23rd ABCM International Congress of Mechanical Engineering
December 6-11, 2015, Rio de Janeiro, RJ, Brazil

ENTROPY AND GIBBS FREE ENERGY OF SUGAR CANE BAGASSE

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Abstract. *Sugar cane bagasse (Saccharum officinarum ssp.) is commonly used as burning raw material for energy recovery in sugar and ethanol plants. However its proper use requires adequate stock conditions. The knowledge of the associated energy with hygroscopic products during processing and storage is strategic for the optimization of processes involved in these steps. Thus, the present study has the objective of determining the differential entropy and Gibbs free energy. The studies enabled to verify that for the intervals of relative humidity from 10 to 85% and temperatures from 20 to 70^{0}C. As the product equilibrium water content decreases the desorption process becomes increasingly less spontaneous and the entropy of the product decreases.*

Keywords: *Sugar cane bagasse, Gibbs free energy, entropy.*

1. INTRODUCTION

Over the past few years, the increasing importance of waste recovery from industrial processes was verified. This situation was not different in the case of sugar cane that began to be processed not only for the production of sugar and alcohol, but also for the energy use of its biomass by burning its straw and bagasse.

The importance of studying the cogeneration involved in sugar cane processing is due to the amount of energy provided by burning waste straw and bagasse, which is sufficient, in most cases, to meet the energy needs not only of the plant itself, but also to allow the commercialization of a surplus (Guerra et al., 2014). It is important to notice that this is a clean and renewable source of energy that generates no direct competition with food production.

Therefore, in order to analyze the efficiency and to plan the production, the energy needs and the energy capacity, the characteristics related to heat and mass transfer phenomena during drying and storage of hygroscopic products, such as sugar cane bagasse must be known (Aviara and Ajibola, 2002). According to Thys et al. (2010), the thermodynamic properties of agricultural products related to entropy and Gibbs free energy can be obtained from sorption isotherms determined by studying the hygroscopicity and enthalpy, the latter also being called isosteric sorption heat.

Thus, due to the importance of knowing these energy characteristics for the optimization processes of sugar cane bagasse burning, this study aims at determining the differential entropy and the free energy Gibbs of sugar cane bagasse considering controlled conditions of the product water content, from enthalpy data analysis.

2. MATERIALS AND METHODS

Entropy and Gibbs free energy were calculated using the hygroscopic equilibrium equations adjusted for a modified Henderson model (Eq. (1)) and differential enthalpy (Eq. (2)), presented below, defined for sugar cane bagasse in the study of Teixeira et al. (2012) for a temperature range between 20 and 70^{0}C and relative humidity between 10 and 85%.

$$U_e = \left[\frac{ln\left(1 - a_w\right)}{-0.337\left(T + 37.3575\right)} \right]^{\frac{1}{1.3902}} \tag{1}$$

$$q_{st} = 657.5507 \times \exp\left(-7.844079 \times U_e\right) \tag{2}$$

in what U_e represents the equilibrium moisture content in wet base, q_{st} the isosteric heat (differential enthalpy) in kJ kg^{-1}, T is the temperature in ^{0}C and a_w is the water activity in percentage.

According to Mcminn et al. (2005), the enthalpy changes due to the product water content allow determining the interaction modifications between water molecules and the constituents of the product. Rizvi (1995) stated that this degree of order or disorder existing in the system water-product is called entropy (Eq. (3)). Also, according to Mcminn et al. (2005), this entropy can be associated with binding or repulsion forces in the system and is related to the spatial arrangement of the product-water ratio

$$\Delta S = \frac{\Delta q_{st} - \Delta G}{T_{abs}} \tag{3}$$

in which ΔS is the differential sortion entropy in kJ kg^{-1}K^{-1} , Δq_{st} is the isosteric heat variation in kJ kg^{-1}, ΔG is of Gibbs free energy variation in kJ kg^{-1} and T_{abs} is the absolute temperature in K.

Gibbs free energy corresponds to the energy required to transfer water molecules from a solid surface to vapor state or vice-versa. In other words, it would be equivalent to the work executed by the system to perform a desorption or an adsorption process (Thys et al., 2010). According to Telis et al. (2000), the spontaneity of the process of water gain or loss between the product and the environment can be verified by the determination of the Gibbs free energy. Negative Gibbs free energy values indicates a spontaneous process, while positive values correspond to a non-spontaneous one (Telis et al., 2000). When Gibbs free energy equals zero then there is equilibrium regarding the process spontaneity (Nayak and Pandey, 2000). Gibbs free energy can be estimated by (Simal et al., 2007)

$$\Delta G = R_{va} \times T_{abs} \times \ln\left(a_w\right) \tag{4}$$

The results of the analyses performed in this study allowed proposing empirical correlations for predicting the Gibbs free energy and the differential entropy, depending on the product water content. These models were validated by comparison with experimental data. This comparison required estimating the coefficient of determination (R^2), the mean relative error (P) and the estimated average error (SE) represented by Equations (5) and (6), respectively.

$$P = \frac{100}{n}\sum\left(\frac{\left|Y - \hat{Y}\right|}{Y}\right) \tag{5}$$

$$SE = \sqrt{\frac{\sum\left(Y - \hat{Y}\right)}{GLR}} \tag{6}$$

where P is the average relative error in %, SE is the estimated average error in decimal; Y is the experimentally observed value; $\hat{Y}$ is the value calculated by the model; GLR is the model degree of freedom and n is the number of performed experiments.

The degree of adjustment of the empirical correlations to the experimental data is based on the magnitude of the coefficient of determination and on the relative and estimated average errors. According to Lomauro et al. (1985), the coefficient of determination (R^2) values should be close to unity. Also, Draper and Smith (1981) state that the model's ability to faithfully describe the physical process is inversely proportional to SE value. According to Mohapatra and Rao (2005), models with average relative error (P) greater than 10% do not have a satisfactory fit to experimental data, being unable to adequately represent the analyzed phenomenon.

3. RESULTS

From the determination of the differential enthalpy through Eq. (2), taking into account the Gibbs free energy (Eq. (4)), the differential entropy of sorption can be calculated. Table 1 shows the differential entropy of sorption values and Gibbs free energy, calculated as a function of the equilibrium water content.

Table 1. Values related to the differential entropy of sorption and Gibbs free energy, depending on the water content of sugar cane bagasse.

Equilibrium water content (d.b.)	**Differential enthalpy ($kJ\ kg^{-1}$)**	**Differential Entropy ($kJ\ kg^{-1}kg^{-1}K^{-1}$)**	**Gibbs free energy ($kJ\ kg^{-1}$)**
0.0142	560.2847	3.67	-644.89
0.0151	558.4371	3.56	-664.62
0.0244	535.3421	3.42	-537.11
0.0270	527.9517	3.28	-547.48
0.0306	517.7899	3.12	-552.67
0.0355	503.4710	3.08	-506.00
0.0496	460.4219	2.86	-434.49
0.0515	454.4172	2.75	-449.60
0.0521	452.2925	2.68	-468.32
0.0644	412.8462	2.47	-434.72
0.0671	404.1625	2.54	-390.78
0.0674	403.1001	2.47	-408.82
0.0718	388.8736	2.54	-356.65
0.0802	362.0834	2.40	-341.67
0.0833	352.2449	2.27	-359.50
0.0897	332.2909	2.08	-382.20
0.0993	302.8678	2.10	-312.75
0.1401	193.3975	1.50	-297.91
0.1492	172.7044	1.43	-275.19
0.1695	132.4267	1.27	-240.34

The results allow verifying that the Gibbs free energy is negative, increasing as the water content of the product increases, showing, for this condition, the occurrence of decreasing non-spontaneity of the sorption phenomenon, as depicted in Fig. 1. Similarly, the increase of water content in sugar cane bagasse provokes a reduction in the entropy, indicating a smaller force in the system involved with the spatial arrangement of water-product, as depicted in Fig. 2, favoring the conditions for the development of the drying process.

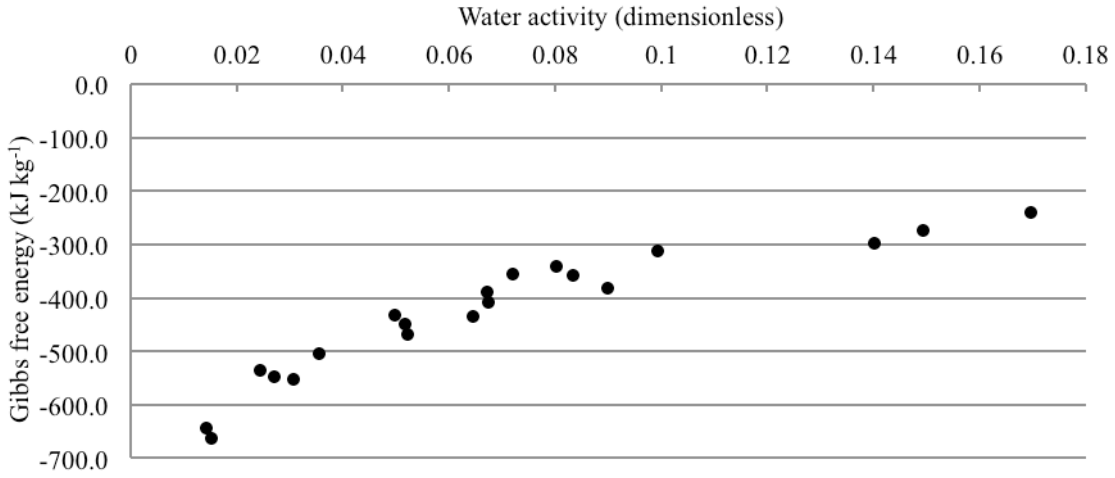

Figure 1. Theoretical values of Gibbs free energy for sugar cane bagasse, with water content between 0.0142 and 0.1695 (d.b.).

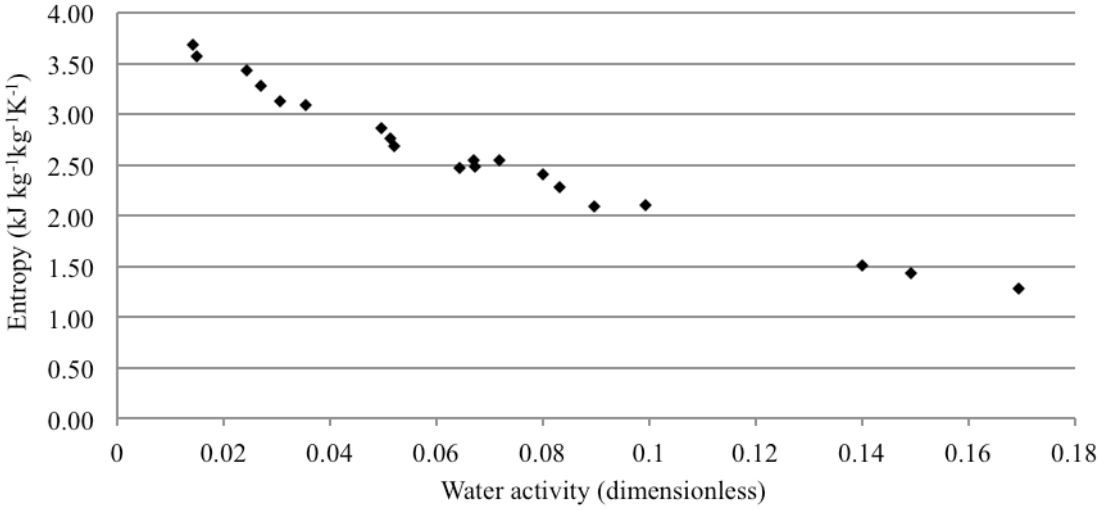

Figure 2. Theoretical values of Entropy for sugar cane bagasse. with water content between 0.0142 and 0.1695. (d.b.).

From the obtained data, the behavior of the Gibbs free energy and the entropy function depending on the variation in water content were simulated. The parameters were determined using the STATISTICA program, version 5.0 (STATSOFT, 2004). The nonlinear simulation employed a quasi-Newton method. Equations (7) and (8) simulate, respectively, the Gibbs free energy and entropy for the water contents between 0.0142 and 0.1695 (d.b.).

$$\Delta S = 164.45 \times \ln\left(a_w\right) + 43.89 \tag{7}$$

$$\Delta G = 3.96 \times \exp\left(-6.76 \times a_w\right) \tag{8}$$

For temperature ranges between 20 and 70^{0}C, relative humidity between 10 and 85% and water contents between 0.0142 and 0.1695 (d.b.), the proposed correlations for Gibbs free energy and differential entropy of sugar cane bagasse presented, respectively, determination coefficients (R^2) of 0.97% and 0.99%, average relative errors (P) of 4.12 and 2.11 and estimated average errors (SE) of 0.62 and 0.002.

Figures 3 and 4 show theoretical and simulated values of the Gibbs free energy and the differential entropy of sugar cane bagasse, respectively.

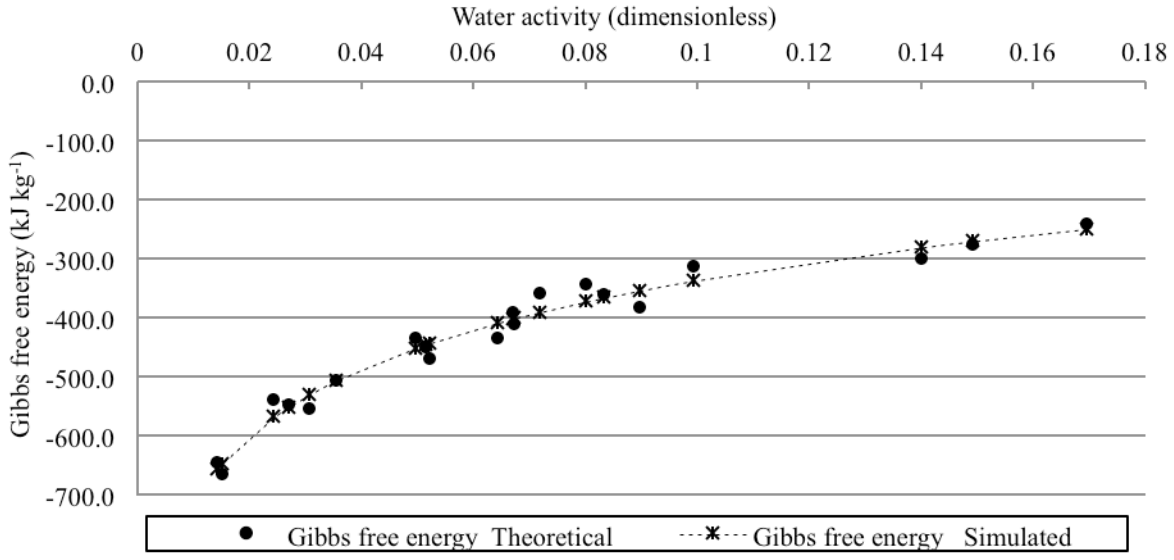

Figure 3. Theoretical and simulated values of Gibbs free energy for sugar cane bagasse with water content between 0.0142 and 0.1695 (d.b.).

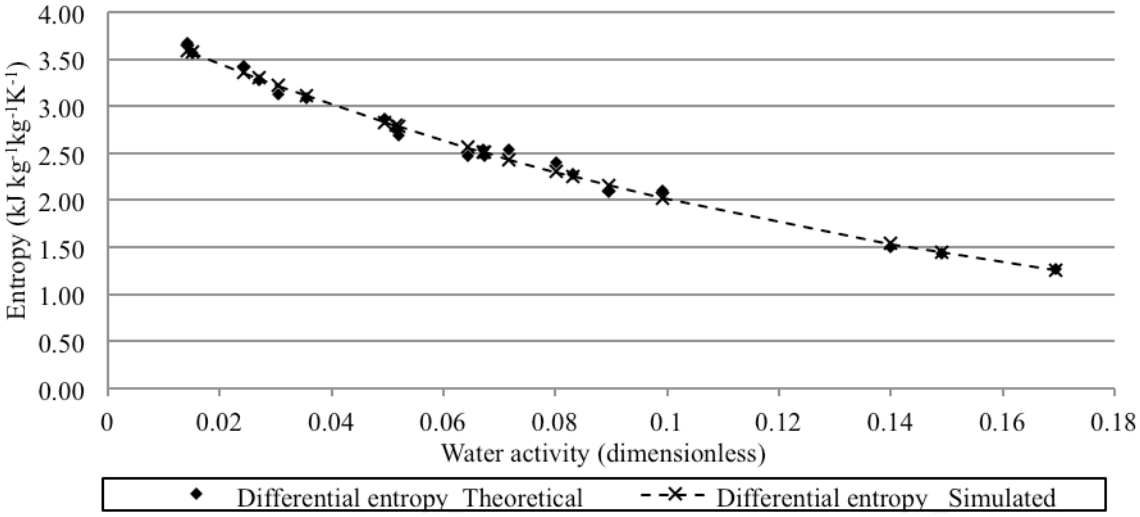

Figure 4. Theoretical and simulated values of Entropy for sugar cane bagasse with water content between 0.0142 and 0.1695 (d.b.).

The analysis of the thermodynamic characteristics of sugar cane bagasse allowed verifying an increase in Gibbs free energy as the water activity increases, although Gibbs free energy is negative and the differential entropy of the product is reduced. Also, the proposed empirical correlations adequately represent the product behavior for the conditions studied.

4. CONCLUSION

This study was performed considering a range of temperature between 20 and 70^{0}C, air relative humidity between 10 and 85% and water contents between 0.0142 and 0.1695 (d.b.). Its results allowed observing that as the equilibrium moisture content of sugar cane bagasse decreases the more spontaneous the sorption process becomes. In other words, the smaller the amount of water present in the product is, the easier the sorption process of water from the environment.

Likewise, it was observed an increase in the differential entropy as the water content was reduced, thus suggesting a greater interaction between the water molecules with the product constituents. Consequently, more energy would be required to transfer the water molecules from the surface of the solid product to the vapor state; indicating a decrease in the spontaneous characteristics of the sugar cane bagasse desorption process as its water content diminishes.

5. ACKNOWLEDGEMENTS

The authors L. P. Teixeira and M. L. Martins-Costa gratefully acknowledge the financial support provided by the Brazilian agencies CAPES and CNPq, respectively.

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