DETERMINATION OF HYGROSCOPIC EQUILIBRIUM AND THE ISOSTERIC HEAT OF BAGASSE OF SUGAR CANE

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Abstract: In order to analyze the dynamics of sorption and vaporization latent heat of the bagasse of sugar cane, the present study objectived to determine the hygroscopic equilibrium and the isosteric heat, for different controlled conditions of temperature and relative humidity, and assess, among various models described in the literature, which best represents the sorption isotherm. As result was verified that the model that best adjusted the empirical data of sorption of bagasse of sugar cane was the Modified Henderson Model, with coefficient of determination of 0.972, while the integral isosteric heat of desorption ranged of 2524.09 to 2951.95 kJ kg⁻¹.

Keywords: bagasse of sugar cane, hygroscopic equilibrium, isosteric heat.

1. INTRODUCTION

Over the past decades, the sugar cane is no longer processed only for the production of sugar and alcohol, from today, also present as an important source of biomass energy by burning its straw and, especially, bagasse. This process, that also can be called co-generation, since is the simultaneous production of thermal and electrical energy from biomass's use or other simultaneous energy source.

According to Santos (2011), approximately 30% of the processing of sugar cane only correspond the bagasse. As result, the bagasse of sugar cane present appropriate quantitative conditions to be used as an important material base for making pellets or briquettes for use in co-production of electric power for the sugar and alcohol industry.

In order to analyze the efficiency and production planning, the capacity's and the energy needs, useful becomes the knowledge of the thermal characteristics of the bagasse of sugar cane, especially, regarding its the isosteric heat. Besides the necessity of direct use of this product for energy generation, another point that deserves special mention is the storage of bagasse produced in order to ensure the formation of stocks for periods off-season (Santos, 2011). In reason of large part of the bagasse not to be burned immediately after the processing of the sugar cane, it is necessary the knowledge of their behavior towards different conditions of temperature and relative humidity, the characterization of the bagasse of sugar cane.

Thus, this study has objective to analyze the hygroscopic equilibrium of the bagasse of sugar cane for controlled different conditions of temperature and relative humidity, as well as from the data analyzed also determine its isosteric heat.

2. MATERIALS AND METHODS

This study was conducted at Fluminense Federal University, in Niterói - RJ. The material used for the study was the bagasse of sugar cane (*Saccharum officinarum*,L.) from the municipality of Campos - RJ. The samples were minced until obtaining a homogeneous material and small, and were, subsequently, to the drying process with an average temperature of 45 °C for 24 hours. The moisture content of samples was determined from the oven method at a temperature of $105 \pm 1^{\circ}$ C for 24 hours (Adolfo Lutz Institute, 2008).

The hygroscopicity tests were performed in a climatic chamber with controlled temperature and relative humidity, and used combinations of ten relative humidity of ambient air, ranged 10, 12, 17, 18, 30, 40, 45, 50, 60 and 85% and four temperatures 20, 40, 55 and 70 °C for 24 hours. For verification and quantification of sorption and desorption phenomena, samples were weighed on an analytical balance with an accuracy of three decimal places before and after they are respectively placed and removed from the chamber, after coming into thermal equilibrium with airtight conditions in the environment, being used for each combination four replicates. Thus, were checked various levels of equilibrium moisture content for the various combinations of temperature and relative humidity.

The mathematical models obtained from the literature and representative of the hygroscopicity of agricultural products, used in this study were chosen based on the evaluation of temperature and relative humidity, for checking that

best fits the empirical reality of the product, so the best represent its isotherm (Brooker et al., 1992, Andrade *et al.*, 2010; Morais, 2010). The models used are presented in Table 1.

Model	Equation	
Chung Pfost	$U_e = a - b \ln[-(T + c) \ln(a_w)]$	(1)
Copace	$U_e = exp[a-(bT) + (ca_w)]$	(2)
Modified GAB	$U_e = \frac{ab(c / T)a_w}{\{[1 - ba_w][1 - ba_w + b(c / T)a_w]\}}$	(3)
Modified Halsey	$U_e = [exp(a - bT) / - ln(a_w)]^{1/c}$	(4)
Henderson	$U_e = [ln(1 - a_w) / (- aT_{abs})]^{1/c}$	(5)
Modified Henderson	$U_e = \{ ln(1 - a_w) / [-a(T + b)] \}_{1/c}^{1/c}$	(6)
Oswin	$U_e = (a - bT) / [(1 - a_w) / a_w]^{1/c}$	(7)
Sabbah	$U_e = a \left(a_w^{\ b} / T^c \right)$	(8)
Sigma Copace	$U_e = exp\{a(bT) + [c exp(a_w)]\}$	(9)

Table 1. Models used to the verify the behavior of the isotherm.

In that, U_e is the moisture content of the product, b.s.; a_w is the water activity, decimal, T is the ambient air temperature, °C; T_{abs} is the absolute temperature of ambient air, K; a, b and c are parameters that depend on the nature of the product.

According to Andrade *et al.* (2010) and Anselmo *et al.* (2006), for the analysis of the data, was considered the water activity (a_w) as being equal to the relative humidity, in decimal. To estimate the parameters of the mathematical models was using the program Statistica 5, already, for the representativeness of the hygroscopicity of the models, the experimental data were compared with the calculated values, verifying the percentage of relative average error (P) and the estimated average error (SE) in accordance respectively with Equations 10 and 11.

$$P = \frac{100}{n} \times \sum \left(\frac{|Y - \hat{Y}|}{Y} \right) \tag{10}$$

$$SE = \sqrt{\frac{\Sigma(Y-\hat{Y})^2}{GLR}}$$
(11)

Where, Y is the experimentally observed value; \hat{Y} is the calculated value by the model; and GLR is the degree of freedom of the model.

According to Resende (2006), the additional energy required to remove the water associated with a hygroscopic material in relation the energy required to vaporize the same amount of free water, under the same conditions of temperature and pressure, is characterized as isosteric heat of desorption. The isosteric heat is a parameter able to predict the demand of energy required for drying and burning of organic materials (Brooker *et al*, 1992).

For the calculation of isosteric heat (Q_{st}) were applied the exponential model of Sopade Ajisegiri (Eq. 12) that representing the behavior of the sorption isosteric heat as a function only of the equilibrium moisture content (Silva *et al.*, 2002), and the Clausius-Clapeyron equation (Eq. 13), modified by Wang and Brennan (Andrade *et al.*, 2010), which considers beyond the equilibrium moisture content, also the temperature, and is largely used in the literature.

$$qst = A \times exp\left(-B \times Ue\right) \tag{12}$$

$$ln(aw) = -\binom{qst}{R}/Tabs + C \tag{13}$$

Where, q_{st} is the liquid isosteric heat of sorption, kJ kg⁻¹; R is the universal gas constant, 8.314 kJ mol⁻¹ K⁻¹, and for water vapor 0.4619 kJ kg⁻¹ K⁻¹; A, B and C are coefficients of adjustment. In the Clausius-Clapeyron equation, the liquid isosteric heat of sorption (q_{st}) was determined from the slopes of the curves of the graph ln (a_w) x (1/T_{abs}) for different equilibrium moisture contents from the mathematical model that best adjusted for the experimental data (Eq. 14). In addition for the liquid isosteric heat of sorption, or, the additional heat required to remove water associated with the product, was also calculated the integral isosteric heat of sorption, which beyond of the liquid isosteric heat of vaporization of the free water in accordance with Eq. 15 (Andrade *et al.*, 2010).

$$qst = (slop of the \ line) \times R \tag{14}$$

$$L = 2502.2 - 2.39 \times T_m \tag{15}$$

Where, L is the latent heat of vaporization of the free water, kJ kg⁻¹; T_m is the average temperature used on the study, in °C. From the data presented it is possible to determine with the Eq.16 the integral isosteric heat of sorption.

$$Qst = A \times exp\left(-B \times Ue\right) + L \tag{16}$$

3. RESULTS

For each representative model of the hygroscopic equilibrium was determined the parameters, coefficients of determination (R^2) , the average error relative (P) and estimate (SE), shown in the Table 2. Considering the analysis of the results of the hygroscopic equilibrium of bagasse of sugar cane, it can check that the Modified Henderson Model was the one that best represented the phenomenon

Table 2. Estimated parameters, coefficient of determination, and average relative errors and estimated for each model analyzed.

Modal	Parameters			\mathbf{P}^2	$\mathbf{D}(0/2)$	SE
Widder	а	b	с	К	r (70)	(decimal)
Chung Pfost	0.2359	0.0442	18.9893	0.948	14.4980	0.0307
Copace	-3.4033	0.0101	2.1985	0.971	12.8121	0.0229
Modified GAB	0.0915	0.6150	98.2672	0.957	12.6417	0.0282
Modified Halsey	-4.4888	0.0185	1.7731	0.959	18.7602	0.0273
Henderson	0.0836	-	1.3407	0.907	13.6551	0.0583
Modified Henderson	0.3770	37.3575	1.3902	0.972	7.5061	0.0228
Oswin	0.0697	-0.0002	2.1617	0.900	19.4152	0.0428
Sabbah	0.5643	1.2128	0.3377	0.949	14.1186	0.0305
Sigma Copace	-4.2726	0.0104	1.1803	0.960	18.4670	0.0269

Figure 1 shows the experimental values of the equilibrium moisture contents (b.s.) and the calculated values of the sorption isotherms that best had adjusted to experimental model.



Figure 1. Experimental and estimated values for the Henderson Modified Model of equilibrium moisture contents in function of the water activity (a_w) and temperature.

Given the representation of the phenomenon of hygroscopicity, the Modified Henderson Model was used to the determination of the values of water activity (a_w) in the analysis of the isosteric heat of sorption of bagasse of sugar cane. From calculation of the values of $ln(a_w)$, they are represented in Figure 2, the curves of natural logarithm of the water activity of the bagasse of sugar cane as a function of inverse of the absolute temperature $(1/T, K^{-1})$ for different levels of equilibrium moisture contents (b.s.) and their linear equations.



Figure 2. Values of ln (a_w) for different equilibrium moisture contents (b.s.).

In function of the slope of the line were calculated (Eq. 14) values of liquid isosteric heat of sorption. To determine the integral isosteric heat of sorption (Eq. 16) was also considered the value of the latent heat of vaporization of free water. For this calculation was considered the average temperature used this study, that was 46.25 °C, that resulted on a latent heat of vaporization of 2391.6625 kJ kg⁻¹. The values of the integral and liquid isosteric heat of sorption are shown in Table 3.

Table 3. Values of isosteric heat liquid and isosteric heat integral of sorption for different equilibrium moisture contents.

Equilibrium	Slope	Isosteric heat	Isosteric heat	Equilibrium	Slope	Isosteric heat	Isosteric heat
	1:me	$(l_{L}L_{h}, -l)$	(LLL_{-l})			$(l_1 L_{l_2}, -l_1)$	$(l_1 l_{1} e^{-l})$
(0.8)	line	(KJ Kg)	(KJ Kg)	(0.8)	line	(KJ Kg)	(KJ Kg)
0.0142	-1213	560.2847	2951.9472	0.0671	-875	404.1625	2795.8250
0.0151	-1209	558.4371	2950.0996	0.0674	-872.7	403.1001	2794.7626
0.0244	-1159	535.3421	2927.0046	0.0718	-841.9	388.8736	2780.5361
0.0270	-1143	527.9517	2919.6142	0.0802	-783.9	362.0834	2753.7459
0.0306	-1121	517.7899	2909.4524	0.0833	-762.6	352.2449	2743.9074
0.0355	-1090	503.4710	2895.1335	0.0897	-719.4	332.2909	2723.9534
0.0496	-996.8	460.4219	2852.0844	0.0993	-655.7	302.8678	2694.5303
0.0515	-983.8	454.4172	2846.0797	0.1401	-418.7	193.3975	2585.0600
0.0521	-979.2	452.2925	2843.9550	0.1492	-373.9	172.7044	2564.3669
0.0644	-893.8	412.8462	2804.5087	0.1695	-286.7	132.4267	2524.0892

Based on these data, and using the program Statistica 5, was reached the equation that represent the integral isosteric heat of sorption for the bagasse of sugar cane (Eq. 17) as a function of equilibrium moisture contents (b.s.) and the average temperature of 46.25° C.

$$Qst = 657.5507 \times exp (-7.844079 \times Ue) + 2391.6625$$
(17)

The values of estimated parameters and determination coefficient were, respectively, A = 657.5507, B = 7.844079 and $R^2 = 0.977$. Thus, the Figure 3 presents the integral isosteric heat of sorption obtained from Equation 14 (Qst₁), and the integral isosteric heat of sorption obtained from Eq. 17 (Qst₂), both as function of equilibrium moisture contents, b.s.



Figure 3. Theoretical (Qst₁) and modeled (Qst₂) values of the integral sorption isosteric heat in function of the equilibrium moisture contents

From the analysis of the Figure 3, as mentioned by Lima *et al.* (2008), is possible to verify that as the moisture content of the product decreases, more energy is required to remove the same amount of water. From these data, it appears that the integral isosteric heat of sorption of the bagasse of sugar cane for the moisture content range from 0.014 to 0.170 (b.s.), ranged from 2524.09 to 2951.95 kJ kg⁻¹, being in accordance with the results obtained for other agricultural products available in the literature.

4. CONCLUSION

Based on the results obtained it was concluded that the equilibrium moisture content of the bagasse of sugar cane varies proportionately according to the relative humidity of the air, for a same temperature, and decreases with increasing temperature, for a same relative humidity of the air, being characterized as a hygroscopic product. Since, from the analysis this dynamic and based on statistical parameters, the Modified Henderson Model was the that best represented the phenomenon of hygroscopicity of the product studied.

The integral isosteric heat of desorption for equilibrium moisture content, of 0.014 to 0.170 b.s., varied, respectively, from 2524.09 to 2951.95 kJ kg⁻¹, and the smaller the equilibrium moisture content, more is the amount of energy required to remove the water contained in the product.

5. REFERENCES

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