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Modelisation of desorption isotherms and estimation of the thermophysic and thermodynamic properties of tropical woods in Cameroon: The case of Ayous and Ebony woods

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Abstract - *A review at various models illustrates the necessary of choosing a model that can best describe each wood in relation to its isotherms of desorption. The theoretical models enable us to deduce several thermo physical parameters. The models of Dent and G.A.B are quite appropriate in the evaluation of the isotherms of desorption of Ayous and Ebony woods taking the humidity of the atmosphere air into consideration. The parameters of Dent's model vary favourably with regard to the theoretical precisions. The level of humidity at fiber saturation points are at 0.2944 for Ayous wood and 0.19141 for Ebony wood. The specific surface area occupied by the woods under study decreases when there is a consequent increase in temperature. The specific surface area of Ayous wood ranges between 295 and 162* m^2/g *whereas that of Ebony ranges between 183 and 96* m^2/g*, while the wood temperatures vary between 20 and 60°C. It is realised that, there is a powerful relationship existing between the primary hydrophiles of Ebony and the first layer of mater molecules. The desorption heat of multi layers of our woods are superior to latent heat condensation of pure water. The heat condensation of water vapour constitutes a specific given which is superior to the heat isosteric adsorption of the woods in question. The soret effect is more important in the drying of Ayous wood than that of Ebony. However, temperature does not influence the soret effect for Ebony wood, relative air humidity is less than 0.85. This limits Ayous wood at 0.9. Above these limits soret effect increases when there is an increase in atmospheric air temperature.*

Résumé - *Un examen des différents modèles illustre le besoin de par de choisir un modèle qui peut décrire mieux chaque bois par rapport à son isotherme de désorption. Les modèles théoriques nous permettent de déduire plusieurs paramètres thermo physiques. Les modèles de Dent et de GAB sont tout à fait appropriés dans l'évaluation des isothermes de désorption des bois, d'ayous et d'ébène. Les paramètres du modèle Dent sont favorables, surtout pour des précisions théoriques. Le taux d'humidité dans les points de saturation des fibres est égal à 0,2944 pour le bois d'ayous et de 0,19141 pour le bois d'ébène. La surface spécifique occupée par le bois diminue, lorsqu'il y a une augmentation conséquente de la température. La surface spécifique pour le bois d'ayous est comprise entre 295 et 162* m^2/g*, tandis que pour le bois d'ébène, elle est comprise entre 183 et 96* m^2/g*, alors que les températures de bois varient entre 20 et 60 °C. Il va s'en dire qu'il existe un puissant lien entre la couche hydrophile primaire de l'ébène et la première couche de molécules mater. La chaleur de désorption des couches multiples des bois est supérieure à la chaleur latente de condensation de l'eau pure. La chaleur de*

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condensation de la vapeur d'eau constitue une donnée spécifique qui est supérieure à la chaleur d'adsorption isostérique du bois en question. L'effet Soret est plus important dans le séchage du bois d'ayous que celui de l'ébène. Cependant, la température n'a aucune influence sur l'effet Soret de l'ébène, et l'humidité relative de l'air est inférieure à 0,85. Cela limite le bois d'ayous à 0,9. Au-delà de ces limites, l'effet Soret augmente quand il ya une augmentation de la température de l'air.

Keywords: Desorption isotherms - Mathematical models - Specific surface area - Fiber saturation points - Soret effect - Thermophysical and thermodynamical properties - Tropical woods.

1. INTRODUCTION

When wood is well dried it is used to good effect. To better control the drying operation, it is important to better estimate the necessary energy that will enable the attainment of objectives. It is equally important to take note of the equilibrium of every species of wood. The characteristics of drying air vary during the process and it becomes useful to better estimate the thermo physical level in relation to temperature and relative humidity.

In the review of literature we evaluate isotherms desorption of tropical woods at given and precise temperatures while others have done other works using empirical models [1-5]. These types of models neither permit one to describe the evolution and state of equilibrium of the wood nor enable them to be used to deduce the point of a certain thermo physical level. Again, for this to be adapted to the drying process, same parameters ought to vary in relation or function to the existing temperature. It is of prime important to indicate the model that best describes the isotherm of desorption of tropical wood in order to facilitate the numerical simulation of woods.

This study sets out to analyse one of the theoretical and empirical models of isotherms of desorption in order to determine the ideal model which enables us to estimate the isotherms of Ayous wood and Ebony wood. This in done in order to avoid repenting experiences which can last for weeks and it functions in sample and thickness. Besides, we estimate the humidity of fiber saturation points, heat desorption, specific surface area, heat condensation and Soret effect of both the Ayous wood and Ebony wood. These levels favor amelioration in theoretical previsions of numerical simulations of wood drying while indicating the necessary level of energy. This favors an extraction of a good quantity of water contained in the wood.

2. MATHEMATICAL MODELS

The are many isotherms of desorption models in the review of literature [1-11]. Van Den Berg and Bruin [6] in their literature present a review which groups these models into four categories: the desorption model with a single localised layer, the desorption model with multi layers, the desorption model which is used in science of polymers and the empirical models. In this study, a distinction shall be made in two categories': both the theoretical and empirical models.

The empirical models are studied with the objectives of describing the experimental points of hygroscopic materials in isotherm desorption as in wood. Generally, there is no physical interpretation expected on the parameters obtained. The empirical models of Chung-Pfost and that of Henderson are tested in the literature [1].

This gives a false estimation to humidity which is relatively weak compared to Chung-Pfost's model as well as a stronger relative humidity when compared to the model of Henderson.

$$X_{eq} = -\frac{1}{B}\ln\left(-\frac{\ln(HR)}{A}\right) \tag{1}$$

$$X_{eq} = \left(-\frac{\ln(1 - HR)}{A}\right)^{1/B} \tag{2}$$

The theoretical models developed in the review of literature are based on gas absorption and the extrapolation based on water absorption [9]. Dent's model postulates that water is absorbed in two forms. One constitutes primary water molecules which are strongly binded on the wood. The other constitutes secondary water molecules which deposit themselves on the primary water molecules. The thermodynamic properties of secondary water molecules are identical but quite different from those of ordinary water [6, 9]. It's mathematical formula is given thus [6, 9]:

$$X_{eq} = \frac{b_1 X_m HR}{(1 - b_2 HR)(1 - b_2 HR + b_1 HR)} \tag{3}$$

If we take $b_2 = 1$, that is the binding water energy over its secondary form is equal to that of free water [9]. Here we affirm BET's model [9]. But if we rather go by $b_2 = 0$, that is to say, the water binding energy over its secondary form is approximate to that of conditioned binding water.

Here, we obtain the model of Langmuir [9]. GAB's model is an improvement on the BET model. It is obtained by adjusting the value of the binding energy of the secondary layers by passing though $b_1 = C b_2$ [10]. The GAB model is given thus:

$$X_{eq} = \frac{C b_2 X_m HR}{(1 - b_2 HR)(1 - b_2 HR + b_2 C HR)} \tag{4}$$

Avec

$$0 < b_2 < 1 \qquad \text{and} \quad b_2 = b_0 \exp\left(\frac{\Delta H_k}{RT}\right) \quad , \; C = C_0 \exp\left(\frac{\Delta H_c}{RT}\right) \tag{5}$$

The models of GAB and that of BET assume that the thermodynamic properties of both primary and secondary water molecules are identical as those of ordinary water [9]. In order to estimate the quantity of water in wood at the fiber saturation point that is when the wood is destroyed by water fibers and the wood bindings or vents saturated by water, we take $HR = 1$. The model of Dent gives:

$$H_s = \frac{b_1 X_m}{(1 - b_2)(1 - b_2 + b_1)} \tag{6}$$

The specific surface area is given by the relation [11]:

$$S_m = 3516 X_m \tag{7}$$

The Soret effect enables us to estimate temperature gradient during wood drying. This is given by the formula [12]:

$$\alpha = \frac{dX_{eq}}{dT} = \frac{E_b\,HR}{R\,T^2}\frac{\partial X_{eq}}{\partial HR} \tag{8}$$

If we take Dent model, we obtained:

$$\alpha = \frac{E_b \times HR \times b_1 \times X_m \left[1 + HR^2 \times b_2\,(b_1 - b_2)\right]}{R\,T^2 \times \left[1 + (b_1 - 2b_2)\,HR - b_2\,(b_1 - b_2)\,HR^2\right]^2} \tag{9}$$

Where E_b is energy of desorption estimated by [13]:

$$E_b = 4.18\left(9200 - 7000\,X_{eq}\right) \tag{10}$$

The heat absorbed by one water mole at the state of adsorption enables us to evaluate the amount of heat need in order to dry wood. This can be obtained by using the Clausius-Clapeyron formula as seen below [14, 15]:

$$\Delta H_b = \frac{R}{(1/T_2) - (1/T_1)} \times \ln\left(\frac{HR_2}{HR_1}\right) \tag{11}$$

We have used the relations below for to estimate entropy and standard free energy of Gibb respectively [16]:

$$\Delta S_T^0 = \frac{\Delta H_b^0}{T} + R \times \ln(HR) \tag{12}$$

$$\Delta G_T^0 = -R\,T \times \ln(HR) \tag{13}$$

For to estimate the total energy when we needed to extract all bounded water, we have used the relation below [9]:

$$Q = \int_{H_s}^{0} \Delta H_b \times dX_{eq} \tag{14}$$

In order to estimate the effect of temperature gradient, it is necessary to estimate the activation energy of the wood. To this end, we are going to use two methods:

* *First method*: The method of infinite plate without transfer resistance:

When drying occurs only by diffusion, we have according to Crank [17]:

$$X_{red} = \frac{X - X_{eq}}{X_0 - X_{eq}} = \frac{8}{\pi^2} \times \exp\left(\frac{-\pi^2 D}{e^2} t\right) \tag{15}$$

* *Second method*: Global transfer coefficient:

When the free water is absent in our samples, we can write [18]:

$$\rho_0\,V\frac{dx}{dt} = -k_X\,S\left(X - X_{eq}\right) \tag{16}$$

3. MATERIALS AND METHODS

The value of wood isotherms of desorption to be studied are made available in the literature review. The woods are from Cameroon and are sliced in to 50 samples with the dimension of 25 × 10 × 5 mm^3 [4]. The saturate solutions are used in order to maintain relatively constant air humidity.

We have determined the parameters of Dent's model where their correlation coefficients permit us to judge the model rate.

The model validated is used to estimate the thermophysical strength of wood while taking the formula below into consideration.

* *First method*

$$\ln\left(X_{red}\right) = \ln\left(\frac{8}{\pi^2}\right) - \frac{\pi^2 D}{e^2} t \tag{17}$$

The function $\ln\left(X_{red}\right) = f\left(t\right))$ should be linear and its slope can be used to estimate the diffusion coefficient D of bound water at each temperature. Then supposing that D varies according to the Arrhenius' relation, we have:

$$D = D_0 \exp\left(\frac{-E_a}{RT}\right) \tag{18}$$

Then we have:

$$\ln\left(D\right) = \ln\left(D_0\right) - \frac{E_a}{R}\frac{1}{T} \tag{19}$$

The slope of the function $\ln\left(D\right) = g\left(1/t\right)$ can be used to estimate the activation energy E_a .

* *Second method*

The global transfer coefficient k_X is considered constant when air humidity and temperature are constant during the drying process. We would have:

$$X_{red} = \frac{X - X_{eq}}{X_0 - X_{eq}} = \exp\left(\frac{-k_X}{\rho_0 e} t\right) \tag{20}$$

Then we have:

$$\ln\left(X_{red}\right) = -\frac{k_X}{\rho_0 e} t \tag{21}$$

A plot of the function $\ln\left(X_{red}\right) = h\left(t\right)$ can be used to estimate k_X at each temperature. If we assume an Arrhenius type variation, we would have:

$$k_X = k_{X0} \exp\left(\frac{-E_a}{RT}\right) \tag{22}$$

Then we have:

$$\ln\left(k_X\right) = \ln\left(k_{X0}\right) - \frac{E_a}{R}\frac{1}{T} \tag{23}$$

A plot of the function $\ln\left(k_X\right) = K\left(1/T\right)$ enables us to estimate E_a.

In order to obtain good results, it is necessary to know the moment during which transfer is only by diffusion when drying the samples. In this regard, let us determine the humidity when the pores are saturated.

This humidity is given by the relation [19]:

$$X_s = 10^3 \times \frac{1500 - \rho_0}{1500\,\rho_0} \tag{24}$$

We can assume that the moisture content transfer only by diffusion if the initial moisture content of the samples is much smaller than the moisture content at the saturation of the pores.

4. RESULTS AND DISCUSSION

Figures 1 and 2 shows that Dent's model better describes the isotherms of desorption of ebony than the model of Henderson. Henderson's model gives an inappropriate result for relative humidity which is greater than 0.8.

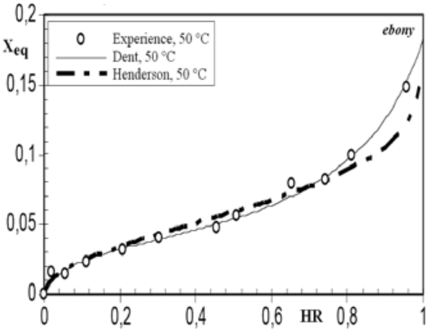

Fig. 1: Experimental and theoretical isotherms of desorption of *Ebony* wood at 50 °C

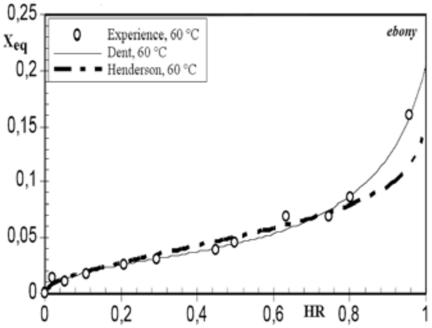

Fig. 2: Experimental and theoretical isotherms of desorption of *Ebony* wood at 60 °C

Figures 3 and 4 shows that the model of Dent better describes the isotherms of desorption of ayous wood than the model of Chung-Pfost. However, the model of better describes the isotherms of desorption when the temperature is important but it does not gives a satisfactory result when the relative air humidity is above 0.9.

Table 1 presents the parameters of Dent's model and the correlation coefficients. We realise that the theoretical presumptions of varying parameters are obtained and that the specific surface area have a linear variation with the temperature as have below:

$$S_m = 3516 \times \left(A_1 \times T + A_2\right) \tag{25}$$

Where A_1 and A_2 are given in **Table 1**.

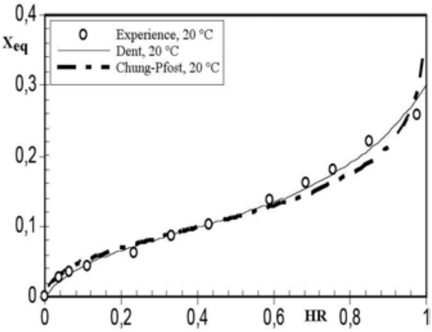

Fig. 3: Experimental and theoretical isotherms of desorption of *Ayous* wood at 20 °C

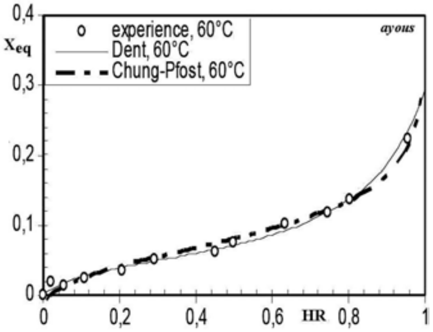

Fig. 4: Experimental and theoretical isotherms of desorption of *Ayous* wood at 60 °C

Table 1: Estimation of the parameters of Dent model and coefficient of specific surface area equation of the *Ayous* and *Ebony* woods

Wood	b_0	ΔH_k	c_0	ΔH_c	A_1	A_2
Ayous	2.2527	-2760.576	27.085	-2203.14	-0.0009	0.3608
	$R^2 = 0.9505$		$R^2 = 0.5395$		$R^2 = 0.9887$	
Ebony	2.9686	-3444.23	0.0655	8374.33	-0.0006	0.2347
	$R^2 = 0.9789$		$R^2 = 0.9966$		$R^2 = 0.9968$	

The figure 5 shows that humidity at the fiber saturation point varying with temperature and can be estimated averagely from 0.2944 for Ayous wood and from 0.19141 for ebony wood.

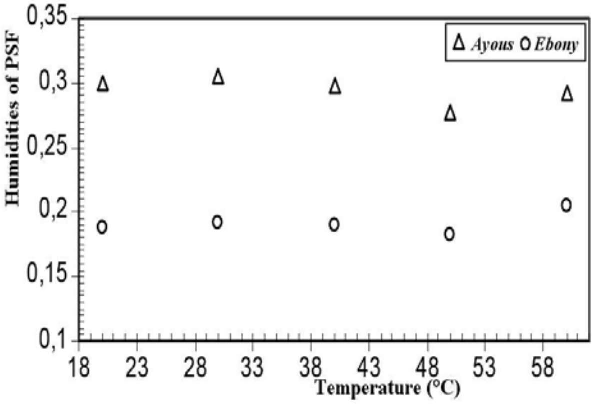

Fig. 5: Humidity at the fiber saturation point of *Ebony* and *Ayous* woods

Table 1 shows that heat condensation of pure water vapour is -2760.576 J/mol for Ayous wood and -3444.23 J/mol for Ebony wood.

For these woods, the latent heat condensation of water is less than the total heat desorption of multi layers. The integral heat desorption of secondary layers is at -2203.14J/mol for Ayous and 8374.33J/mol for Ebony.

Nonetheless, the total heat desorption of primary layers is less than that of total heat desorption of multi layers for Ayous. The contrary is observed in Ebony wood.

Figures 6 and 7 indicate that the model of GAB equally gives a satisfactory experimental description of isotherms of desorption of our woods.

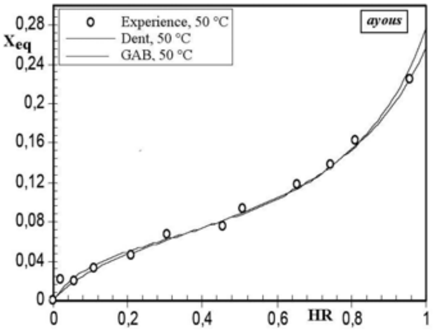

Fig. 6: Different between Dent and GAB models, *Ayous* wood, T = 50°C

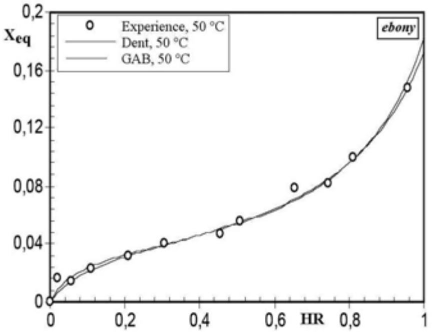

Fig. 7: Different between Dent and GAB models, *Ebony* wood, T = 50°C

Figures 8, 9 and 10 indicate the evolutions of heat desorption, of entropy and standard free energy of Gibb respectively with the stability of water equilibrium. We have used Henderson’s model for ebony and the Chung-Pfost for ayous wood, because these models permit us to better estimate relatively air humidity when the equilibrium water content and temperatures are known. We have equally used from 40°C and 50°C isotherms.

These suppose that heat desorption is constant in the given temperature range. The $\mathrm{HR} < 0.8$ is obtained because the two models are interesting. We observe that heat desorption, entropy and standard free energy of Gibb are important to weak water content. This indicates that there is a strong interaction between water and wood.

When water content increases, these thermophysical parameters decrease indicating a reduction in surface desorption. In weak water content, more energy is needed to extract water molecules linked to ebony wood.

The difference reduces when water content increases to an inverse point. The variation obtained is shared in the review of literature using agricultural products [14]. The stabilise the difference in figure 8, we used the correlation as obtained below in Perré [9].

As a result, we get, for ayous wood:

$$-\Delta H_b = 7847.61 \times \exp\left(-12.38 \times X_{eq}\right) \tag{26}$$

and for ebony wood, we get:

$$-\Delta H_b = 7847.61 \times \exp\left(-12.38 \times X_{eq}\right) \tag{27}$$

with ΔH_b in cal/mol.

In used a good number of treated wood and an estimated average of coefficients is obtained. Perré [9] obtained:

$$-\Delta H_b = 5040 \times \exp\left(-14 \times X_{eq}\right) \tag{28}$$

It is noticed that wood types influence the coefficients as well as the conserved order in grandeur.

For to extract all binded, we have needed $Q = 616.403 \text{ cal/mol}$ for Ayous and $Q = 692.453 \text{ cal/mol}$ for ebony.

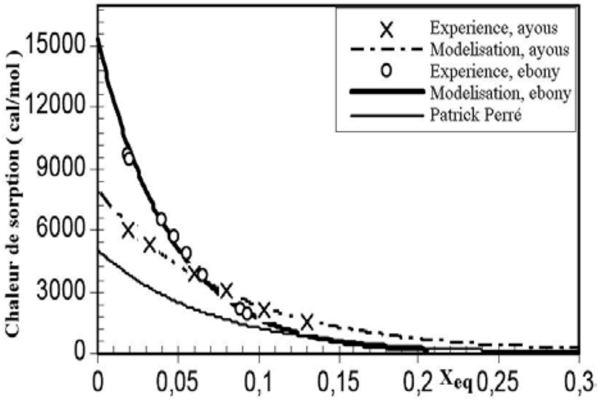

Fig. 8: Variation of heat desorption with equilibrium moisture content. Comparison between experiment point and theoretical models

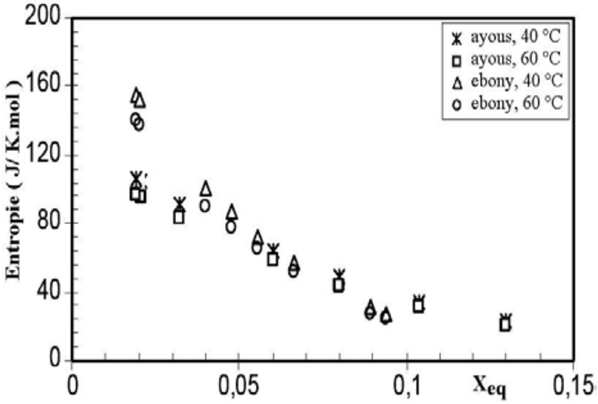

Fig. 9: Variation of entropy with equilibrium moisture content of *Ayous* and *Ebony* woods at 40 °C and 50 °C

From the literature, we have [20, 21], ρ_0 = 336 kg/m^3 for the Ayous wood and ρ_0 = 994 kg/m^3 for the Ebony wood. Thus we obtain $X_s = 2.06$ for the Ayous wood and $X_s = 0.339$ for the Ebony wood.

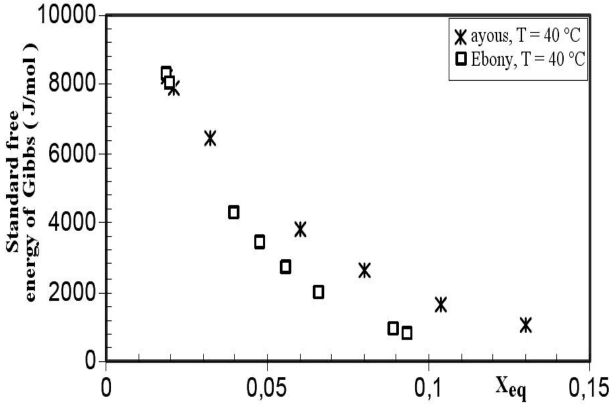

Fig. 10: Variation standard free energy of Gibbs with equilibrium moisture content of *Ayous* and *Ebony* woods at 40 °C

We can assume that the moisture transfer occurs only by diffusion in the case of the ayous wood, given that the initial moisture content of its samples ($X_0 = 0.6$) is much smaller than the moisture content at pore saturation.

Consequently we have used all the experimental points for the Ayous wood. Figure 11 shows that the theoretical previsions are respect at each temperature. The case of the Ebony wood ($X_0 = 0.28$) is different.

We need the experimental drying kinetics curve in order to consider the sequence of points that have a linear behavior, that is after 20hrs of drying, according to the figure 12. These kinetic experimental points are taken in the literature [21-23].

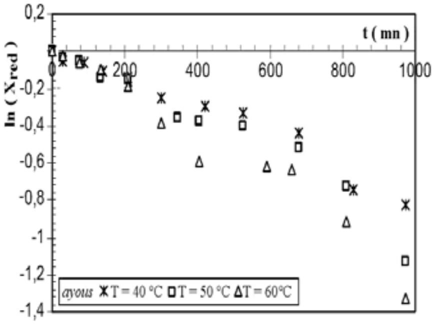

Fig. 11: Drying kinetic of *Ayous* wood at 40 °C, 50 °C and 60 °C

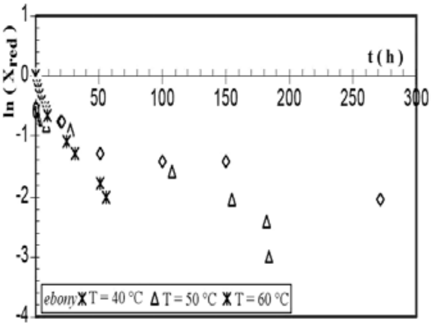

Fig. 12: Drying kinetic of *Ebony* wood at 40 °C, 50 °C and 60 °C

Figures 13 and 14 present a good agreement between experiment and theory for to estimate a coefficient diffusion of bound water.

We have obtained the following correlations:

$$D\,[m^2/s] = 1.78\times10^{-6} \times \exp\left(-\frac{17605.12}{R\times T(K)}\right) \qquad \text{for Ayous} \qquad (29)$$

$$D\,[\mathrm{m}^2/\mathrm{s}] = 774.33 \times \exp\left(-\frac{78015}{R \times T(K)}\right) \qquad \text{for Ebony} \qquad (30)$$

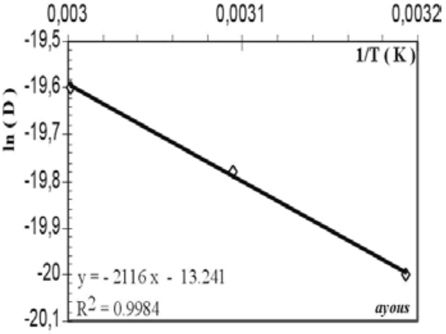

Fig. 13: Variation of logarithmic of diffusion coefficient of *Ayous* wood with the inverse of the temperature

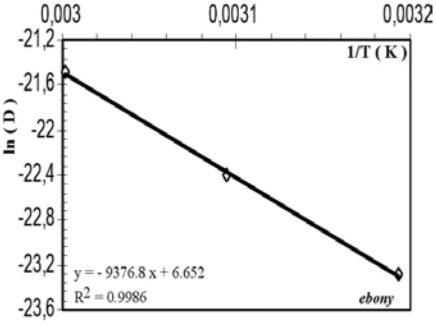

Fig. 14: Variation of logarithmic of diffusion coefficient of *Ebony* wood with the inverse of the temperature

$$k_X\left(\mathrm{kg/m^{-2}\,s^{-1}}\right) = 1.41 \times \exp\left(-\frac{17472}{R \times T(K)}\right) \qquad \text{for Ayous} \qquad (31)$$

$$k_X\left(\mathrm{kg/m^{-2}\,s^{-1}}\right) = 4.28\times10^{-9} \times \exp\left(-\frac{84864}{R \times T(K)}\right) \qquad \text{for Ebony} \qquad (32)$$

Table 2: Estimation of activation energy of *Ayous* and *Ebony* woods of our two methods

E_a [J/mol]			
Ayous		***Ebony***	
First method	Second method	First method	Second method
17605.12	17472	78015	84864
Difference = 133.12		Difference = 6849	

We observe that the values obtained for the activation energies are close to each other, thus agreeing with our estimation (**Table 2**). Temperature has a reasonable effect on the structure of the ebony wood inasmuch as it is less diffusive. As a consequence, specialists use low temperature (about 40 °C) to dry the ebony wood.

We have used the activation energy values obtained by the method of global transfer coefficient in order to estimate the effect of temperature gradient. This is because the method is more specific to wood as it uses the dry density and the drying kinetics of each wood type.

Figures 15 and 16 present the evolution of the coefficients of Soret effect for Ayous wood and Ebony wood respectively. This effect increase alongside relative air humidity and slightly vary with temperature when relative air humidity is less than 0.85 for these two woods.

Above this limit, this effect increase with an increase in temperature. To obtain these variants Dent's model is used.

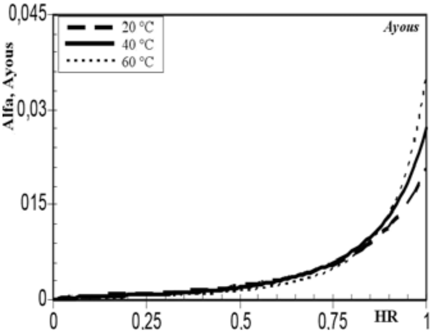

Fig. 15: Variation Soret effect coefficient of *Ayous* wood with the relative humidity at 20 °C, 40 °C and 60 °C

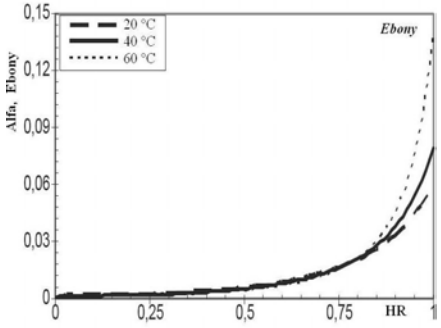

Fig. 16: Variation Soret effect coefficient of *Ebony* wood with the relative humidity at 20 °C, 40 °C and 60 °C

5. CONCLUSION

The models of Dent and that of GAB better describe the isotherms of desorption of the woods of Ayous and Ebony in very respect of relative air humidity. Humidity at fiber saturation point deduced from the model of Dent is 0.2944 for Ayous wood whereas that of Ebony is 0.1914.

The specific surface area decrease in a linear manner from 295 to 162 m^2/g for Ayous wood and 183 to 96 m^2/g for Ebony, this leads to an increase in temperature moving from 20 to 60 °C.

The Soret effect temperature varies with temperature in general and more energy is needed to extract water contained in ebony when water content is weak. When water content increase, the heat use to desolve the water molecules go toward each other.

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