ISOSTERIC HEAT, ENTROPY, AND GIBBS FREE ENERGY OF PUMPKIN SEEDS (*Cucurbita moschata*)

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ABSTRACT

To maintain seed and soil quality of pumpkin, energy knowledge associated with processing and storage stages is strategic for the optimization of the thermodynamic processes needed for product stabilization. Thus, the objective of this study was to determine isosteric heat, differential entropy, and Gibbs free energy within a temperature range from 20 to 70° C, and relative air humidity levels between 10.75 and 85.11%. The study was based on empirical data for water activity determination. As a result, we verified that as moisture content decreased, the integral isosteric heat of the product increased from 2502.35 to 6231.17 kJ kg^{-1}, differential entropy raised from 1.18 to 12.43 kJ kg^{-1} K^{-1}, and Gibbs free energy ranged from -243.84 to -432.59 kJ kg^{-1}. Thus, we concluded that the lower the water availability in seeds, the greater the energetic requirement for its removal, as there is a major interaction between water and the product (seeds), indicating an increasingly less spontaneous desorption process.

INTRODUCTION

From pumpkin (*Cucurbita moschata*), both the fruit and its grains are consumed, which can be used roasted or as raw material for oil production liable to be utilized in food and energy (Adams et al., 2012; Veronezi & Jorge, 2012; Schinas et al., 2009). Pumpkin grains are consumed in several countries, being important sources of proteins (32 to 40%), lipids (44 to 50%) and fibers (23 to 27%), rich in fatty acids, mono and polyunsaturated (Trucom, 2006), submitting an equivalent production to 450g of oil per each 1 kg of pressed grains, with approximately 30% of moisture content, on wet basis (wb) (El-Soukkary, 2001).

After removed from the fruit, these grains, which present germinative characteristics easily influenced by their moisture content alteration (Bee & Barros, 1999), when exposed to the environment can also suffer deterioration due to microorganisms attack and enzymatic modifications. For this reason, the proper application of techniques and processes capable of controlling moisture content is essential to ensure maintenance stability of product quality.

In the same way, the knowledge about grains and seeds properties are decisive for analyses related to heat and mass transfer effects during the drying and storage of products (Resende et al., 2011, Caetano et al., 2012, Silva et al., 2016), energy requirement for drying performance, and for oil quality maintenance in the inner grain (Rosa & Telis-Romero, 2013). The study of such characteristics is important since it covers thermodynamic analysis involved in adsorption and desorption processes, allowing optimization and a better understanding of water properties in relation to the product, and energy calculation requirements associated with heat and mass transfer in these biological products (Oliveira et al., 2013).

For a clearer analysis on the biological components and water interactions in products, as well as to verify sorption process spontaneity, specific thermodynamic studies can be adopted, such as integral isosteric heat of sorption, liquid isosteric heat of sorption or differential enthalpy, entropy, and Gibbs free energy. According to Thys et al. (2010), data on product hygroscopic characteristics are used to determine these thermodynamic properties.

According to Corrêa et al. (2010), through integral isosteric heat variations, due to product moisture content, water molecule changes and interactions among product constituents can be determined, as well as to analyze through entropy the energy associated with bonding or repulsion forces in the system, which is related to water-product spatial arrangement relation. In a complementary way to this study, there is Gibbs free energy, which relates

to the required energy for transferring water molecules from a solid surface to vapor state or vice versa, that is, represents the measurement of the system effort to perform desorption or adsorption processes (Oliveira et al., 2014).

Taking into account the importance associated with oil production from pumpkin grains, for both food and energy purposes, studying the required energy demand for the proper processing of products would allow an optimization of processes and improve accuracy in product quality control. For this reason, the objective of this paper was to determine isosteric heat, entropy, and Gibbs free energy of pumpkin grains under controlled temperature conditions and product moisture content.

MATERIAL AND METHODS

This study was carried out at Federal Fluminense University. For the assessments, pumpkin grains with an initial moisture content of 0.096 db were used. To determine the amount of water activity (a_w) required to analyze the isosteric heat of sorption for pumpkin grains, an equilibrium moisture content equation (Equation 1) was employed, adjusted for Modified Halsey model, at temperature ranges of 20 to 70° C, and relative air humidity levels between 10.75 and 85.11%, defined through hygroscopicity study developed by Teixeira et al. (2014). This equation, adjusted for the pumpkin grains, presented determination coefficient of 98.30%, mean relative error of 3.24%, and mean estimated error of 0.0105.

$$X_e = \left[\frac{\exp(-8.3762 - 0.0225.T)}{-\ln(a_w)} \right]^{1/3.8973} \quad (1)$$

where,

Xe - equilibrium moisture content on a dry basis;

T - temperature, in° C;

a_w - water activity, in decimal.

Once water activity was determined, isosteric heat or enthalpy was forecasted through the estimation of the liquid isosteric heat of sorption (or differential enthalpy), by means of Sopade and Ajisegiri exponential model (Equation 2), and Clausius-Clapeyron modified equation (Equation 3). In this case, equilibrium moisture content and temperature (Wang & Brennan, 1991) are also considered.

$$q_{st} = = A \exp(-B \, U_e) \quad (2)$$

$$\ln(a_w) = -\left(\frac{q^{st}}{R} \right) \frac{1}{T_{abs}} + C \quad (3)$$

where,

qst - liquid isosteric heat of sorption, in kJ kg^{-1};

Tabs - absolute temperature, in K;

R - universal gas constant for water vapor, 0.4619 kJ kg^{-1} K^{-1};

A, B, C - adjustment coefficients.

For integral isosteric heat forecast, which also adds to the liquid isosteric heat of sorption the energy associated with the latent heat of free water vaporization (Equation 4), [eq. (5)] was applied (Chaves et al., 2015).

$$L = 2502.2 - 2.39. \, Tm \quad (4)$$

$$Qst = qst + L \quad (5)$$

where,

Qst - liquid isosteric heat of sorption, in kJ^{kg-1};

L - latent heat of free water vaporization, in kJ^{kg-1};

Tm - study range mean temperature, in °C.

Yet for order or disorder degree analysis and characterization in the water-product system, entropy (Equation 6) was measured associated with the product, according to Goneli et al. (2010).

$$\Delta S = \frac{\Delta q_{st} - \Delta G}{T_{abs}} \quad (6)$$

where,

ΔS - differential entropy of sorption, in kJ kg^{-1}K^{-1};

ΔG - Gibbs free energy, in kJ kg^{-1}.

For spontaneity analysis of water gain and loss process between product and environment, as indicated by Oliveira et al. (2014), Gibbs free energy calculation was enforced. For Gibbs free energy negative values, the process is spontaneous, and for positive values, it is non-spontaneous, yet when it is zero, then equilibrium was reached in relation to process spontaneity (Corrêa et al., 2010). According to Oliveira et al. (2013), Gibbs free energy can be estimated using [eq. (7)].

$$\Delta G = R_{va} \, T_{abs} \ln(a_w) \quad (7)$$

RESULTS AND DISCUSSION

Equilibrium moisture content empirical data, related to hygroscopicity analysis, adopted for isosteric heat, entropy and Gibbs free energy calculations are available in Table 1. Equation 1 was used in determining the water activity in pumpkin seeds at temperatures between 20 and 70°C. Table 2 discloses water activity values (a_w), in decimal, for pumpkin grains, determined by Modified Halsey model.

TABLE 1. Equilibrium moisture content of pumpkin grain at different temperatures and relative air humidities.

Relative Humidity (%)	Temperature (°C)	Mean equilibrium moisture content (db)
11.31	20	0.0858
33.07	20	0.0976
54.38	20	0.1234
85.11	20	0.1652
11.28	30	0.0808
21.61	30	0.0825
32.44	30	0.0952
51.4	30	0.1148
83.62	30	0.1488
11.03	55	0.0727
29.93	55	0.0747
50.15	55	0.0940
80.70	55	0.1290
10.75	70	0.0653
27.77	70	0.0683
49.70	70	0.0888
79.49	70	0.1126

TABLE 2. Water activity values (a_w) estimated by Modified Halsey model for the pumpkin grains, according to temperature and equilibrium moisture content.

Equilibrium moisture content (db)	Temperatures (°C)			
	20	30	55	70
0.065	0.0022	0.0076	0.0617	0.1369
0.068	0.0059	0.0166	0.0967	0.1887
0.073	0.0181	0.0405	0.1607	0.2711
0.075	0.0268	0.0555	0.1922	0.3081
0.081	0.0696	0.1191	0.2971	0.4205
0.083	0.0859	0.1407	0.3269	0.4501
0.086	0.1212	0.1854	0.3825	0.5035
0.089	0.1582	0.2292	0.4318	0.5490
0.094	0.2284	0.3074	0.5104	0.6187
0.095	2.457	0.3259	0.5277	0.6336
0.098	0.2793	0.3611	0.5594	0.6605
0.113	4.816	0.5578	0.7169	0.7885
0.115	0.5084	0.5825	0.7348	0.8025
0.123	0.6003	0.6652	0.7926	0.8471
0.129	0.6508	0.7095	0.8223	0.8696
0.149	0.7818	0.8215	0.8939	0.9231
0,165	0,8487	0,8772	0,9280	0,9481

Through Table 2 data, we could verify that as moisture content and/or temperature increase, there is an upsurge in water activity, indicating an increased water availability in the product. Oliveira et al. (2014) observed the same behavior for jatropha.

Based on water activity data, the liquid isosteric heat of sorption was determined from the angular coefficients of curves according to ln (a_w) x (T_{abs}^{-1}), shown in Figure 1, for different equilibrium moisture contents, as indicated by [eq. (3)].

From angular coefficients measurement, applied to [eq. (3)], the isosteric heat values of pumpkin seeds could be established. According to Equation 4, the average empirical temperature used as latent heat of free water vaporization was 42.94 °C, resulting in a latent heat of vaporization of 2399.57 kJ kg^{-1}. Table 3 reports liquid and integral isosteric heat of sorption values and their corresponding moisture contents and angular coefficients.
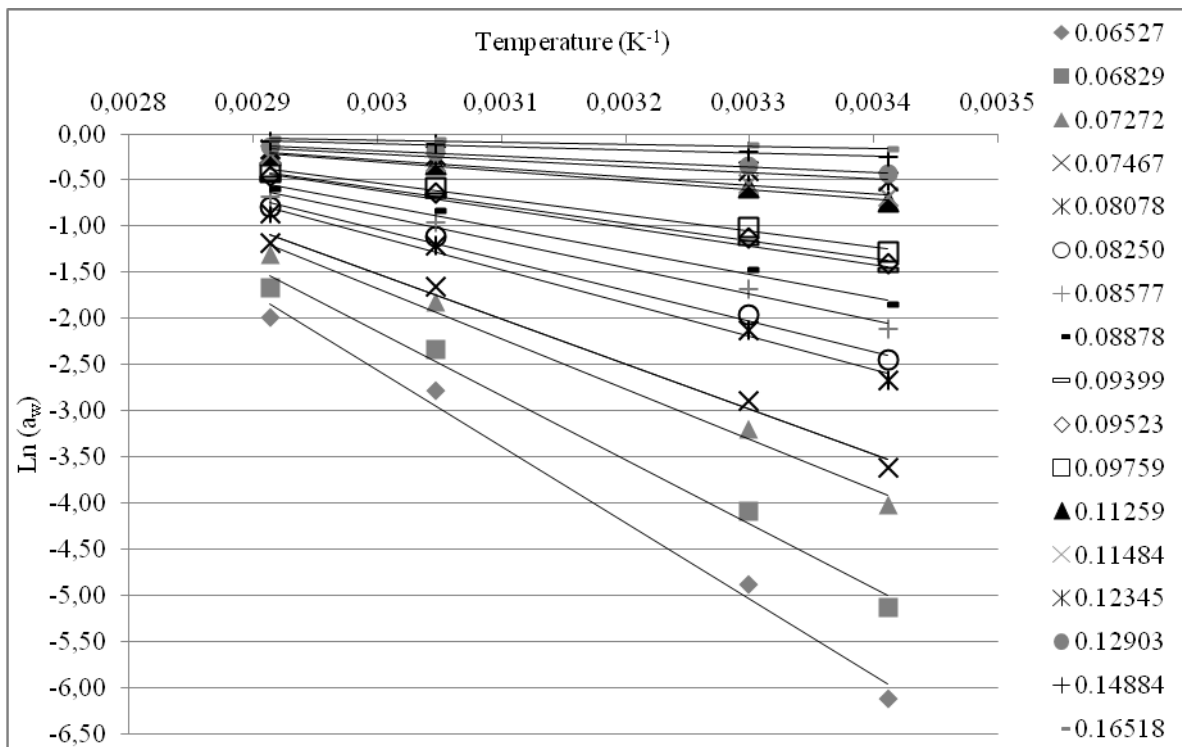
FIGURE 1. Angular coefficient values for different equilibrium moisture contents (db) of the pumpkin grains.

TABLE 3. Liquid and integral isosteric heat values of the pumpkin grains for different equilibrium moisture contents (db).

Equilibrium moisture content (db)	Angular Coefficient	Liquid isosteric heat (kJ kg^{-1})	Integral isosteric heat (kJ kg^{-1})
0.065	8295.3	3831.60	6231.17
0.068	6956.7	3213.30	5612.87
0.073	5444.3	2514.72	4914.29
0.075	4910.0	2267.93	4667.50
0.081	3613.4	1669.03	4068.60
0.083	3329.2	1537.76	3937.33
0.086	2861.7	1321.82	3721.39
0.089	2500.9	1155.17	3554.74
0.094	2002.6	925.00	3324.57
0.095	1903.5	879.23	3278.80
0.098	1729.7	798.95	3198.52
0.113	991.0	457.74	2857.31
0.115	917.5	423.78	2823.35
0.123	692.2	319.73	2719.30
0.129	582.6	269.12	2668.69
0.149	333.9	154.21	2553.79
0.165	222.5	102.78	2502.35

Figure 2 and Table 3 results show that as equilibrium moisture increases, angular coefficient decreases and, consequently, liquid and integral isosteric heats decline as well (Thys et al., 2010). From these data attainment, we reached the equation that provides integral isosteric heat of sorption for the pumpkin grains (Equation 8), according to equilibrium moisture content (db) and mean temperature of 42.94 °C. Estimated parameters and determination coefficient values were, respectively,

A = 90543.14 and B = - 48.93, where R^2 was equivalent to 99.5%.

$$Q_{st} = 90543.14 \exp(-48.93\ U_{eq}) + 2399.57 \qquad (8)$$

From the obtained results, Figure 2 features theoretical and estimated (simulated) values of integral isosteric heat of sorption according to equilibrium moisture content, in db.
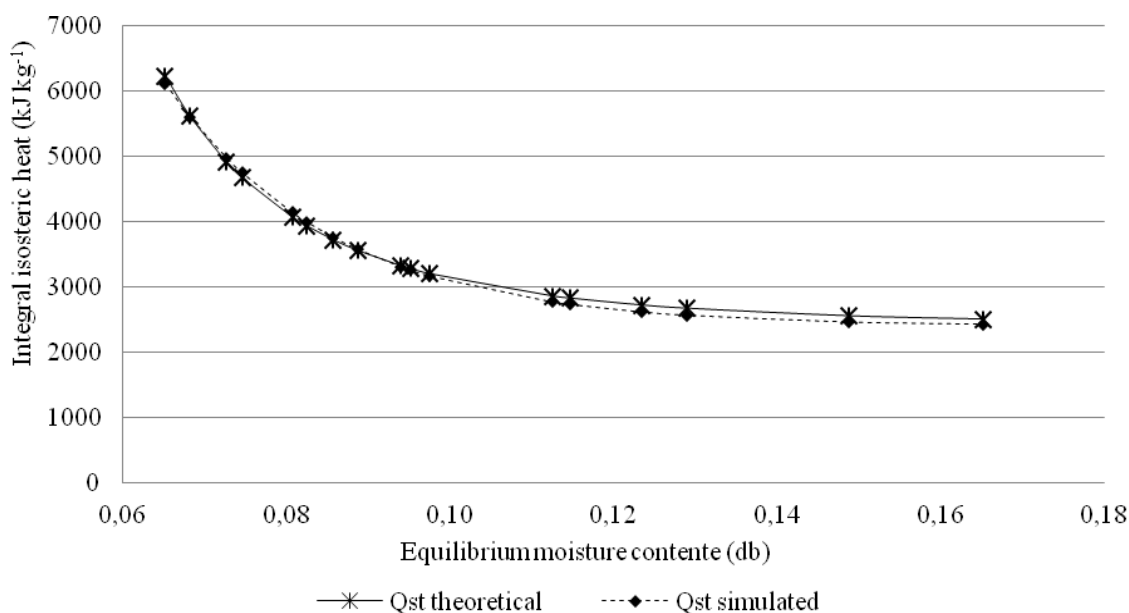
FIGURE 2. Theoretical (Q_{st} theoretical) and estimated (Q_{st} simulated) integral isosteric heat of sorption values of the pumpkin grains according to equilibrium moisture content.

Figure 2 makes it clear that as long as moisture content decreases, more energy is needed to remove it, as already mentioned by Oliveira et al. (2014). Thus, the integral isosteric heat of sorption values for the pumpkin grains, in moisture content range from 0.0653 to 0.1652 (db), were observed to vary from 6231.17 to 2502.35 kJ kg^{-1}. This behavior is corroborated as well by Caetano et al. (2012) for *Anacardium othonianum* Rizz seeds. Due to liquid isosteric heat or differential enthalpy determination, the differential entropy of sorption could be calculated (Equation 6), considering Gibbs free energy (Equation 7). Table 4 reports related values to the differential entropy of sorption and Gibbs free energy, according to liquid isosteric heat.

TABLE 4. Differential entropy of sorption and Gibbs free energy values according to the liquid isosteric heat of the pumpkin grains.

Equilibrium moisture content (db)	Temperature (°C)	Liquid isosteric heat (kJ kg^{-1})	Differential entropy of sorption (kJ kg^{-1} K^{-1})	Gibbs free energy (kJ kg^{-1})
0.065	70	3831.60	12.43	-432.59
0.068	70	3213.30	10.60	-425.44
0.073	55	2514.72	8.87	-397.31
0.075	55	2267.93	8.11	-393.29
0.081	30	1669.03	6.67	-352.31
0.083	30	1537.76	6.22	-349.37
0.086	20	1321.82	5.64	-332.59
0.089	70	1155.17	4.48	-383.83
0.094	55	925.00	3.91	-358.41
0.095	30	879.23	3.99	-329.28
0.098	20	798.95	3.80	-315.09
0.113	70	457.74	2.34	-346.18
0.115	30	423.78	2.40	-303.06
0.124	20	319.73	2.06	-283.27
0.130	55	269.12	1.77	-310.39
0.149	30	154.21	1.39	-266.74
0.165	20	102.78	1.18	-243.84

Since the adopted empirical method was based on an adsorption process, from the results shown in Table 4, we may infer that the greater the interaction of water molecules with product constituents (lower equilibrium moisture content), the larger the energy needed for transferring these molecules from the solid surface of the product to vapor state. Hence, desorption process presents increasingly less spontaneous characteristics. Therefore, for the pumpkin grains, as equilibrium moisture content is reduced, the water absorption in the product becomes progressively more spontaneous. Rosa & Telis-Romero (2013) also noticed this behavior for orange seeds and by Silva et al. (2016) for pepper seeds.

Mathematically, the relationship among enthalpy, entropy, and Gibbs free energy can demonstrate this trend. As enthalpy (isosteric heat) and entropy are positive, then Gibbs free energy is negative, characterizing a desorption process becoming increasingly less spontaneous when

there is a decrease in the moisture content of the product. In addition, through Gibbs free energy and entropy results, we can confirm that the energetic analysis of sorption process can be influenced by both moisture content and temperature.

CONCLUSIONS

Moisture content influences thermodynamic properties of pumpkin seeds, as well as technical parameters definition over processing and storage stages.

The lower the water availability in the product, the greater the energy required for its removal, and the stronger the interaction between water and product.

As the moisture content in product decreases, integral isosteric heat, differential entropy, and Gibbs free energy increases, in absolute values.

Gibbs free energy revealed a negative signal, indicating that desorption process becomes increasingly less spontaneous as product moisture content decreases.

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