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ANALYSIS OF MOISTURE ADSORPTION ISOTHERMS FOR ROASTED AND RAW BIOMASSES

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Abstract. Biomass, renewable and abundant source of carbon is one of the new energy sources under study. The high renewable and productive potential of wood can express an environmentally healthier energy matrix. However, the potential for energy generation is difficult as the percentage of moisture increases, since part of the combustion energy must be destined to evaporate a water in the biomass. This paper presents an analysis about the relevant aspects of wood moisture gain in some conditions and roasting and raw, which can be obtained through the study and evaluation of adsorption isotherms. The research is based on studies focused on food isotherms, but it was verified that the use of isotherms can be applied to the wood with the aid of mathematical models as the GAB model, the results prove this affirmation and allow to describe with quality the humidity gain of the biomass for several different conditions. The static gravimetric method was used to follow the moisture gain of the wood and to construct the adsorption isotherms of each sample. It was observed an unexpected behavior of the sample of 300 °C that differs from the others, being able to be explained by increase of the porosity in the sample or changes observed in the adsorption of humidity are attributed to changes in the surfaces of cellulose crystallites.

Keywords: Biomass, moisture, adsorption, energy, sustainability.

1. INTRODUCTION

Global energy demands have grown steadily as a result of population growth and increasing investment in industrialization. The most widely used and widely used energy source is fossil fuels and their derivatives, such as coal. However due to the imminent future shortage of these resources, new sources of energy and technologies capable of generating energy have been studied, being these sustainable and renewable.

Brazil has a privileged position in relation to resources for the use of renewable energy sources in its energy matrix. The Brazilian electricity matrix is very diversified, with emphasis on water resources and fossil fuels, corresponding to 61.34% and 16.85% of installed capacity, respectively, according to the Generation Information Bank (BIG). February 2017. It is also possible to emphasize as an alternative energy source, the use of biomass that, although they do not yet have an expressive percentage in the world's energy production, can open the way to new means of energy generation. Studies on biomass as an energy source have intensified more recently.

However, due to the low conversion rate in energy, biomass is still not widely used worldwide because it mostly has high moisture content, high oxygen-to-carbon (O/C) ratio, and so on. Consequently, biomass has a lower calorific value compared to fossil fuel, about 10-40% of most fossil fuels, Scurlock (2001). However, the high renewable and productive potential of wood can express an environmentally healthier energy matrix and, in addition, decreases dependence on exhaustible energy sources, Brito et al. (2007).

To overcome these disadvantages, a pretreatment process for biomass was developed, called roasting. This process promotes an improvement in biomass characteristics, for example by reducing the proportion of oxygen and hydrogen when compared to the original biomass Arias et al., (2007) and occurs in a reduced or oxygen-free environment, at temperatures below 300 ° C. The process also allows the biomass to acquire greater hydrophobicity.

The moisture content is a parameter to be considered when the best biomass energy utilization conditions are desired; high moisture contents are not interesting. The presence of more water in the combustion process indicates that more energy is required to vaporize it, and less energy will be available for the endothermic reactions responsible for H₂ and CO production, Rendeiro (2008). The study of water activity can be done by evaluating isotherms, which consist of curves describing the relationship between moisture content of food and water activity (*a_w*) for constant temperature and pressure according to Iglesias & Chirife (1982).

Biomass as organic material may also be available in this study and the work carried out has the objective of verifying the validity of moisture adsorption isotherms to describe the moisture adsorption behavior of Cupiúba (*Goupia glabra*) samples for some roasting conditions.

2. EXPERIMENTAL PROCEDURE

Raw cupiúba samples were used to generate the adsorption isotherms at temperatures of 220, 240, 260, 280 and 300 °C / 30 minutes. The preparation of the samples involved the grinding of these samples and subsequent classification of the samples granulometry between 35 and 60 mesh. The static gravimetric method was used, using saturated solutions of six salts at 25 °C. The salts used and their relative humidity at 25°C were CH₃COOK (22.60%), K₂CO₃ (43.80%), Mg(NO₃)₂ (52.86%), NaCl (75.32%), KCl, 32%) and BaCl₂ (90.26%).

The salts solutions were placed in hermetically sealed plastic containers and stored in an environment temperature controlled at 25 ° C. Eppendorf tubes were placed in the containers, in styrofoam disks, containing 1g of sample each. The samples were confined until they reached equilibrium. All assays were performed in triplicate of sample. The residence time of the samples in the pots was 30 days. The dry basis equilibrium moisture for the samples were obtained from the Eq. 1.

$$U_{eq} = \frac{m_{\acute{a}gua}}{m_{seca}} \times 100 \quad \text{Eq.1}$$

U_{eq}: equilibrium moisture (% dry basis);
m_{água}: mass of water adsorbed by the sample (g);
m_{seca}: dry mass of the sample (g)

The mathematical adjustment of the moisture adsorption isotherms of the roasted wood, the mathematical model of GAB (Eq. 2) was used.

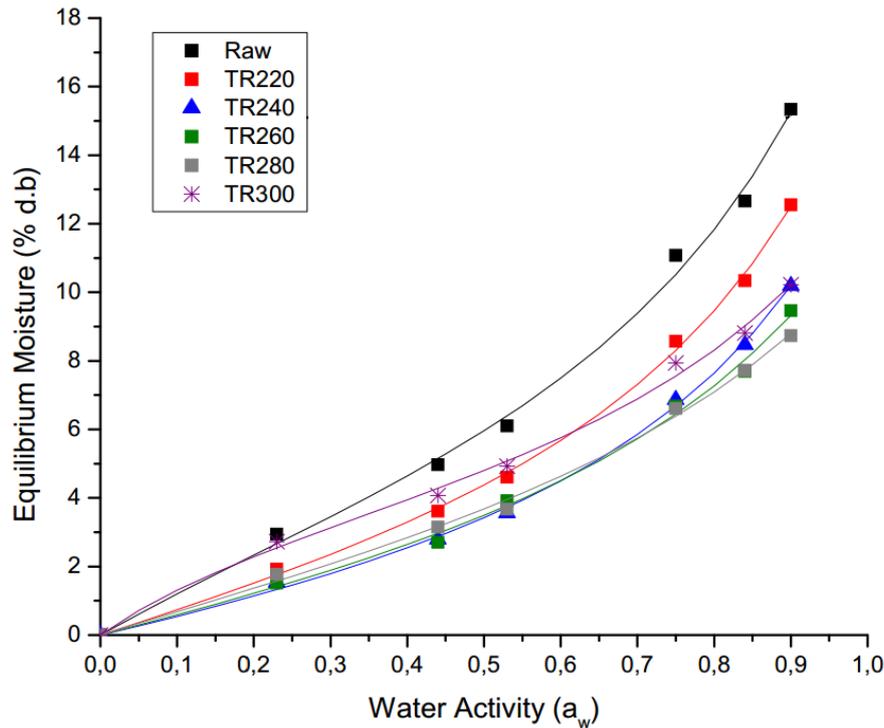
$$X = \frac{X_m C_g K_{sm} a_w}{[(1 - k_{sm} a_w)(1 - k_{sm} a_w + C_g K_{sm} a_w)]} \quad \text{Eq.2}$$

X: equilibrium moisture;
X_m: moisture in the monolayer;
C_g: Guggenheim constant;
k_{sm}: sorption heat of multilayers;
a_w: water activity.

The parameters of the models were determined using MATLAB software 7.10 using non-linear regression. The quality of the isotherm in relation to the experimental points will be evaluated by the coefficient of determination of statistical adjustment R² and error bars of the experimental points.

3. RESULTS AND DISCUSSIONS

The results of experimental and theoretical equilibrium moisture (GAB model) of the samples of raw and roasted wood at the temperatures of 220, 240, 260, 280 and 300 °C and their respective water activities at 25 °C are shown in Figure 1. Through of the results it is observed that the *U_{eq}* grows with *a_w*, in general the roasting process tends to make the samples more hydrophobic.



However, the sample roasted at 300°C presented a different behavior, with equilibrium moisture values higher than the samples roasted at 280, 260 and 240°C. According to Felfli et al. (2005) and Chiou et al., (2016) this behavior may be due to the intense emission of volatiles with increasing roasting temperature, resulting in increased porosity. Under these conditions, a higher moisture uptake may occur within the pores.

While, Hill et al. (2013) speculate that observed changes in moisture adsorption are attributed to cellulose crystal surfaces. Where, the increase in hydrophobicity at low roasting temperatures is attributed to dehydration of cell wall polymers, causing an increase in polymer-polymer interactions by substituting polymer-water interactions. Under severe roasting conditions the polymers are degraded, resulting in increased hydrophilicity of the sample. The parameters found by the adjustment are shown in Table 1 and the error bars for each curve in Figure 2.

Table 1. Adjustment parameters of adsorption isotherms of raw and roasted wood to the GAB model, determination coefficients (R^2).

Samples	GAB model parameters			
	X_m	K	C	R^2
Raw wood	6,022	0,739	2,835	0,996
TR 220 °C	5,235	0,743	1,873	0,999
TR 240 °C	4,420	0,743	1,608	0,999
TR 260 °C	4,712	0,692	1,780	0,996
TR 280 °C	4,959	0,644	2,133	0,997
TR 300 °C	4,174	0,701	5,453	0,997

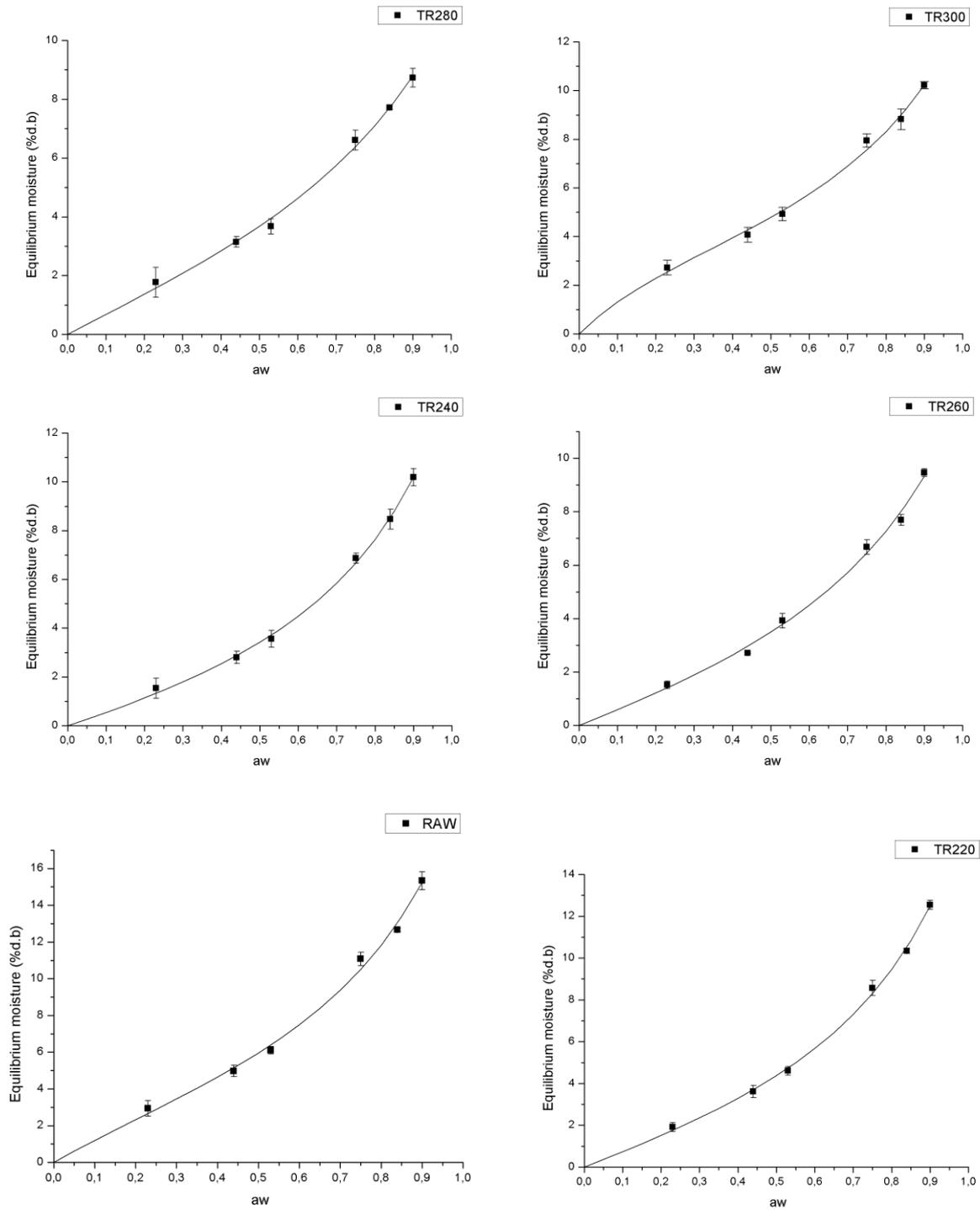


Figure 2. Isotherms of the 300, 280, 260, 240, 220 °C and raw with the error bars.

The parameters found for the GAB isotherms (Eq. 2) are presented in Table 2. A good indicator of the isotherms' validity is given by the moisture in the monolayer (X_m) being decreasing from the raw wood. The R^2 values of approximately 0.99 for all isotherms allied to the error bars which show that the curves did not distant significantly from the experimental points are factors that can validate the generated isotherms as reliable.

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5. REFERENCES

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