PARTICLE SIZE AND ROASTING ON WATER SORPTION IN CONILON COFFEE DURING STORAGE

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ABSTRACT: The aim of this work was to evaluate alterations on the water sorption of coffee due to the effect of roast, grind and storage in two temperatures (10 and 30 ºC) during 180 days. Crude grain coffee (Coffea canephora) with average initial moisture content of 12.61 % (d.b.) was used. Grain was roasted at two levels: medium light (ML) and moderately dark (MD). Afterwards, grain was processed in three different particle sizes: fine (0.59 mm), medium (0.84 mm) and coarse (1.19 mm), besides the whole coffee lot. Samples prepared were then stored in two temperatures (10 and 30 ºC). These were analyzed during six months, at five distinct times (0, 30, 60, 120 and 180 days) regarding moisture content and water activity. Furthermore, mathematical modeling and thermodynamic properties acquisition of the coffee moisture adsorption process were accomplished. A split plot design was used, in which plots consisted of storage period and split-plots consisted of a 2 x 4 x 2 factorial (two roasting degrees, four particle sizes and two storage temperatures), with five repetitions.It was concluded thatparticle size did not significantly affectedmoisture content of coffee, independently of roast degree; Sigma-Copace model best represented hygroscopic equilibrium for sorption of roasted coffee; with moisture content reduction, an increase of differential enthalpy and entropy of sorption and Gibbs free energy occurs.

Index terms: Adsorption isotherms, mathematical modeling, thermodynamic properties, *Coffea canephora.*

GRANULOMETRIA E TORREFAÇÃO NA SORÇÃO DE ÁGUA EM CAFÉ CONILON DURANTE O ARMAZENAMENTO

RESUMO: *Objetivou-se, nesse trabalho, avaliar as alterações na sorção de água de café, devido ao efeito da torrefação, moagem e armazenamento em duas temperaturas (10 e 30 ºC), durante 180 dias. Café cru (Coffea canephora), com teor de água inicial médio de 12,61 % (b.u.) foi utilizado. Os grãos foram torrados em dois níveis: média clara (MC) e moderadamente escura (ME). Posteriormente, os grãos foram processados em três diferentes granulometrias: fina (0,59 mm), média (0,84 mm) e grossa (1,19 mm), além do lote de café inteiro. As amostras foram armazenadas em duas temperaturas (10 e 30 ºC). Estas foram analisadas durante seis meses, em cinco diferentes tempos (0, 30, 60, 120 e 180 dias), acerca do teor de água e atividade de água. Posteriormente, a modelagem matemática e a aquisição das propriedades termodinâmicas do processo de adsorção foi realizada. Um esquema de parcelas subdivididas foi usado, em que as parcelas consistiram no tempo de armazenamento e as subparcelas um fatorial 2 x 4 x 2 (dois níveis de torrefação, quatro níveis de granulometria e duas temperaturas de armazenamento), com cinco repetições. Foi concluído que a granulometria não afetou significativamente o teor de água de café, independentemente da torra; o modelo de Sigma-Copace é o que melhor representa o equilíbrio higroscópico de sorção de café torrado; com a redução do teor de água há um aumento da entalpia e entropia diferenciais de sorção e da energia livre de Gibbs.*

Termos para indexação: *Isotermas de adsorção, modelagem matemática, propriedades termodinâmicas, Coffea canephora.*

1 INTRODUCTION

Storage of agricultural products is historically an important post-harvest procedure with the aim of achieve food safety and economic strength for agribusiness. However, in order to ensure product quality and higher shelf life, temperature and relative humidity of the environment surrounding the product are primordial parameters to be considered during storage (CORRÊA et al., 2014). They determine the water activity (a_w) of the product and, thus, the water exchange between the product, which is hygroscopic, and the environment (HENAO; QUEIROZ; HAJ-ISA, 2009).

Agglomeration is an important issue for industry, which may lead to complicating product handling and transport and, therefore, the processing of the final product, directly influencing profit.Ground roasted coffee may absorb water from the atmosphere because of its low moisture content. Coffee agglomeration occurs when the moisture content ranges from 7 to 8% (OLIVEIRA

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et al., 2014; ROBERTSON, 1993; SILVA et al., 2006).

Particle size and roasting also affects the hygroscopic capacity of the product and thus agglomeration index (OLIVEIRA et al., 2014; ROBERTSON, 1993; SILVA et al., 2006). Thus, studies on the influences of particle size and roasting level on water absorption and storage are required to understand product-environment interactions.

Grinding coffee grain aims to increase the specific surface area for extraction, increasing components transfer related to flavor, affecting cup quality (ILLY; VIANI, 1996). Baptestini (2011) observed that smaller particle-sized coffees had higher a_w values after 120 days of storage. In addition, the rupture of coffee tissues and cells caused by grinding leads to easier release of the volatile compounds that perfume the drink (ANDUEZA; DE PEÑA; CID, 2003). Therefore, coffee drink quality is expected to decrease with storage time because of the loss of volatile compounds from ground coffee.

Roasting also affects the degree of moisture sorption, coffee being more (dark roasts) or less (light roasts) hygroscopic according to its degree of roasting. Different researchers stated this trend (BICHO et al., 2012; SCHMIDT; MIGLIORANZA; PRUDÊNCIO, 2008).

Sorption isotherms are indispensable to determine and analyze water sorption changes during storage. Mathematical models are used to construct isotherms aiding the prediction and simulation of the performance of materials in a certain environment.Different works stated sorption isotherms of coffee beans, ground coffee, dehulled coffee or roasted coffee (CORRÊA et al., 2014; FURMANIAK et al., 2009; HENAO; QUEIROZ; HAJ-ISA, 2009; IACCHERI et al., 2015; RAMÍREZ-MARTÍNEZ et al., 2013), however, research were not made regarding different particle sizes and roasting degrees of coffee.

Water sorptionand thermodynamic sorption properties of a materialmay be monitored by assessing the a_w. According to Corrêa, Oliveira and Santos (2012), thermodynamic properties of agricultural products is a key resource that can inform assessments of the effect of a_w on storage and can inform the understanding of the adsorbed water properties and food microstructure. This information enables the study of the physical phenomena that occur on food surfaces.

Given the importance of knowledge of the hygroscopicity of agricultural products, as well as the interaction of water with the product, the objective of this study was to determine the adsorption isotherms of coffee in different roasting and particle size degrees, stored at either 10 or 30 ºC. In addition, to determine the thermodynamic properties of water sorption as a function of a_w.

2 MATERIALS AND METHODS

Sample preparation

Dried raw coffee grain (*Coffea canephora* Pierre ex A. Froehner) were purchased at the local market in Zona da Mata, MG.The coffee grain were sorted to remove deteriorated, damaged, and bored coffee grain to obtain a homogeneous raw material with minimal defects.

The mean initial moisture content of the coffee beans was 12.61% on a dry basis (db), which was determined gravimetrically using a forced-air oven at 105 ± 1 °C for 24 h.

Coffee grain were subjected to the roasting process after sorting. A roaster of direct gas burn (LPG), with rotary cylinder at 45 rpm, with capacity of 350 g, was used to roast (brand Rod-Bel).The degree of roasting was determined by a trained professional by monitoring the sample color and comparing it with the Agtron/Specialty Coffee Association of America (SCAA) standard roast number (ASSOCIAÇÃO BRASILEIRA DA INDÚSTRIA DE CAFÉ - ABIC, 2015). Two roasting degrees were obtained: medium light (ML) and moderately dark (MD), corresponding to Agtron numbers of SCAA#65 and SCAA#45, respectively (Figure 1).

The mass loss parameter was determined to ensure roasting uniformity, and the coffee beans lost, on average, 15.85 and 18.74 gof mass under ML and MD roasting, respectively, at a temperature of 285 ºC (VARGAS-ELÍAS, 2011). Roaster temperature and roasting time tests were performed to evaluate their influence on mass losses. The product was removed from the roaster when reaching the aforementioned degrees of roasting and immediately cooled to room temperature.

Following the roasting process, the coffee beans were processed in a Mahlkönig mill (Germany, model K32 S30LAB) at three different particle sizes: fine (0.59 mm), medium (0.84 mm), and coarse (1.19 mm), and a batch of coffee was maintained as whole beans(without milling).

FIGURE 1 - Roasting degrees employed: medium light (A) and moderately dark (B) (ABIC, 2015).

The prepared samples were then placed in polypropylene bags and refrigerated at two storage temperatures (10 and 30 ºC)in BOD chambers. The treatments were sampled and analyzedduring storageat five period(0, 30, 60, 120, and 180 days).

Figure 2 summarizes the sample preparation for further analyzes described below.

The changes in the water activity (a_w) of the roasted whole bean and ground coffee samples were assessed using an AquaLab 4TE(Decagon Devices, USA) water activity meter with an a_w accuracy of ± 0.003. Five replicates were measured.The equilibrium moisture content of a coffee sample was defined as the content assessed after each five storage times (0, 30, 60, 120 and 180 days) because the samples were stored in permeable plastic bags and the time elapsed was deemed sufficient to reach equilibrium.

Mathematical models commonly used to describe sorption phenomena in agricultural products were fitted to the collected hygroscopic equilibrium data (Table 1).

The standard deviation of the estimate (SDE), mean relative error (MRE) values and residual plot were analyzed to assess the goodness of the model fit. The SDE and MRE values of each model were calculated using Equations 6 and 7, respectively:

$$MRE = \frac{100}{n}\sum\frac{|Y - \hat{Y}|}{Y} \tag{6}$$

$$SDE = \sqrt{\frac{\Sigma(Y - \hat{Y})^2}{DF}} \tag{7}$$

In which: *MRE* = mean relative error, %; *SDE* = standard deviation of the estimate, % d.b.; *Y* = observed value; Ŷ = estimated value by the model; *n* = number of observed data; and, *DF* = residue degrees of freedom (number of observed data minus number of model parameters).

Thermodynamic parameters: differential entropy of desorption (Δ*S*), differential enthalpy (Δ*H*), Gibbs free energy (Δ*G*) and enthalpy-entropy relationship, were obtained by means of a known methodology [1], which an approximate (1-α)100% confidence interval for isokinetic temperature was used. These parameters are expressed respectively by Equations 8-12:

$$ln a_w = \pm\left(\frac{\Delta H_{st}}{RT_k} - \frac{\Delta S}{R}\right) \tag{8}$$

$$\Delta H = \Delta H_{st} - \Delta H_{vap} \tag{9}$$

$$\Delta G = \pm RT_k ln(a_w) \tag{10}$$

$$T_B = \hat{T}_B \pm t_{m-2,\alpha/2}\sqrt{Var(T_B)} \tag{11}$$

$$T_{hm} = \frac{n}{\Sigma_{i=1}^{n}\left(\frac{1}{T_i}\right)} \tag{12}$$

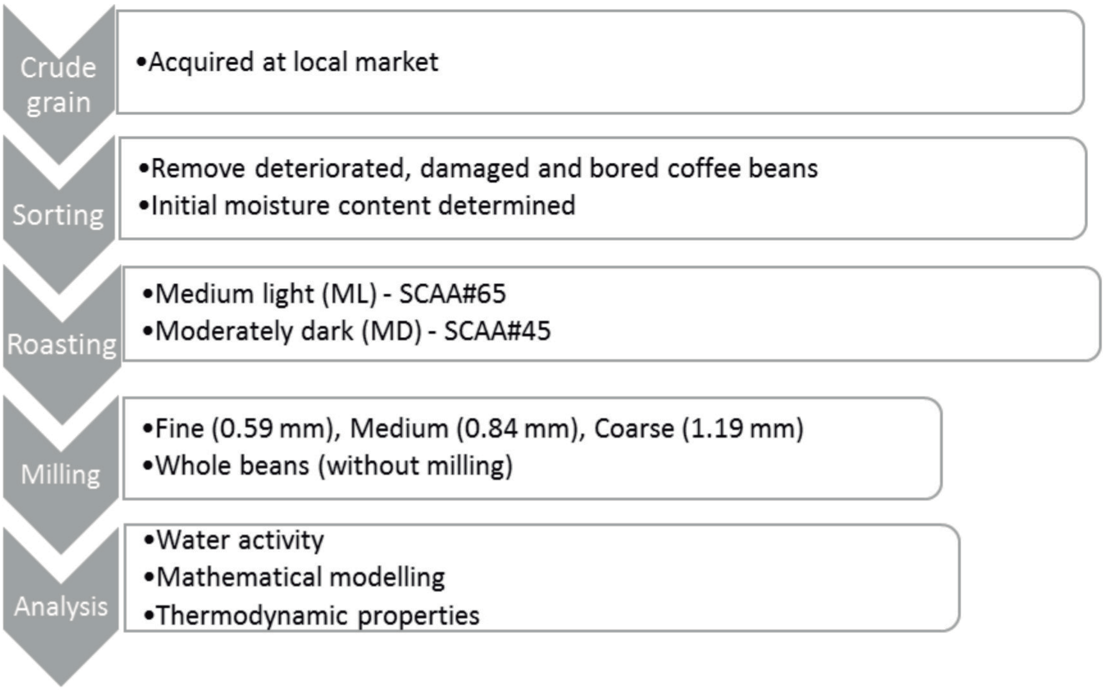

FIGURE 2 - Stages for sample preparation.

TABLE 1 - Mathematical models used to represent sorption isotherms.

Modelname	Model	
Copace	$U_e = exp(a - bT + ca_w)$	(1)
Modified GAB	$U_e = \frac{ab(c/T)a_w}{\{[1 - ba_w][1 - ba_w + b(c/T)a_w]\}}$	(2)
Halsey	$U_e = \left[\frac{exp(a - bT)}{-ln a_w}\right]^{1/c}$	(3)
ModifiedOswin	$U_e = \frac{a + bT}{\left(\frac{1-a_w}{a_w}\right)^{1/c}}$	(4)
Sigma-Copace	$U_e = exp(a - bT + ca_w)$	(5)

in which: U_e = equilibrium moisture content, % d.b.;a_w = water activity, dimensionless;*a, b, c* = model parameters which depends on the product; and,*T* = temperature, ºC.

In which: ΔH = differential enthalpy of sorption, kJ kg-^{1}; ΔH_{vap} = latent heat of vaporization of pure water, kJ kg^{-1}; ΔH_{st}= net isosteric heat of sorption, kJ kg^{-1}; ΔS = differential entropy of sorption, kJ kg^{-1} K^{-1}; and ΔG = Gibbs free energy, kJ kg^{-1} mol^{-1}; T_B = isokinetic temperature, K; m = number of data pairs of enthalpy and entropy; t is the t value at (m-2) degrees of freedom; T_{hm} = harmonic mean temperature, K; and, *n* = number of temperatures utilized.

The "+" and "-"signs in Equation 8 and others related to thermodynamic properties express the direction of heat transfer, which is associated with the spontaneity of the process studied. Thus, a positive sign corresponds to the adsorption processes in the present study.

A split plot design was used, in which plots consisted of storage period and split-plots consisted of a 2 x 4 x 2 factorial (two roasting degrees, four particle sizes and two storage temperatures), with five repetitions.

3 RESULTS AND DISCUSSION

Tables 2 and 3 present the coefficients of the models fitted to the observed data for the hygroscopic equilibrium of coffee in the different conditions used.

MRE values lower than 10% indicate a good fit for practical purposes (SAMAPUNDO et al., 2007) and description of a specific physical process is inversely proportional to the SDE value. A maximum SDE of the model estimate of 0.5 % (d.b.) was considered acceptable. In order to conclude the best model, suitability of the model to respond all variables (storage temperature, roast degree and particle size degree) was taken into account. Among all the models tested, the Sigma-Copace model had the best results regarding residual plots, MRE and SDE values at all storage temperatures, roast and particle size degree, followed by Halsey model (Tables 2and3). This trend can be seen at coffee grain roasted at moderately dark degree, with fine particle coffee (Table 3).Copace and Modified GAB models present biased residual plots whilst Modified GAB and Modified Oswin presented MRE value higher than 10% (Table 3).

The Sigma-Copace model has also been reported to satisfactorily describe the hygroscopicity of soluble coffee (CORRÊA; AFONSO JÚNIOR; STRINGHETA, 2000) and conilon coffee cherries (CORRÊA et al., 2014). However, because the Sigma-Copace model is an exponential model, the inflection of the isotherm should not be used to predict moisture content values as the a_w tends toward zero. This is a limitation of the model.

Figures 3 to 6 present the mean equilibrium moisture contents and standard deviation at each storage period (0, 30, 60, 120, and 180 days), obtained by adsorption,of the roasted conilon coffee beans for the evaluated particle sizes, as well as their isotherms by Sigma-Copace model.

As can be seen in Figures 3 to 6, water activity increased throughout storage, regardless of roast and particle size degree. This trend is due to adsorption process during storage, in which finer products are more hygroscopic, presenting higher potential to exchange moisture with the environment; in this case, gaining moisture.

Storage temperature affects the hygroscopicity of roasted coffee samples, regardless of particle size. At a given constant water activity, the equilibrium moisture content decreases with a decrease in storage temperature. As the temperature increases, molecular vibrations also increase, thereby increasing the distance between molecules and, consequently, decreasing the attractions between molecules.

At higher water activities, the equilibrium moisture contents increase sharply, especially for samples roasted to MD. This trend is related to roasting degree (more hygroscopic)which at MDcoffee may adsorb a greater amount of water from the environment. Similar increases in water adsorption isotherms have been observed by Anese, Manzocco and Nicoli (2006), Baptestini (2011) and Corrêa, Afonso Júnior and Stringheta (2000), for roasted ground coffee stored at 30 ºC for 1 month and for roasted ground coffee stored in various packages.

A good correspondence was observed between the data estimated using the Sigma-Copace model and the experimentally observed data. However, it should be noted the Sigma-Copace model is an exponential model. Therefore, the inflection of the isotherm should not be used to predict moisture content values as the a_w tends toward zero, which is a limitation of the model. Future studies are recommended to experimentally assess the equilibrium moisture contents for a_w values ranging from 0.5 to 0.9 and analyze the resulting ground roasted coffee adsorption isotherms, especially for coffee roasted to MD, because there may be an overestimation of the equilibrium moisture content values at these a_w levels.These levels were not achieved at the present study probably to the lower storage period (six months), requiring higher period to achieve higher levels of a_w.

TABLE 2 - Parameter estimates of hygroscopic equilibrium models of medium light roasted coffee, whole, fine, medium and coarse particle sizes and its respective determination coefficients (R^2), standard deviation of the estimate (SDE), mean relative error (MRE) and residual plot (B – biased; R – random)at temperatures of 10 and 30 ºC.

Models	Fittedparameters			MRE	SDE	R^2	Residual plot
	a	b	c	(%)	(% d.b.)	(%)	
			WholeCoffee				
Copace	0.2217	- 0.0026	2.0712	3.87	0.17	92.64	R
Modified GAB	1.5018	58697490	1.2655	4.33	0.18	91.55	R
Halsey	1.3059	- 0.0035	1.3272	3.87	0.17	92.62	R
ModifiedOswin	3.4227	0.0010	2.1947	3.87	0.17	92.79	R
Sigma-copace	- 1.1543	- 0.0026	1.4793	3.86	0.16	92.88	R
			Fine Coffee				
Copace	0.5888	0.0016	2.2271	6.92	0.33	89.20	R
Modified GAB	2.1534	1086	1.2614	7.31	0.35	87.85	R
Halsey	1.8295	0.0019	1.3063	6.58	0.32	89.84	R
ModifiedOswin	5.011	- 0.0057	2.4113	6.12	0.31	90.59	R
Sigma-copace	- 1.0349	0.0017	1.6950	7.22	0.34	88.47	R
			MediumCoffee				
Copace	0.3490	0.0060	2.8808	6.69	0.25	93.62	R
Modified GAB	1.9438	265.6907	1.3547	6.95	0.26	93.02	R
Halsey	1.3829	0.0059	0.9827	6.71	0.25	93.55	R
ModifiedOswin	5.5280	- 0.0295	1.7415	6.77	0.26	93.19	R
Sigma-copace	- 1.7023	0.0060	2.1542	6.64	0.25	93.76	R
			CoarseCoffee				
Copace	0.5589	0.0036	2.0645	4.37	0.18	93.57	R
Modified GAB	2.0411	826.4070	1.1647	4.80	0.20	92.48	R
Halsey	1.8138	0.0049	1.3789	4.48	0.19	93.26	R
ModifiedOswin	4.6036	- 0.0148	2.4715	4.78	0.19	92.59	R
Sigma-copace	- 0.9290	0.0036	1.5581	4.27	0.18	93.93	R

TABLE 3 - Parameter estimates of hygroscopic equilibrium models of moderately dark roasted coffee, whole, fine, medium and coarse particle sizes and its respective determination coefficients (R^2), standard deviation of the estimate (SDE), mean relative error (MRE) and residual plot (B – biased; R – random) at temperatures of 10 and 30 ºC.

Models	Fittedparameters			MRE	SDE	R^2	Residual plot
	a	b	c	(%)	(% d.b.)	(%)	
			WholeCoffee				
Copace	- 1.2570	- 0.0006	6.3450	9.02	0.27	93.08	R
Modified GAB	0.7449	3071165	2.0371	8.07	0.25	94.17	B
Halsey	0.4668	- 0.0003	0.4340	9.11	0.27	92.97	R
ModifiedOswin	6.1339	0.0049	0.7282	9.43	0.28	92.54	R
Sigma-copace	- 5.5530	- 0.0005	4.5920	8.76	0.26	93.38	R
			Fine Coffee				
Copace	- 0.6566	- 0.0058	4.7150	9.71	0.36	92.86	R
Modified GAB	1.0058	10259337	1.8935	10.09	0.41	90.51	R
Halsey	0.6369	- 0.0034	0.5909	9.86	0.36	92.75	R
ModifiedOswin	4.9883	0.0314	1.0159	10.11	0.37	92.52	R
Sigma-copace	- 3.9327	- 0.0059	3.4666	9.57	0.36	92.92	R
			MediumCoffee				
Copace	- 0.5796	- 0.0021	4.8426	8.75	0.25	95.09	B
Modified GAB	1.0019	30517074	1.9552	7.73	0.23	96.00	B
Halsey	0.6927	- 0.0012	0.5777	9.01	0.26	94.75	R
ModifiedOswin	5.6483	0.0121	1.0044	9.53	0.28	94.00	R
Sigma-copace	- 3.9768	- 0.0022	3.5867	8.40	0.24	95.52	R
			CoarseCoffee				
Copace	- 0.9357	- 0.0011	5.9178	6.30	0.27	94.89	R
Modified GAB	0.8648	4774015	2.0777	5.72	0.28	94.61	R
Halsey	0.5813	- 0.0005	0.4687	6.38	0.27	94.87	R
ModifiedOswin	6.7563	0.0064	0.8029	6.60	0.27	94.78	R
Sigma-copace	- 5.0459	- 0.0012	4.3541	6.14	0.27	94.93	R

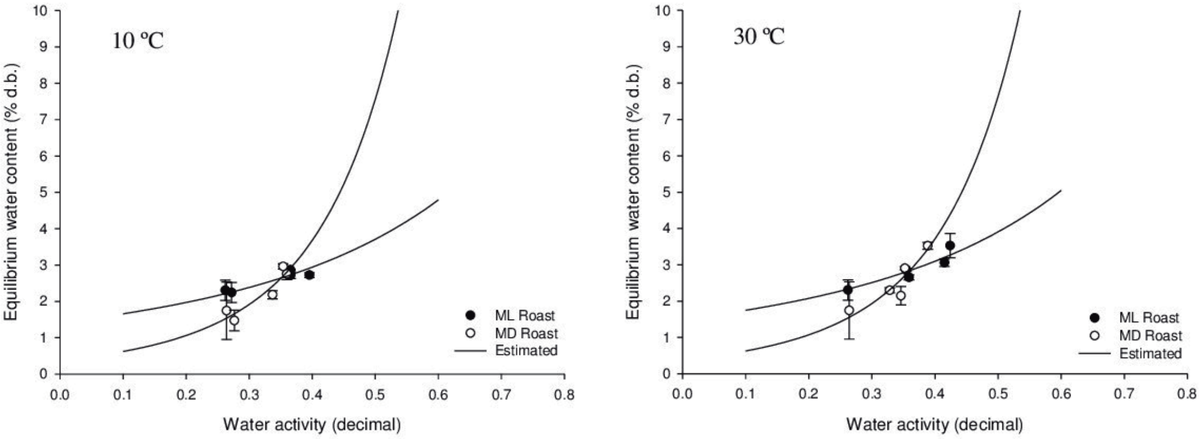

FIGURE 3 - Observed and estimated values, obtained by means of Sigma-Copace model, of equilibrium adsorption moisture contents of the roasted conilon coffee beans, whole particle size, stored at 10 and 30 ºC.

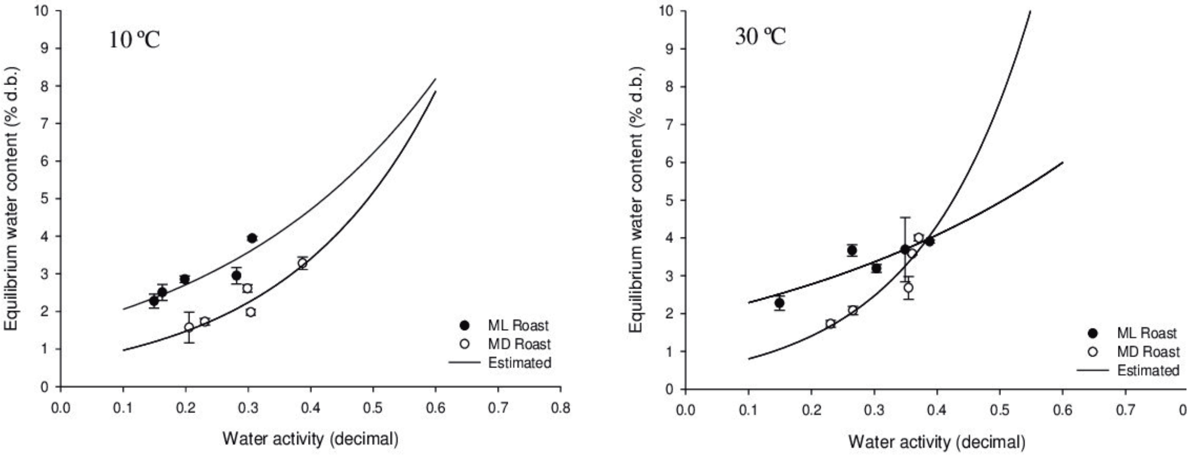

FIGURE 4 - Observed and estimated values, obtained by means of Sigma-Copace model, of equilibrium adsorption moisture contents of the roasted conilon coffee beans, fine particle size, stored at 10 and 30 ºC

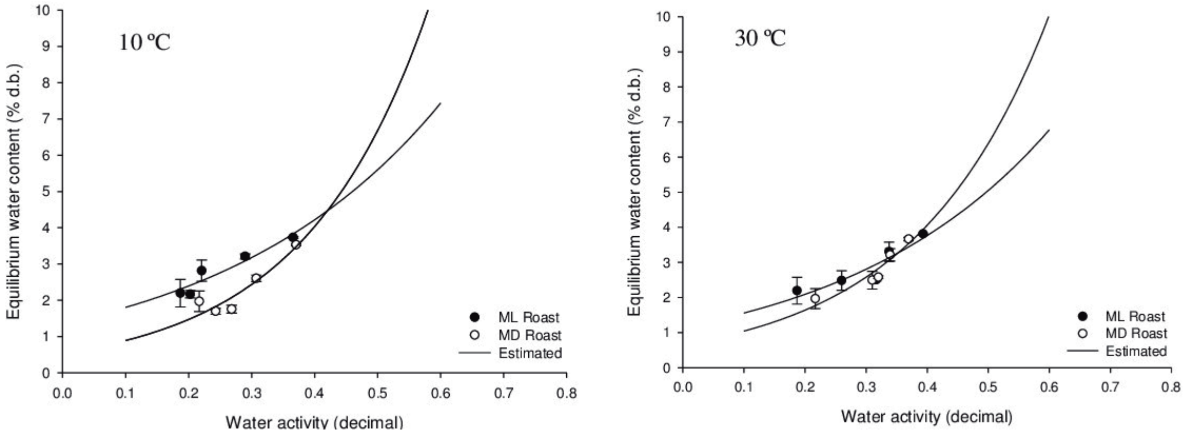

FIGURE 5 - Observed and estimated values, obtained by means of Sigma-Copace model, of equilibrium adsorption moisture contents of the roasted conilon coffee beans, medium particle size, stored at 10 and 30 ºC.

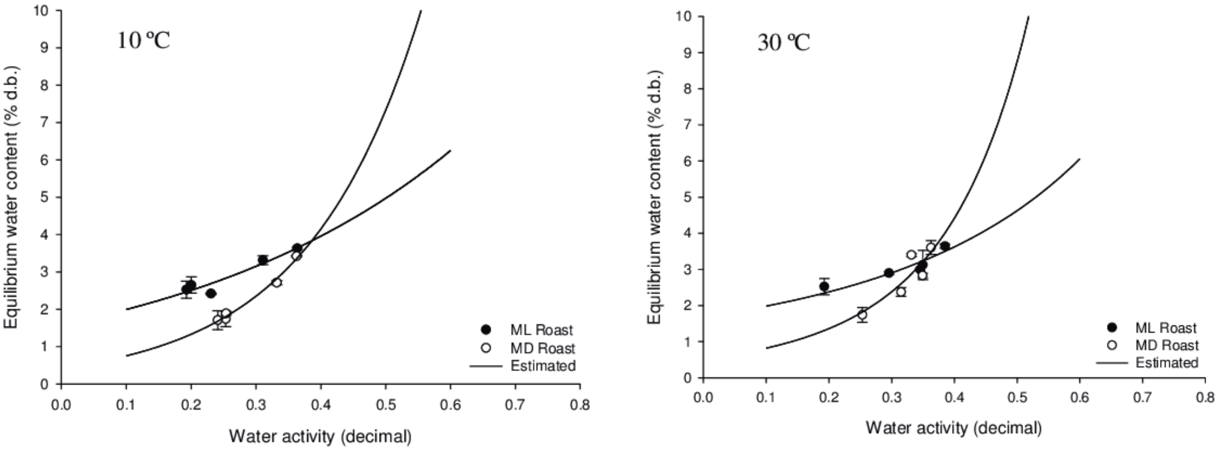

FIGURE 6 -Observed and estimated values, obtained by means of Sigma-Copace model, of equilibrium adsorption moisture contents of the roasted conilon coffee beans, coarse particle size, stored at 10 and 30 ºC.

Brunauer (1945) classified sorption isotherms based on the van der Waals forces of nonpolar gases adsorbed onto several non-porous solid substrates.A comparison analysis of the results indicates that the whole bean and ground roasted-coffee adsorption isotherms may be classified as type III isotherms. Type III isotherms,known as the Flory–Huggins isotherms, mainly correspond to food consisting of crystalline components, a state characterized by a three-dimensional regular arrangement of molecules based on their orientation (HASSINI et al., 2015).

Observed and estimated values of differential enthalpies and entropies of adsorption are shown in Figures 7 and 8, respectively.

Positive values of differential enthalpy represent a process with heat absorption (endothermic) and negative values of differential enthalpy, which is the case of the present study, indicates an exothermic and energetically favorable transformation process, in other words, with heat release (CHU et al., 2004; SHAFAEI; MASOUMI; ROSHAN, 2016). Furthermore, Chu et al. (2004) states that negative values of differential entropy explains the exothermic nature of the adsorption process, along with increase of molecules organization.

It can be noticed that an increase in moisture content, the differential enthalpy of adsorption tends to reach the latent heat value of pure water (2442.45 kJ kg^{-1}). This trend indicates that the number of bonds formed between water molecules and the active adsorption sites of the product are close to the potential maximum (saturation).

This increase is explained by the change in the bond strength between water and the sorbent surface (coffee), which, according to Al-Muhtaseb, McMinn and Magee (2004), at the beginning of sorption, has numerous highly active polar sorption sites with high interaction energies that, with time, are covered by water molecules, forming a monomolecular layer. As water molecules continue to bind chemically to the highly active sorption sites, sorption begins to occur in less-active sites (high moisture content) with lower interaction energies; therefore, the differential enthalpy of adsorption is lower. This trend occurred for whole coffee (without grinding) and grinded coffee samples roasted at MD level (Figure 7-B). At these samples, adsorption occurred at vapor form, because the released energy of this process did not attained the value of latent heat of condensation.

However, coffee roasted to ML presented different behavior for grinded coffee (fine, medium, coarse), as can be seen in Figure 7-A. Higher values of ΔH indicates that, during adsorption, there are more polar sites or sorption sites at the adsorbent surface of coffee. Viganó et al. (2012) reported that higher values reflect higher interaction energies and a greater heterogeneity of water molecules, suggesting that these products are more strongly affected by changes in relative humidity.

ΔH values as a function of the particle size of roasted coffeemay be analyzed by evaluating roasting. Coffee ground MD samples were statistically similar ($p < 0.05$) but differed from the pattern for whole roasted coffee. Baptestini (2011) also concluded that arabica coffee samples that were roasted and ground to the fine, medium, and coarse particle sizes were statistically equivalent. However, coffee roasted to ML presented random pattern. The medium and coarse particle sizes of conilon coffee are statistically equal ($p < 0.05$).

Differential entropy of adsorption had the same tendency as ΔH. A similar result was reported by Al-Muhtaseb, McMinn and Magee (2004) for starch powder and by Baptestini (2011) for ground roasted coffee stored in various packages.

Coffee samples roasted to ML and grinded exhibited a pattern opposite to the above-described. According to Rizvi (2005), there are two opposite patterns for the differential entropy of water adsorption in food: a loss of entropy because of the water location or an increase in entropy as a result of the formation of a solution, for example, during food solubilization and product expansion. Therefore, the increase in ΔS indicates the formation of water molecule layers that will be subsequently removed from the product surface. This trend indicates that samples roasted to MD permits the formation of water layers.

The observed and estimated values of the change in the Gibbs free energy are shown in Figure 9.

Regardless of roast and grind degree, Gibbs free energy values were negative. This is typical of an exergonic reaction or spontaneous process, which does not require the addition of energy from the environment surrounding the product. Whole bean coffee had lower ΔG values than the ground samples, regardless of roasting degree (Figure 9). Lower absolute ΔG values are related to lower product hygroscopicity.

Throughout storage, is expected a decrease in ΔG values, because coffee samples adsorb moisture from the environment, decreasing the number of adsorption sites and, therefore, reducing the potential for spontaneous water sorption. This trend can be noticed at Figure 9.

Temperature affects ΔG, increasing its values at higher temperatures (Figure 9). This trend is related to the higher level of excitation of molecules comprising the product, accelerating gas exchange, increasing the rate and degree of spontaneity of water sorption.

To validate the theory of enthalpy-entropy compensation, the isokinetic temperature should be compared with the harmonic mean (Thm) of the temperature range used to determine the sorption isotherms. The calculated Thmwas 292.82 K. The results (Table 4) indicate thatthe enthalpy-entropy compensation theory may be applied because TB ≠ Thm, except for the ML roasted and finely ground conilon coffee sample.

The enthalpy-entropy compensation theory is, most likely, not valid for this sample because the ΔS values recorded for this sample (Figure 8A) were close to zero.According to Table 4, the water sorption mechanism of roasted conilоncoffee may be controlled by either the enthalpy or entropy, with a greater number of samples controlled by entropy (5) than enthalpy (2).

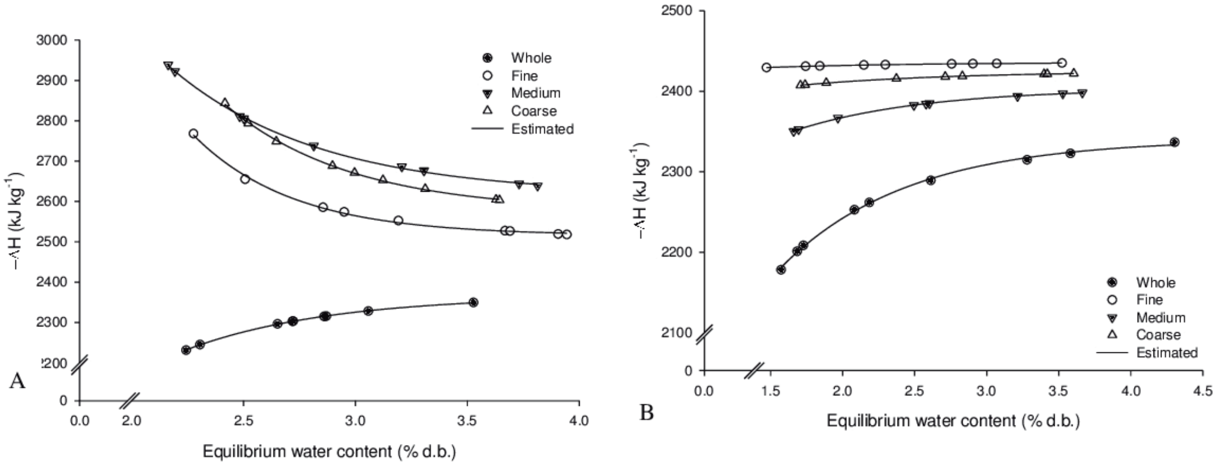

FIGURE 7 - Observed and estimated values of differential enthalpy of adsorption(Δ*H*) of conilon coffee roasted at medium light (A) and moderately dark (B), in different particle sizes.

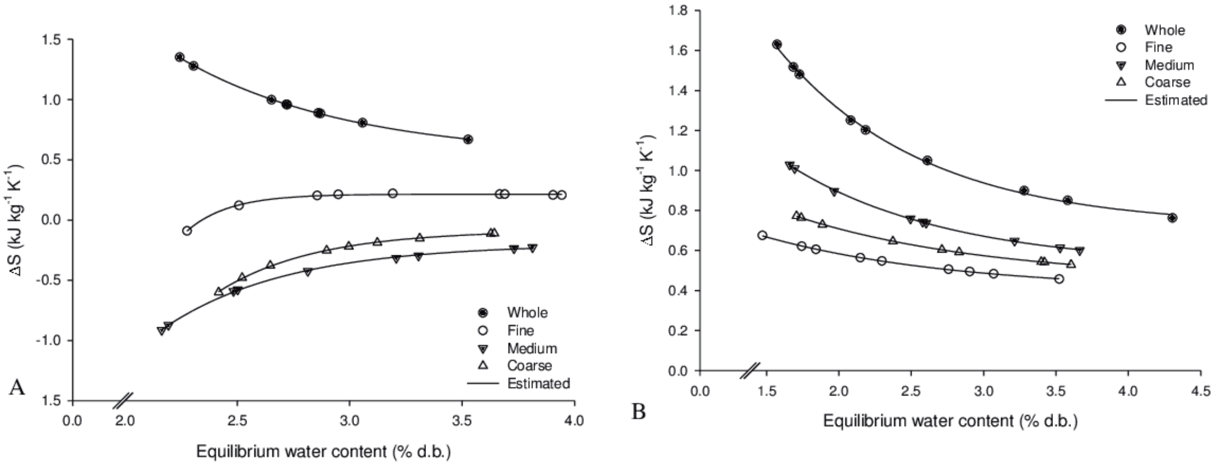

FIGURE 8 - Observed and estimated values of differential entropy of adsorption(Δ*S*) of conilon coffee roasted at medium light (A) and moderately dark (B), in different particle sizes.

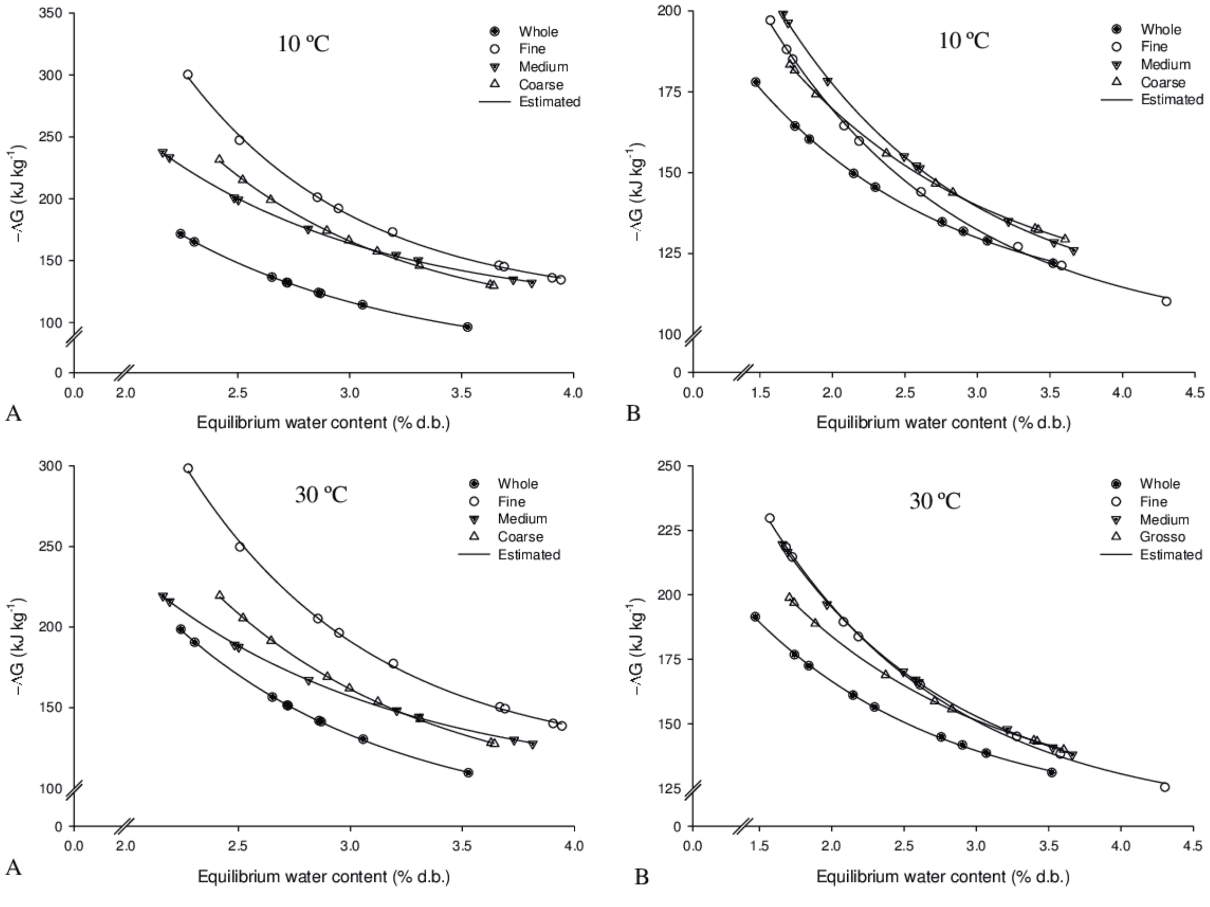

FIGURE 9 -Observed and estimated values of Gibbs free energy (Δ*G*) of conilon coffee roasted at medium light (A) and moderately dark (B), in different particle sizes, stored at 10 and 30 ºC

TABLE 4 -Isokinetic temperature (T_B) and Gibbs free energy at isokinetic temperature (ΔG_B) in order to evaluate the enthalpy-entropy compensation theory of Conilon coffee, in two roasting degrees (ML – medium light; MD – moderately dark) and in four particle sizes.

Part.Size	ML		MD	
	T_B (K)	ΔG_B (kJ kg^{-1})	T_B (K)	ΔG_B (kJ kg^{-1})
Whole 174.82 ± 13.95		-2469.36	25.82 ± 2.91	-2446.99
Fine	768.90 ± 516.31	-2710.43	183.15 ± 12.52	-2479.41
Medium	434.73 ± 41.46	-2547.20	112.58 ± 10.69	-2467.04
Coarse	490.92± 67.55	-2557.00	60.73 ± 4.81	-2454.45

4 CONCLUSIONS

Roasting coffee to moderately dark (MD) increased the hygroscopicity of these samples compared to coffee roasted to medium light (ML).

The Sigma-Copace model best describes the hygroscopic equilibrium, followed by Halsey model.

The equilibrium moisture content of roasted coniloncoffee decreases with an increase in temperature at a given value of a_w.

Differential enthalpy (ΔH)and differential entropy (ΔS) values altered with moisture content variation of coffee.

The enthalpy-entropy compensation theory may be satisfactorily applied to water sorption by coffee.

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