8] [13]. 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 equation [14], [15], [16]. The enthalpy-entropy compensation theory has been widely investigated for different physical and chemical processes [17],[ 18]. This theory states that the enthalpy and the specific reaction entropy are linearly correlated [19].

To our knowledge, they are no published works concerning the effect of natural cellulosic fibers on the thermodynamic equilibrium properties of a clay mixture material has been published.

Inside this context, this work is intended to measure the desorption equilibrium isotherms of a clay mixture, with and without cellulosic fibers, at temperature ranging from 60°C to 80°C and at relative humidity ranging between 5% and 90%. Furthermore, we aim at establishing the predictive correlations of some fundamentals thermodynamic properties versus the desorption state variables (the moisture content and the temperature). Five theoretical and empirical models available on isotherm and drying literature and frequently used in clay studies were tested for fitting the experimental equilibrium data. The isosteric heat of desorption at different moisture content was evaluated on the basis of Clausius-Clapeyron formula applied 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. Beside, for both products, desorption process was defined as a spontaneous or as a non-spontaneous one regarding the free energy value sign. The comparison between isokinetic temperature and harmonic mean temperature values allowed us to check if the desorption process is enthalpy-driven or entropy-controlled.

## II. MATERIALS AND METHODS

### A. Samples Preparation

The clay mixture used in this study is a commercial product obtained from BIBLIONTEK Company [20]. This mixture contains clay RR32, halloysite, vermiculite, clay 24: Sereilhac clay with moisture content dry basis equal to 35%. As concerns, the clay-cellulosic fiber composite, this innovative product, was obtained after incorporation of plant fibers (7%) in the clay mixture described above, and has a flexural strength of 7 MPa when it is completely dried. The fibers used are mainly composed of cellulose ((C<sub>6</sub>H<sub>5</sub>O<sub>5</sub>)<sub>n</sub>), lignin ((C<sub>9</sub>H<sub>10</sub>O<sub>2</sub>)<sub>n</sub>) and of Pentosan ((C<sub>5</sub>H<sub>10</sub>O<sub>5</sub>)<sub>n</sub>). One of the important applications of such clay mixture and composite is for the processing of boxes devoted to the preservation of heritage and precious objects against fire damage and other degradation (moisture, insects, etc.).

The mineralogical characterization of the studied clay-based samples was performed using a Bruker-AXS D5000 powder diffractometer with the Cu K $\alpha$ 1 radiation (1.5418Å) and a graphite back-monochromator. Fig. 1 shows the X-ray diffraction (XRD) diagrams of the two products. It marks the presence of an intense peak characteristic of quartz (SiO<sub>2</sub>). The two products contain also kaolinite, halloysite, illite, montmorillonite, vermiculite as clay minerals. The goethite is detected as a ferric phase. These results were confirmed by the EDS (Energy Dispersive Spectroscopy) micro-analysis spectra (see Fig. 2 (a) and (b)), which confirms the

existence of alkaline elements (Na, K), alkaline earth metals (Ca, Mg) and the presence of iron element (Fe).

For further information on these two materials, the morphology of the clay mixture and the clay mixture with fiber was reported on Fig. 3. The observation of the morphology of clay mixture (Fig.3.(a)) confirms the presence of the vermiculite platelets. She shows also a strong heterogeneity. This heterogeneity does not prevent strong cohesion clay mixture -cellulosic fibers such illustrated by the state of the interface of the clay mixture-fiber (Fig.3.(b) and (c)).

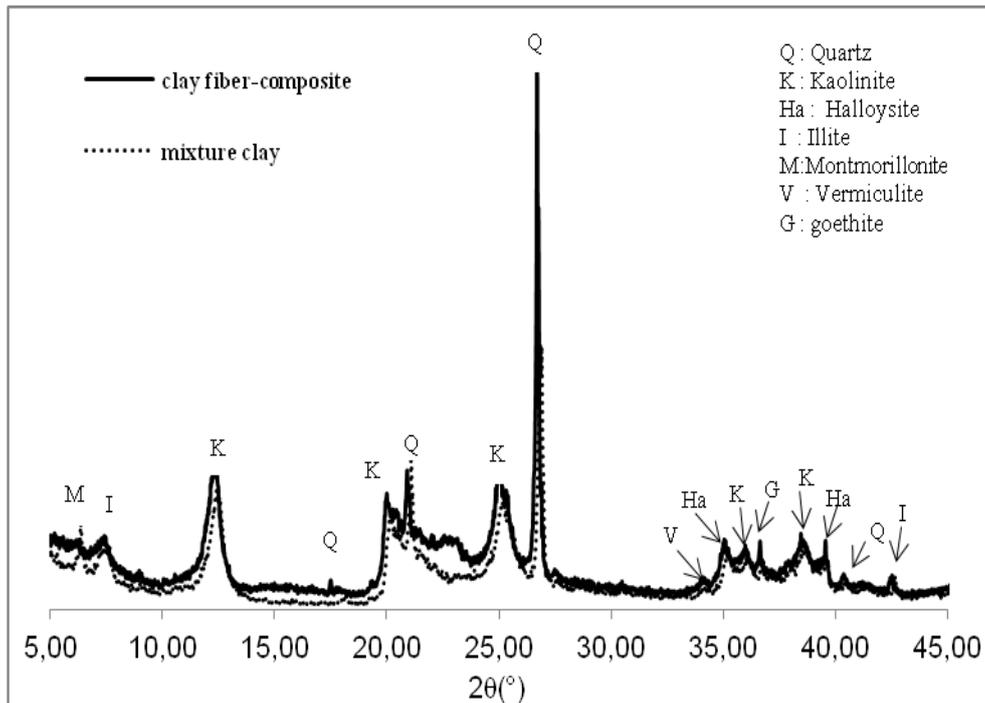


Fig.1: XRD traces of clay mixture and clay-fiber composite.

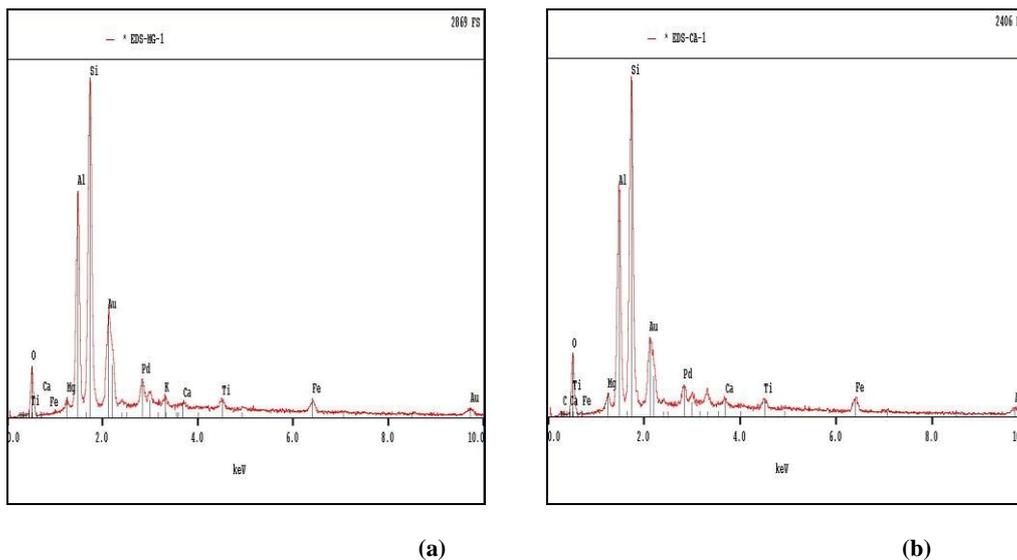


Fig.2: EDS spectra of clay mixture (a) and clay-fiber composite (b)

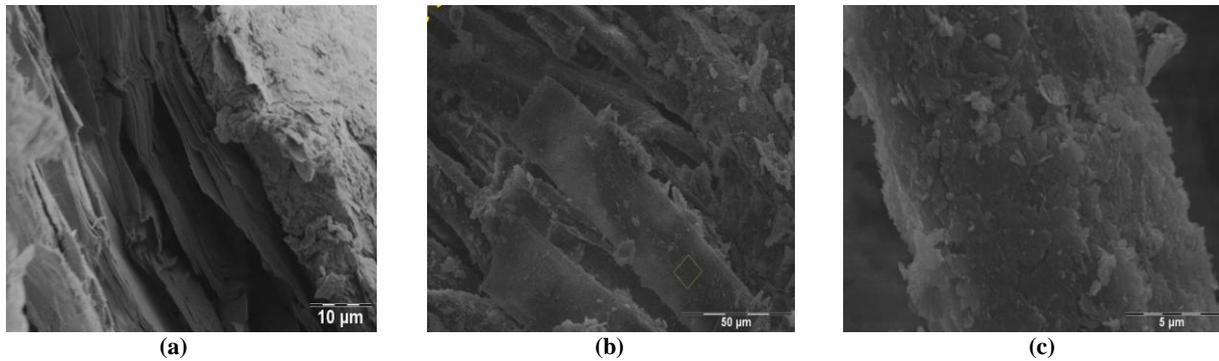


Fig.3: SEM images of clay mixture (a) and clay-fiber composite ((b) and (c))

**B. Experimental Procedure: Static Gravimetric Method**

The equilibrium moisture contents of clay mixture and clay mixture with fibers at 60, 70, and 80°C were determined by using static gravimetric methodology (fig.4) (developed by the European Cooperation Project COST90 [21]). In this method, diffusion is the only way of mass transfer inside the product. Standard saturated salt solutions (LiCl, MgCl<sub>2</sub>, K<sub>2</sub>CO<sub>3</sub>, NaBr, (NH<sub>4</sub>)<sub>2</sub> SO<sub>4</sub>, K<sub>2</sub>SO<sub>4</sub>) 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. The selected saturated salt solutions and corresponding water activities values are reported in Table 1.

Table 1: Selected saturated salt solutions and corresponding air relative humidity [22], [23].

sals	Relative humidity (%)		
	60C°	70°C	80C°
Li Cl	11	10,8	10,5
MgCl <sub>2</sub>	29,3	27,8	26,1
K <sub>2</sub> CO <sub>3</sub>	42,12	42,1	42
NaBr	49,7	49,7	51,4
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	80,3	79,5	78,9
K <sub>2</sub> SO <sub>4</sub>	95,8	95,8	95,8

These saturated solutions were placed inside desiccators with insulated lid (Fig. 4). 1-cm cube of clay mixture (or clay-fiber composite) samples were suspended at the lid of the desiccators without touching the solution. Finally, desiccators were placed in an oven where constant temperature is maintained. This experience was repeated at three temperatures (60, 70 and 80°C) to evaluate the effective influence of temperature.

The thermodynamic equilibrium was considered to be achieved when the mass of the clay sample remained constant after three consecutive measurements at intervals of 24 hours. Each sample was weighed on a Toledo balance with a precision of ±0.001 g. For each product, the dry mass of each sample was determined by putting the six samples in an oven at 105 ± 1°C for at least 24h [24], [25], [26].. The difference of mass before and after drying in the oven gives the moisture content X<sub>eq</sub> of the product at hygroscopic equilibrium:

$$X_{eq} = \frac{m_{eq} - m_d}{m_d} = \frac{m_{water}}{m_d} \quad (1)$$

where,  $X_{eq}$  is the equilibrium moisture content dry basis, expressed in (kg water/kg dry matter),  $m_{eq}$  is the equilibrium mass and  $m_d$  is the dry mass of the sample.

The experiments were carried out using a heating oven referenced DHG-9053A (420 x 395 x 350 mm<sup>3</sup>) (Fig. 4) with a temperature range of +10-250°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. All isotherm measurements were done at least twice in order to check the reproducibility of the desorption isotherms curves.

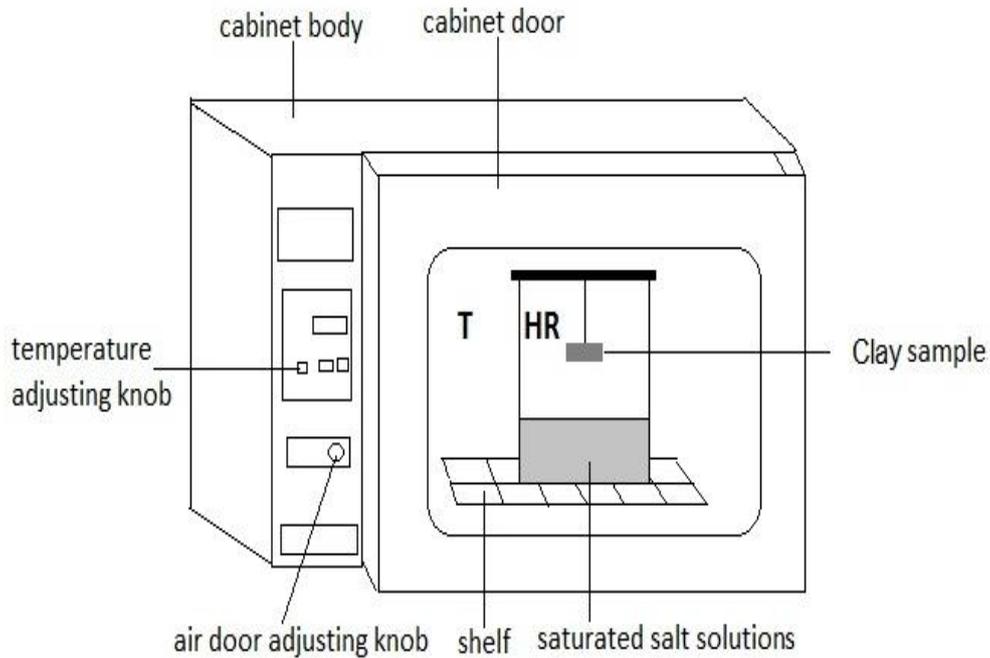


Fig. 4: Experimental set-up for the determination of sorption isotherms (DHG-9053A).

### III. THERMODYNAMIC PROPERTIES

#### A. Moisture Sorption Isotherms Modeling

The experimental desorption data of clay mixture and clay mixture with fibers were fitted by five semi-empirical correlations recommended for hygroscopic products [12], [27]. The corresponding mathematical equations are listed in Table 2. These equations have two or three parameters. These parameters were calculated by non-linear least square regression analysis, using CurvExpert 1.3 software. The quality/accuracy of the fit using different models 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 A.

Table 2: Mathematical models for fitting the desorption isotherms.

Models names	Models equations	Parameters
GAB [8]	$X_{eq} = \frac{X_m \cdot C \cdot k \cdot a_w}{(1 - K \cdot a_w)(1 - k \cdot a_w + C \cdot K \cdot a_w)}$	$X_m, C, K$
Oswin [28]	$X_{eq} = A \left( \frac{a_w}{1 - a_w} \right)^B$	$A, B$



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Volume 4, Issue 2, March 2015

Dent [14]	$X_{eq} = \frac{Hr}{A.Hr^2+B.Hr+C}$	A, B, C
Henderson's [29]	$X_{eq} = \left( \frac{-\ln(1-a_w)}{A(1.8T + 492)} \right)^{1/B}$	A, B
BET [2]	$X_{eq} = \frac{A B a_w}{(1 - a_w)(1+(A-1).a_w)}$	A, B

**B. Net Isotheric Heat of Desorption**

For a given equilibrium moisture content, the isotheric heat of desorption was determined by applying equation (2), which derives from the Clausius–Clapeyron equation [7], using the data obtained from the best fitting desorption model..

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

Then

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

where  $Q_{st,n}$  is the net isotheric heat of desorption (J/mol),  $q_{st}$  is the total isotheric 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 isotheric 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 desorption model. This approach allows us to determine the variation of net isotheric heat ( $Q_{st,n}$ ) with moisture content. Several studies neglected the impact of temperature on isotheric heat [16]. In order to check this behavior, the isotheric heat was determined on the basis of sorption isotherms measured at more than two temperatures.

**C. Differential Entropy**

The differential entropy ( $\Delta S$ ) is related to the number of available sorption sites at a specific energy level [19]. 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 [30]:

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

Where Gibbs free energy ( $\Delta G$ ) is calculated as:

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

Inserting equation (4) in equation (5), we can obtain the equation (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 moistures contents, the differential entropy can be determined as the intercept of the linearized experimental curve and the  $a_w$  axis.

**D. Enthalpy-Entropy Compensation Theory**

The enthalpy-entropy compensation theory has been widely studied for several physical and chemical processes [17]. According to this theory, there is a linear relationship between enthalpy and entropy for a specific reaction which is given by equation (7) [18]:



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International Journal of Engineering Science and Innovative Technology (IJESIT)

Volume 4, Issue 2, March 2015

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

The isokinetic temperature ( $T_{\beta}$ ) represents the temperature at which all series proceed at the same rate, and  $\Delta G_{\beta}$  is the free energy at the specific temperature ( $T_{\beta}$ ). The sign of  $\Delta G_{\beta}$  indicates whether water desorption is a spontaneous (negative) or a non-spontaneous process (positive). ( $T_{\beta}$ ) and  $\Delta G_{\beta}$  were calculated by linear regression from the experimental data using equation (7).

In order to verify the compensation theory, [31] [32]: proposed equation (8) to compare the isokinetic temperature ( $T_{\beta}$ ) with the harmonic mean temperature ( $T_{hm}$ ):

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

In the compensation enthalpy-entropy theory, the isokinetic temperature ( $T_{\beta}$ ) should be different to the harmonic temperature ( $T_{hm}$ ). Leffler and Grunwal [33] 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 equation (6) and equation (7) to obtain the following equation (9). Parameter  $\Delta G_{\beta}$  is neglected for its small contribution in the enthalpy change [1]:

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

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

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

where  $\Psi = ((1/T) - (1/T_{\beta}))^{-1}$  is the temperature correction factor and  $\Phi(X)$  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 [17] 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 equation (11). A power law was proposed in our study:

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

Then

$$\ln(\Psi_T \ln(a_w)) = \ln(K_1) + X \ln(K_2) \quad (12)$$

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

## VI. RESULTS AND DISCUSSION

### A. Equilibrium Moisture Content

Experimental desorption isotherms of the clay mixture and the derived clay-fiber composite are shown in Figs. 5 and 6. The desorption isotherms curves exhibit a sigmoid shape of type III for the clay mixture and type II for the clay-fiber composite, 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 [34]. The difference in the equilibrium moisture content of the two materials can be explained by the difference in internal morphology and microstructure. The sigmoid shape of sorption isotherms is a common behavior for many hygroscopic products reported in the literature such as Kaolin [26]; Palm and Jack pine wood [35].

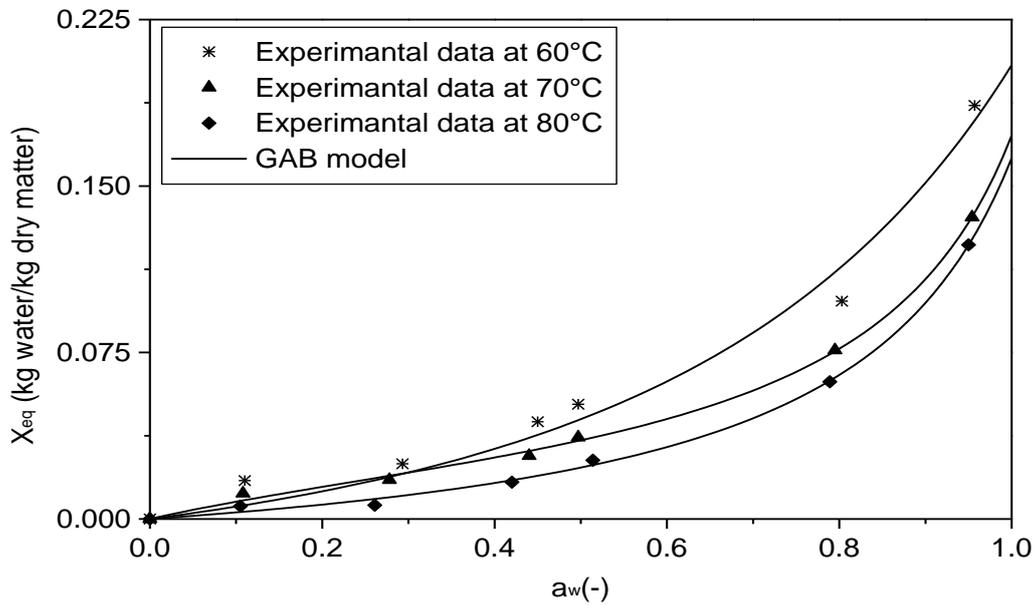


Fig. 5. Influence of temperature on the desorption isotherms of clay mixture.

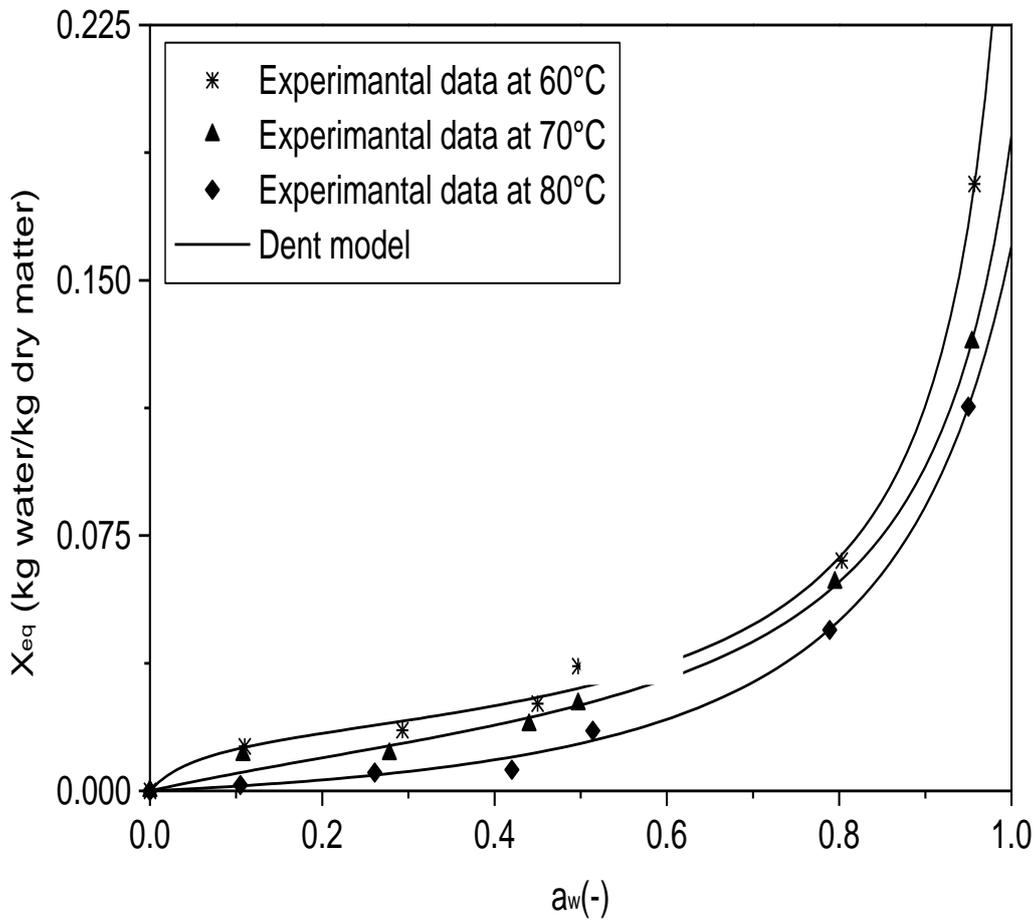


Fig. 6. Influence of temperature on the desorption isotherms of the clay-fiber composite.



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Volume 4, Issue 2, March 2015

**B. Fitting of Sorption Models To Experimental Data**

The results of the non-linear regression of desorption isotherms of the clay mixture and clay-fiber composite, at various temperatures, are shown in Table 3 and Table 4, respectively. For all the models tested, the correlation coefficient (r) and standard error (s) are reported as a comparison criterion to evaluate the fit quality. The lowest values of standard error and highest values of correlation coefficient characterize the best fit. According to these results, the best fit was obtained by the GAB model with physiochemical parameters for the clay mixture and the Dent model for the clay-fiber composite. The comparison between the calculated (by the best models) and the experimental values for the two products at all experimented temperatures is shown in Fig. 7.

Model names	Temperature (°C)	Model Parameters	s	r
GAB	60	K = 0.5575 X <sub>m</sub> = 0.4360 C <sub>g</sub> = 0.2078	0.0114	0.999
	70	K = 0.8452 X <sub>m</sub> = 0.0280 C <sub>g</sub> = 3.6838	0.0026	0.999
	80	K = 0.8343 X <sub>m</sub> = 0.0322 C <sub>g</sub> = 0.8343	0.0026	0.999
Dent	60	A = -23.8803 B = 23.0829	0.0037	0.9988
	70	C = 4.9235 A = -22.0800 B = 16.4913	0.0026	0.999
	80	C = 11.3737 A = -0.06284 B = -30.7978 C = 37.0108	0.0026	0.999
Henderson	60	w <sub>psf</sub> = 0.687 φ = 1.006 a = 1.5536	0.01145	0.997
	70	w <sub>psf</sub> = 0.635 φ = 1.154 a = 1.389	0.011	0.997
	80	w <sub>psf</sub> = 0.5459 φ = 1.254 a = 1.2611	0.00738	0.9984
BET	60	A = 23.41e10 B = 0.00879	0.0326	0.8836
	70	A = 5.14e10 B = 0.0069	0.017	0.9407
	80	A = 82.32e2 B = 0.0065	0.0173	0.9407
Oswin	60	A = 0.04916 B = 0.4333	0.0055	0.9967
	70	A = 0.0361 B = 0.4431	0.0065	0.9923
		A = 0.02527	0.0069	0.9906



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Volume 4, Issue 2, March 2015

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B=0.54519

Table 3 Results of fitting of the desorption isotherms of the clay mixture.

Table 4 Results of fitting of the desorption isotherms of the clay-fiber composite.

Model names	Temperature (°C)	Model Parameters	s	r
GAB	60	K = 0.95207 X <sub>m</sub> =0.01582 C <sub>g</sub> = 17.27e10	0.00536	0.9978
	70	K = 0.9332 X <sub>m</sub> = 0.01451 C <sub>g</sub> = 1.0257e8	0.0063	0.9935
	80	K = 0.8635 X <sub>m</sub> =0.02912 C <sub>g</sub> = 0.4979	0.0026	0.999
Dent	60	<b>A = -52.6556</b> <b>B = 52.3908</b>	<b>0.00431</b>	<b>0.9995</b>
	70	<b>C = 3.4588</b> <b>A = -33.3115</b> <b>B = 20.7427</b>	<b>0.0026</b>	<b>0.999</b>
	80	<b>C = 17.7594</b> <b>A = 34.9179</b> <b>B = -111.5984</b> <b>C = 82.9242</b>	<b>0.0024</b>	<b>0.9998</b>
Henderson	60	w <sub>psf</sub> =0.687 ϕ = 1.006 a = 1.5536	0.01145	0.997
	70	w <sub>psf</sub> =0.635 ϕ =1.154 a=1.389	0.011	0.997
	80	w <sub>psf</sub> =0.5459 ϕ = 1.254 a = 1.2611	0.00738	0.9984
BET	60	A =7.604e11 B =0.007976	0.01873	0.9636
	70	A =2.196e10 B =0.0065	0.017	0.9407
	80	A =26.0624 B =0.00588	0.0096	0.9766
Oswin	60	A=0.03193 B=0.5536	0.00349	0.9987
	70	A=0.0265 B=0.5322	0.0043	0.9963
	80	A=0.01686 B=0.6499	0.005	0.9935

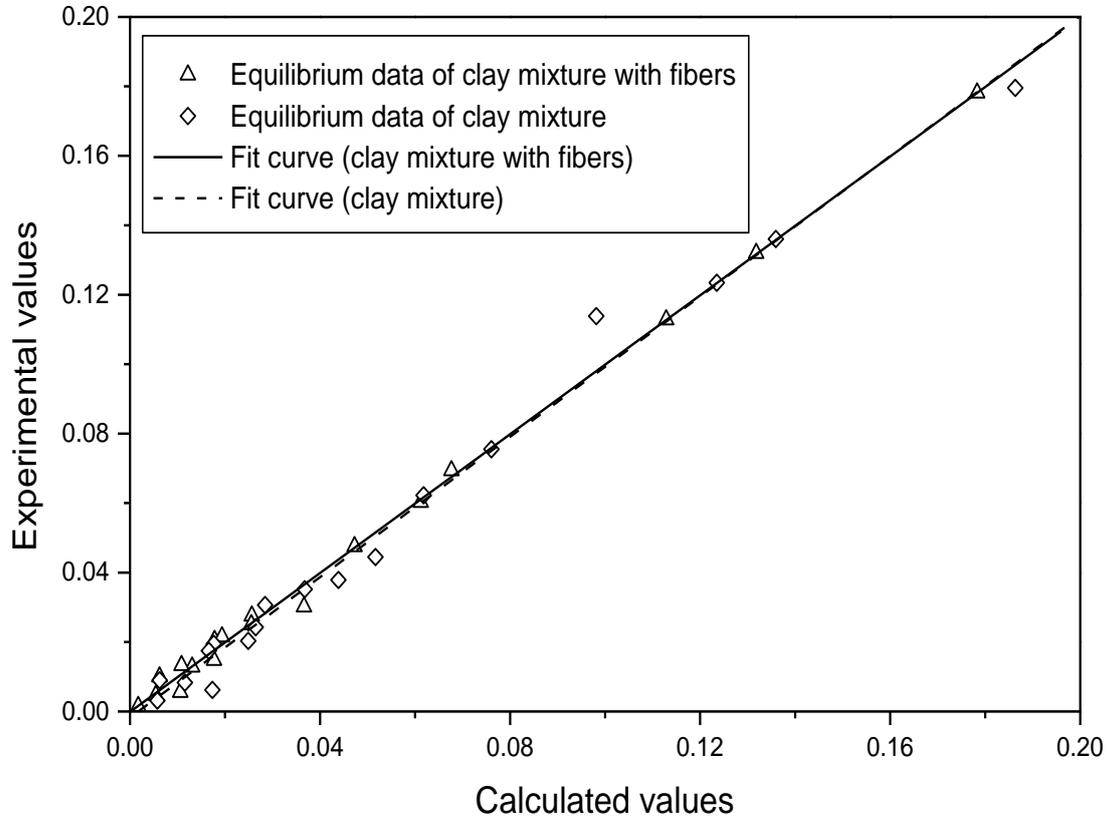


Fig. 7. Experimental and calculated equilibrium moisture content values by GAB model for the clay mixture and by Dent model for the clay-fiber composite at all temperatures.

**C. Isotheric Heat Of Desorption and Differential Entropy**

The desorption isosters for the clay mixture and clay-fiber composite are shown in Figs. 8 and 9. Each curve determines the heat required to evaporate the water in the hygroscopic region for given moisture content.

The net isotheric heat of desorption for the clay mixture and clay-fiber composite versus moisture content obtained by applying Clausius-Clapeyron equation is shown in Fig. 10. As shown in Fig. 10, for both materials, the net isotheric heat of desorption increases strongly with decreasing moisture content. The high value of the net isotheric heat of desorption at low moisture content is relevant of strong water-surface interactions in the product, because the product may contain a lot of free water easy to remove [36], [16]. Similar behavior has been observed for various hygroscopic products such as kaolin [26], palm wood and Jak pine wood [35], Olive leaves [37]: and Mentha pulegium and Mentha rotundifolia [34]. The variation of the net isotheric heat of desorption with moisture content was fitted by a power function (13) for clay mixture and (14) for clay-fiber composite:

$$Q_{st\ pred} = 2.634X_{eq}^{-0.585} : \quad (13)$$

$$Q_{st\ pred} = 0.195X_{eq}^{-1.269} : \quad (14)$$



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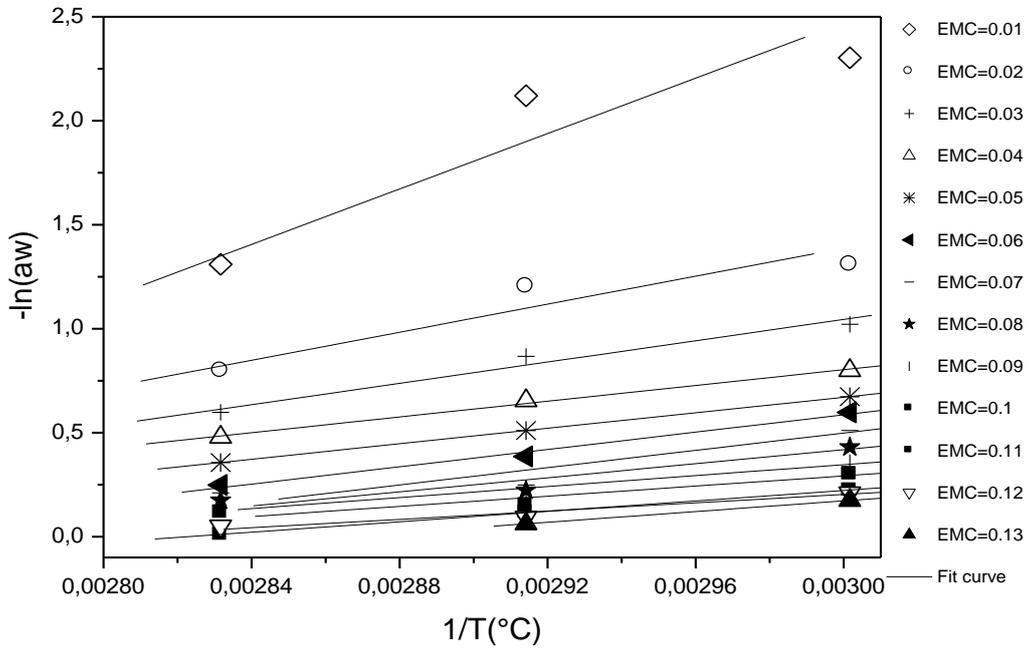


Fig.8: Desorption isothermic curve of clay mixture.

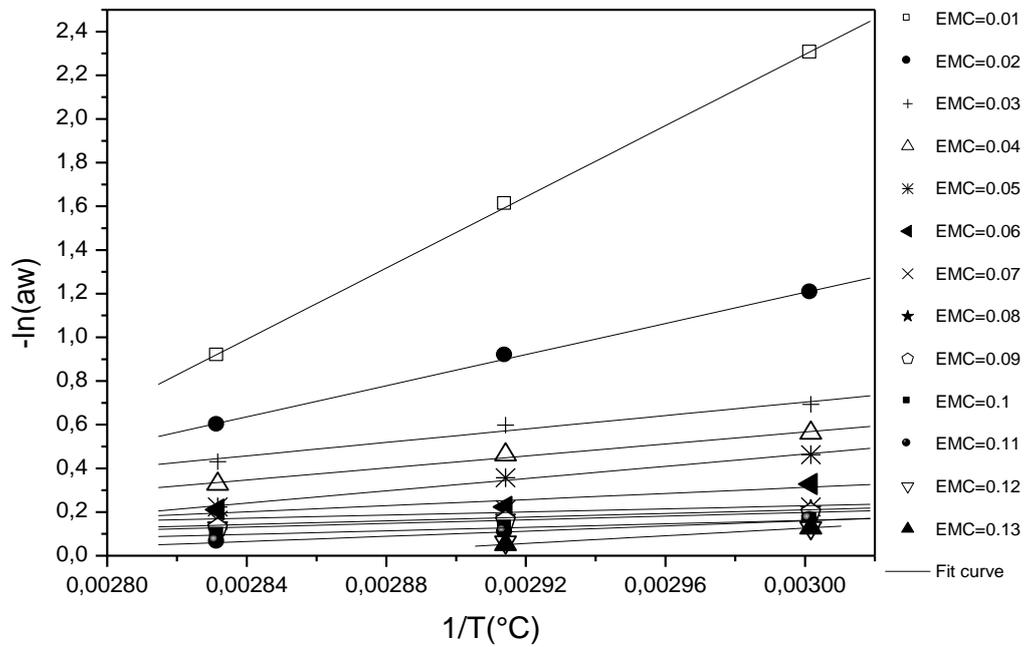


Fig.9: Desorption isothermic curve of clay-fiber composite.

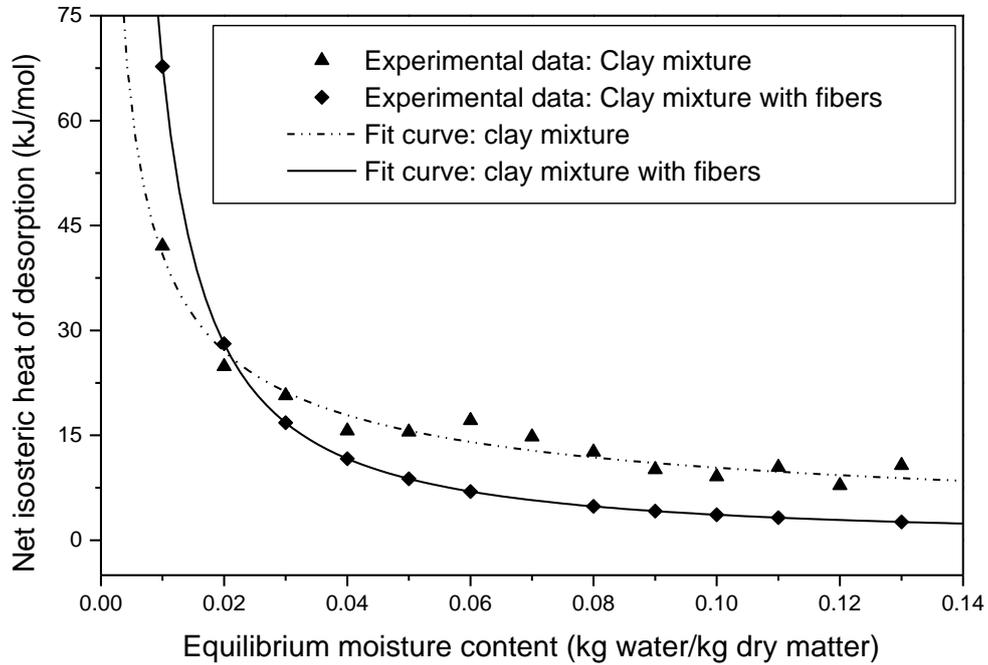


Fig. 10: Variation of isosteric heat of desorption with equilibrium moisture content.

The differential entropy for the clay mixture and clay-fiber composite versus equilibrium moisture content is shown on Fig. 11. It can be seen that the differential entropy increases with decreasing equilibrium moisture content. The entropy data displays a strong dependence on equilibrium moisture content. The variation of desorption differential entropy ( $\Delta S$ ) with moisture content for the two wood species was best fitted by a power function as follows equation (15) for clay mixture and equation (16) for clay-fiber composite:

$$\Delta S = 6.2109X_{eq}^{-0.6381} \quad (15)$$

$$\Delta S = 0.4646X_{eq}^{-1.2988} \quad (16)$$

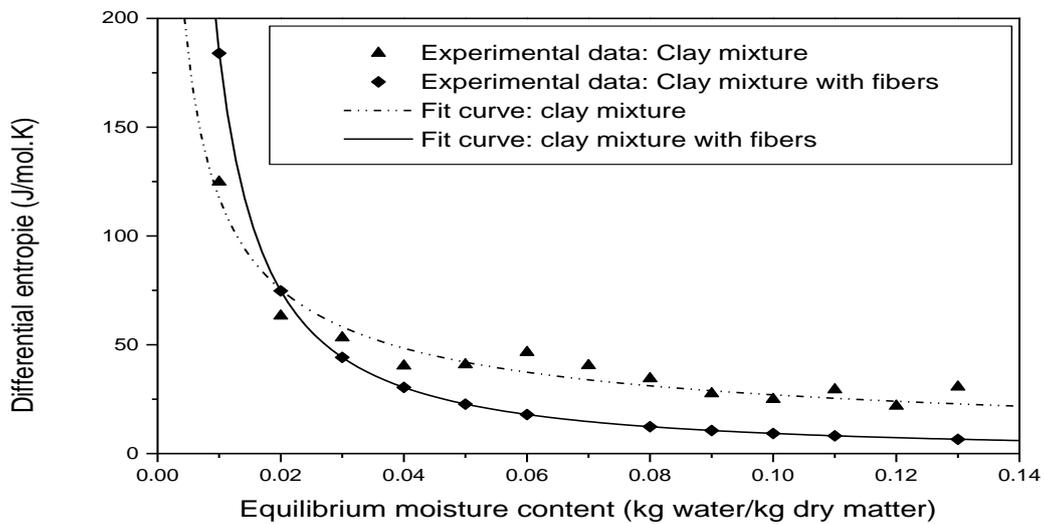


Fig. 11. Variation of differential entropy with equilibrium moisture content.

**D. Enthalpy-Entropy Compensation Theory**

A good straight line related the net desorption isosteric heat and the differential entropy of desorption for the two materials, at all temperatures (Fig. 12). This behavior confirms the enthalpy-entropy compensation hypothesis [33]. It was assumed that at a specific moisture content, the net isosteric heat and differential entropy of desorption are independent with temperature [17]. The isokinetic temperature ( $T_\beta$ ) and the free energy ( $\Delta G_\beta$ ) were determined by linear regression of equation (7). The characteristic parameters for enthalpy-entropy relationship for the clay mixture (equation (17)) and clay-fiber composite (equation (18)) are respectively:

$$Q_{st,n} = 1.22 + 0.338 \Delta S \tag{17}$$

$$Q_{st,n} = 0.286 + 0.367 \Delta S \tag{18}$$

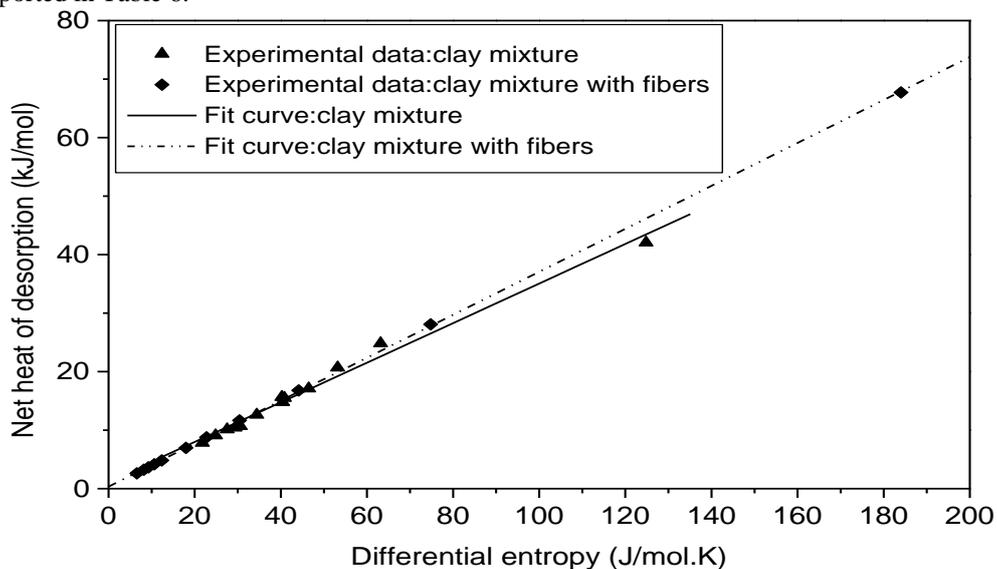
**Table 5: Characteristic parameters for enthalpy-entropy relationship.**

Material	$T_\beta$ (K)	$\Delta G_\beta$ (J/mol)	r
Clay mixture	338	1220	0.987
Clay-fiber composite	367	286	0.999

For the two clay-based materials, the value of ( $\Delta G_\beta$ ) (Table 5) was found to be positive, +1220 J/mol for the clay mixture and +286 J/mol for the clay-fiber composite, indicating a non-spontaneous desorption process. The values of isokinetic temperature ( $T_\beta$ ) for the clay mixture and clay-fiber composite were 338 K and 367 K, respectively. The harmonic temperature ( $T_{hm}$ ) for the clay mixture and clay-fiber composite was found to be  $T_{hm} = 342$  K (calculated on the basis of equation 8). It was observed that  $T_{hm} \neq T_\beta$  for these two materials.

This difference between harmonic and isokinetic temperature corroborates also the enthalpy-entropy compensation theory. Our result shows that ( $T_\beta$ ) is lower than ( $T_{hm}$ ) for the clay mixture and higher than ( $T_{hm}$ ) for the clay-fiber composite. Thus, the desorption process is entropy-controlled for the clay mixture and enthalpy-driven for the clay-fiber composite [33].

The compensation theory was used also to model the temperature influence on moisture sorption according to equation (10) and equation (11). Fig. 13 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 products. This confirms that the temperature effect on moisture sorption follows a power law [17]. The values of parameters K1 and K2 were calculated using linear regression and are reported in Table 6.



**Fig. 12: Plot of enthalpy change against entropy change for water adsorbed.**

Table 6: Values of parameters relative to the equation (11)

Material	$K_1$ (K)	$K_2$	r
Clay mixture	43477.5504	$2.969 \times 10^{-11}$	0.951
Clay-fiber composite	9045.2948	$3.529 \times 10^{-12}$	0.953

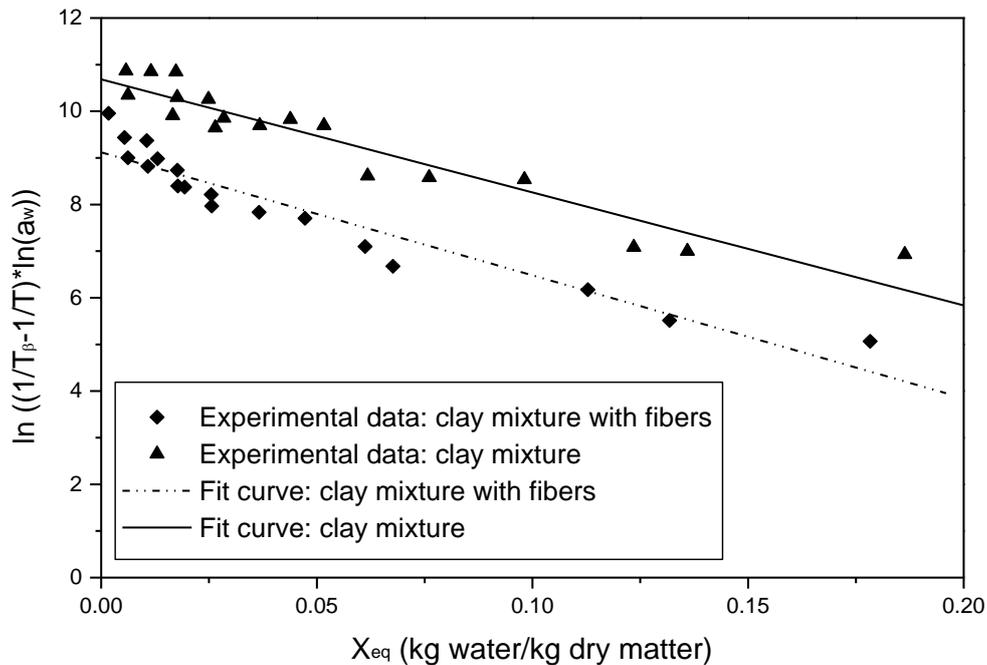


Fig.13: Equilibrium moisture at all temperatures plotted according to equation (11).

### V. CONCLUSION

The purpose of the present was to investigate the influence of natural plant cellulosic fibers on the thermodynamic properties of a clay mixture. A standard gravimetric method has been used to determine the equilibrium moisture content of clay mixture samples, with and without fibers, at 60, 70 and 80°C over a relative humidity domain ranging from 5 to 90%. According to our results, the following conclusions can be proposed.

For the two products: clay mixture and clay-cellulosic fiber composite, the increase of temperature enhances the water desorption for constant values of water activity. At constant temperature, the equilibrium moisture content values increase with increasing water activity. Experimental clay mixture desorption curves were better fitted by the GAB model while the Dent model showed the best fit performance for the clay-cellulosic fibers composite.

The net isosteric heat of desorption, estimated using the Clausius-Clapeyron equation, is a simple power function of the moisture content. The differential entropy evaluated on the basis of the Gibbs-Helmholtz relationship, is also a power function of moisture content. A linear relationship between differential entropy and enthalpy exists, which confirms the enthalpy-entropy compensation theory.

According to the value of the free energy for the two materials, desorption is a non-spontaneous desorption process. As the isokinetic temperature is lower than the harmonic mean temperature for the clay mixture and greater than the harmonic temperature for the clay-fiber composite. The desorption process is then entropy-controlled for the clay mixture and enthalpy-driven for the clay-fiber composite.

The empirical and semi-empirical thermodynamic correlations established in this paper can describe rigorously the hygroscopic behavior of the two innovative materials in order to optimize its drying process and in general its industrial processing. This study can be extended to measure the thermo-mechanical properties of these



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industrial products. The knowledge of mechanical strength and thermal behavior of these materials is normally desired before its use, in particular preservation and insulation against fire.

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APPENDIX

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

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

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