SORPTION ISOTHERMS AND ISOSTERIC HEAT OF PERICARP AND ENDOSPERM TISSUES OF ARABICA COFFEE FRUIT

Camila de A. Dias[1*], Ednilton T. de Andrade[1], Isabella A. Lemos[1], Flávio M. Borém[1], Ezequiel A. Barros[1]

[1*]Corresponding author. Universidade Federal de Lavras/ Lavras - MG, Brasil.
E-mail: camila.almeidadias@gmail.com | ORCID ID: https://orcid.org/0000-0001-8422-7867

ABSTRACT

The aim of this study was to evaluate and model the hygroscopic equilibrium and isosteric heat curves of pericarp and endosperm tissues of arabica (*Coffea arabica*) coffee fruit, in different temperature and relative humidity conditions. Sorption isotherms were drawn under temperatures from 20°C to 70°C and relative humidity ranging between 10% and 90% until the product reached the equilibrium water content with the environment. The experiment was set up in a 4 × 4 factorial scheme (four relative humidity of the drying air and three tissues of the coffee cherry pericarp + endosperm [1: exocarp + part of the mesocarp, 2: mesocarp, 3: endocarp, 4: endosperm]), in a completely randomized design, with three repetitions. The results were examined by analysis of variance and regression using the STATISTICA 5.0 statistical software. Among the analyzed models, the ones that best fit the experimental data were modified GAB, for exocarp + part of mesocarp and mesocarp, modified Henderson, for endocarp, and Sabbab for endosperm. It was observed that, for all treatments, the lower water contents required a higher amount of energy to reach the equilibrium water content, and the integral isosteric heat decreased with the increasing equilibrium water content.

INTRODUCTION

Coffee is an important source of income for the Brazilian economy, because the country has high estimates for each agricultural season, and the production technologies are improved daily. However, regarding drying technology or methodology, the country displays a deficit, making the drying stage the great bottleneck of the Brazilian coffee sector.

Although the technological development in the coffee postharvest area is well advanced, the behavior of each intrinsic coffee part during drying and how the interaction and interdependence occur are still unknown. The resistance imposed by the parts compounding the coffee fruit increases the drying time and, consequently, the energy expenditure.

The study of coffee fruit anatomy, as well as the chemical composition of each pericarp anatomic component and the endosperm, separately, can help to design new drying strategies, because it can promote a better understanding of the interdependent relationship of the components and their influence on the drying process.

Therefore, a correct drying operation requires knowledge of the relationships between the product and the surrounding air. In the case of coffee fruit, the phenomena observed are the water desorption and adsorption, because coffee fruits and beans are hygroscopic and can give water to or adsorb water from the environment (Corrêa et al., 2014).

The sorption isotherms describe the relationship between the equilibrium water content of a specific material and the relative humidity of the surrounding air at a set constant temperature (Simón et al., 2016). Water sorption isotherms are a very important tool, because they can be used to predict eventual changes that may affect the stability of agricultural products (Wani & Kumar, 2016). Each material seeks hygroscopic balance at different speeds under different temperature and relative humidity conditions (Rosentrater & Verbeek, 2017).

Several models had been utilized for representing sorption isotherms, and, although very well adapted to the obtained data, they typically have thermodynamic errors. However, the model development always comprises some simplification of the sorption process (Simón et al., 2015).

The energy required to remove the water associated with a hygroscopic material is always greater than the energy utilized to vaporize an equal amount of free water, under the same pressure and temperature conditions (Wang & Brennan, 1991). This additional energy, a consequence of the bonding forces between water and the surface of the adsorbing substance, is known as isosteric desorption heat in the drying processes, and it is a good parameter for the estimation of the minimum required heat to remove an amount of water from the product.

According to Mulet et al. (1999), the water content at which the isosteric heat of sorption is almost identical to the latent heat of vaporization of free water is generally considered as an indicator of the free water content in the product.

Considering this, the objective of this work was to evaluate the hygroscopic equilibrium curves and the isosteric heat of pericarp and endosperm tissues of arabica coffee, under different controlled air conditions.

MATERIAL AND METHODS

This work was developed at the Agricultural Product Processing Laboratory at the Engineering Department of the Federal University of Lavras (UFLA), Lavras, MG. The experiment used coffee cherry (*Coffea arabica* L. cv. Catuaí Vermelho) fruits, manually harvested in a crop located in Ingaí, MG. After harvesting, the fruits were separated in water, by density difference, removing the lower-specific-mass ones (dried, hollow, damaged by berry borer, and poorly ground).

The next step was the fruit processing to obtain the coffee parts: exocarp (skin + part of mesocarp), mesocarp (mucilage), endocarp (parchment), and endosperm (beans/seed), for performing the individual drying.

Coffee fruits were peeled manually to prevent eventual damages to the exocarp and, with this procedure, the exocarp + part of mesocarp portion was obtained. After the removal of the major part of the mesocarp (mucilage),

adhering to the exocarp, the exocarp was washed in running water and sieved to drain the surface water.

The mesocarp was obtained by processing the peeled beans in a centrifuge (Centriflux). No water was used during this step, to avoid any interference on the amount of obtained mesocarp. After this stage, mesocarp was filtered (plastic sieve), removing the solid impurities. The mesocarp was then placed in a petri dish dryer for proceeding with the drying process.

The endocarp was obtained by peeling the beans manually with tweezers. These beans had been previously peeled manually. However, the drying process was performed for the removed and intact endocarps only, the ones with no damage to their structure.

After removing the beans' endocarp, it was possible to obtain the endosperm. Thus, both endocarp and endosperm were placed in the dryer, in small polyester bags, for drying.

Weight determinations were made during drying, with 10-, 20-, 30-, 60-, and 120-min time intervals. The 10- and 20-min time intervals were used for exocarp + part of mesocarp, mesocarp, and endocarp, given that these tissues reached constant weight rapidly. Thus, after three consecutive weighings showing the same value, with 0. 01-g difference, drying was terminated.

The static-gravimetric method was used to obtain the hygroscopic equilibrium water content of each pericarp (exocarp, mesocarp, and endocarp) and endosperm (bean/seed) tissue, separately of the arabica coffee, with initial water contents of 0.1246 (exocarp + part of the mesocarp), 0.1983 (mesocarp), 0.0804 (endocarp), and 0.1109 (endosperm), on a dry basis (db).

The analysis of the sorption processes utilized different temperature and relative humidity conditions. Table 1 presents the saturated saline solutions used in this work, as well as the air relative humidity provided by each saline solution as a function of the temperature.

TABLE 1. Equilibrium relative humidity (%) of saturated saline solutions.

Temperature (°C)	Salts		Relative Humidity
	Lithium Chloride	LiCl	11.31 ± 0.31
	Potassium Acetate	CH_3COOK	23.11 ± 0.25
20	Magnesium Chloride	$MgCl_2$	33.07 ± 0.18
	Magnesium Nitrate	$Mg(NO_3)$	54.38 ± 0.23
	Potassium Chloride	KCl	85.11 ± 0.29
	Lithium Chloride	LiCl	11.31 ± 0.31
	Potassium Acetate	CH_3COOK	23.11 ± 0.25
30	Magnesium Chloride	$MgCl_2$	33.07 ± 0.18
	Magnesium Nitrate	$Mg(NO_3)$	54.38 ± 0.23
	Potassium Chloride	KCl	85.11 ± 0.29
	Lithium Chloride	LiCl	11.03 ± 0.23
55	Magnesium Chloride	$MgCl_2$	29.93 ± 0.16
	Sodium Bromide	NaBr	50.15 ± 0.65
	Potassium Chloride	KCl	80.70 ± 0.35
70	Lithium Chloride	LiCl	10.75 ± 0.33
	Potassium Chloride	KCl	79.49 ± 0.57

Samples were hermetically placed in a Gerbox plastic box of 50 mL approximately, under temperature and air relative humidity control. The pericarp and endosperm were wrapped in a permeable fabric (voile) to allow air to pass through the tissues, using three repetitions, as an average, for each treatment, with an initial weight of approximately 3 g.

The temperatures of the experiments were set by adjusting the biochemical oxygen demand chamber and the oven; the relative humidity was obtained from the solutions used. Temperatures experienced were 20°C,

30°C, 55°C, and 70°C, for approximately 168 h, until the results of three consecutive weight determinations presented the same value, with a difference of 0.01 g, at intervals of 10, 30, and 240 min and 24 h.

The mathematical models found in the literature, representative of agricultural product hygroscopicity and used in the product analysis, were randomly chosen, as a function of ambient air temperature and relative humidity evaluation. This was a way of verifying what best fit the empirical reality of the products to better represent their isotherms. The models used are in Table 2.

TABLE 2. Mathematical models used for representing the hygroscopic equilibrium.

Model	Equation	
Chung Pfost	$Ue = a - b*ln[-(T + c)*ln(RH)]$	(1)
Copace	$Ue = exp[\ a-(b*T) + (c*RH)]$	(2)
GAB modified	$Ue = \dfrac{ab(c/T)RH}{\{[1 - b\ RH][1 - b\ RH + b(c/T)RH\ ]\}}$	(3)
Halsey modified	$Ue = [exp(a - bT) /- ln(RH)]^{1/c}$	(4)
Henderson	$Ue = [ln(1 - RH\ ) /(- a*T_{abs})]^{1/b}$	(5)
Henderson modified	$Ue = \{ln(1 - RH\ ) /[- a*(T + b)]\}^{1/c}$	(6)
Oswin	$Ue = (a - b*T) /[(1- RH)/RH]^{1/c}$	(7)
Sabbab	$Ue = a\ (RH^{b} / T^{c})$	(8)
Sigma Copace	$Ue = exp\{a-(bT) + [c\ exp(RH)]\}$	(9)

In which:

Ue: Equilibrium water content of the product (db);

RH: Relative humidity of the air (decimal);

T: Temperature of ambient air (°C);

Tabs: Absolute temperature of ambient air (K),

a, b, c: Parameters depending on product nature.

The values of the liquid isosteric heat of desorption (q_{st}) for each equilibrium water content were calculated by [eq. (10)]. Values of water activity, temperature, and equilibrium water content were obtained from the desorption isotherms of coffee pericarp and endosperm tissues, utilizing the best fit to the observed data model.

$$ln(a_w) = -\left(\frac{q_{st}}{R}\right) \cdot \frac{1}{T} + c \qquad (10)$$

In which:

a_w: Water activity (decimal);

q_{st}: Liquid isosteric heat of sorption (kJkg^{-1});

R: Universal gas constant (8.314 kJ kmol^{-1} K^{-1}, equal to 0.4619 kJkg^{-1} K^{-1}) for the water vapor;

T: Absolute temperature (K),

c: Model coefficient.

Equation (11) was used for calculating the values of the integral isosteric heat of desorption (Q_{st}).

$$Q_{st} = q_{st} + L = a.\exp(-b.U_e^*) + L \qquad (11)$$

In which:

Q_{st}: Integral isosteric heat of sorption (kJkg^{-1});

L: Latent heat of free water vaporization (kJkg^{-1});

Ue: Equilibrium water content (db),

a,b: Model coefficients.

The latent heat of free water vaporization L ($kJkg^{-1}$), necessary for calculating Q_{st}, was obtained by the mean temperature T (°C) in the studied range by the following equation:

$$L = 2502.2 - 2.39.T \quad (12)$$

The adjustment of the mathematical models was made through nonlinear regression analyses, by the Gauss–Newton method, using the STATISTICA 5.0 software. The choice of the best model was a function of the following statistical parameters: estimate standard deviation (SE), relative mean error (P), and coefficient of determination (R^2). The standard deviation of the estimate and the relative mean error were calculated, respectively, by the following equations:

$$SE = \sqrt{\sum (Y - \hat{Y})^2 / GLR} \quad (13)$$

$$P = [(100/n) \sum |(Y - \hat{Y})| / Y] \quad (14)$$

In which:

SE: Standard deviation of the estimate (decimal, dimensionless);

Y: Experimentally observed value (dimensionless);

$\hat{Y}$: Model calculated value (dimensionless);

GLR: Model degrees of freedom ("No. of model parameters – 1");

P: Relative mean error (%),

n: Number of observed data.

RESULTS AND DISCUSSION

For modeling the sorption isotherms of the coffee parts (exocarp + part of mesocarp, mesocarp, endocarp, and endosperm), at 20°C, 30°C, 55°C, and 70°C temperatures, the final water contents were used, after reaching the hygroscopic equilibrium with the environment (Table 3).

TABLE 3. Final water content (Tf), dry basis, of coffee parts, after reaching hygroscopic equilibrium with relative humidity (RH%) and temperature (T°C).

Water content (db)	EXOCARP + PART OF MESOCARP							
	T (20)	RH	T (30)	RH	T (55)	RH	T (70)	RH
	0.3191	85.11	0.2995	83.62	0.2863	80.70	0.2509	79.49
	0.2295	54.38	0.2060	51.40	0.1734	50.15	0.0572	10.75
T_f	0.1654	33.07	0.1415	32.44	0.1172	29.93		
	0.1391	23.11	0.1337	21.61	0.0488	11.03		
	0.1027	11.31	0.0950	11.28				
	MESOCARP							
	0.4597	85.11	0.4220	83.62	0.3898	80.70	0.3361	79.49
	0.3771	54.38	0.3470	51.40	0.2708	50.15	0.0637	10.75
T_f	0.3303	33.07	0.2782	32.44	0.1998	29.93		
	0.2827	23.11	0.2354	21.61	0.0884	11.03		
	0.1917	11.31	0.1493	11.28				
	ENDOCARP							
	0.2290	85.11	0.1446	83.62	0.1271	80.70	0.1109	79.49
	0.2045	54.38	0.1357	51.40	0.1067	50.15	0.0782	10.75
T_f	0.1798	33.07	0.1198	32.44	0.0896	29.93		
	0.1718	23.11	0.1104	21.61	0.0692	11.03		
	0.1543	11.31	0.0990	11.28				
	ENDOSPERM							
	0.2387	85.11	0.2295	83.62	0.1906	80.70	0.1821	79.49
	0.1999	54.38	0.1844	51.40	0.1600	50.15	0.0966	10.75
T_f	0.1707	33.07	0.1555	32.44	0.1390	29.93		
	0.1579	23.11	0.1283	21.61	0.0966	11.03		
	0.1350	11.31	0.1122	11.28				

Table 4 shows the coefficient of determination (R^2), relative mean error (P), and standard deviation of the estimate (SE) values, for the different mathematical models, adjusted to the experimental data of sorption isotherms of coffee fruit parts, in different temperatures.

TABLE 4. Coefficient of determination (R², %), relative mean error (P, %) and standard deviation of the estimate (SE, decimal), for the analyzed models, in modeling the sorption isotherms of coffee fruit parts.

MODELS	STATISTICAL PARAMETERS		
	R^2	P	SE
EXOCARP + PART OF MESOCARP			
Chung Pfost	96.81	5.414	0.019
Copace	97.77	4.103	0.012
GAB modified	99.55	1.598	0.006
Halsey modified	98.43	1.760	0.007
Henderson	95.29	4.692	0.192
Henderson modified	86.72	9.261	0.289
Oswin	79.62	17.775	0.518
Sabbab	98.61	1.005	0.314
Sigma Copace	97.75	4.114	0.013
GAB	92.09	1.054	0.023
MESOCARP			
Chung Pfost	99.40	1.870	0.009
Copace	93.63	5.380	0.265
GAB modified	99.72	1.576	0.007
Halsey modified	96.74	5.136	0.025
Henderson	88.62	6.521	0.523
Henderson modified	92.33	2.129	0.106
Oswin	95.87	4.877	0.439
Sabbab	97.49	3.773	0.188
Sigma Copace	93.34	5.531	0.265
GAB	92.65	1.877	0.081
ENDOCARP			
Chung Pfost	90.25	6.321	0.241
Copace	91.33	3.346	0.324
GAB modified	77.82	9.649	0.249
Halsey modified	91.43	3.104	0.142
Henderson	52.43	17.071	0.625
Henderson modified	99.40	0.839	0.002
Oswin	86.08	5.199	0.295
Sabbab	95.91	1.434	0.345
Sigma Copace	91.33	3.229	0.324
GAB	78.30	2.743	0.005
ENDOSPERM			
Chung Pfost	97.93	3.251	0.870
Copace	97.89	2.527	0.682
GAB modified	96.68	4.334	0.395
Halsey modified	93.59	2.921	0.257
Henderson	94.07	1.624	0.181
Henderson modified	90.84	6.998	0.913
Oswin	78.73	7.778	0.977
Sabbab	99.04	0.217	0.006
Sigma Copace	97.88	2.535	0.185
GAB	93.89	1.146	0.002

The adjusted models exhibited satisfactory values of the coefficient of determination ($R^2 > 90\%$), except for the modified Henderson model (exocarp + part of the mesocarp), Oswin model (exocarp + part of the mesocarp, endocarp, and endosperm), Henderson (mesocarp and endocarp), modified GAB, and GAB (endocarp) models. All these models have a relative mean error of less than 10%, the only exception being the Henderson model for exocarp + part of mesocarp and for the endocarp. The standard deviation value was satisfactory for all models, considering that an SE close to zero is ideal (Mohapatra & Rao, 2005). These selection criteria were used for all pericarp and endosperm tissues, thus making it possible to select the model that best describes the studied process.

The best fit for exocarp + part of mesocarp was reached by the GAB-modified model. In the case of the mesocarp, the model best describing the sorption isotherms was the GAB-modified method. The Henderson-modified method offered the best fit of experimental data for the endocarp.

Observing the models used to describe the phenomenon for the endosperm, except for the Oswin model, all other models presented satisfactory adjustments for the coefficient of determination and, regardless of the model, all had relative mean errors of less than 10% and an average standard deviation close to zero, the best adjustments found for the Sabbab model.

There are still few works studying the hygroscopic equilibrium of each part of the fruit separately. Because each part of the coffee fruit has a different chemical composition and anatomy, when subjected to separate analyses, the behavior tends to be different. It is important to highlight that such chemical and anatomical differences have a direct influence on postharvest processes, mainly drying, because each tissue of the coffee pericarp and the endosperm offers different resistance to water outflow (Dias, 2017).

Table 5 shows the coefficients of the chosen mathematical model, based on statistical selection criteria, for modeling the sorption isotherms of coffee fruit parts.

TABLE 5. Coefficients of chosen mathematical model, based on statistical selection criteria, adjusted to the desorption isotherms of coffee fruit parts.

MODEL	COEFFICIENTS		
	EXOCARP + PART OF MESOCARP		
	a	b	c
GAB modified	0.165942	59.24550	380.7321
	MESOCARP		
GAB modified	0.412622	24.32445	580.3091
	ENDOCARP		
Henderson modified	6.919672	-18.3972	4.818797
	ENDOSPERM		
Sabbab	2.136378	0.332360	0.202718

Figures 1(A)–(D) show the sorption isotherms of coffee fruit parts, both based on experimental data and on estimated data from the mathematical models offering the best fit, as a function of water content (dry basis) and water activity (decimal).
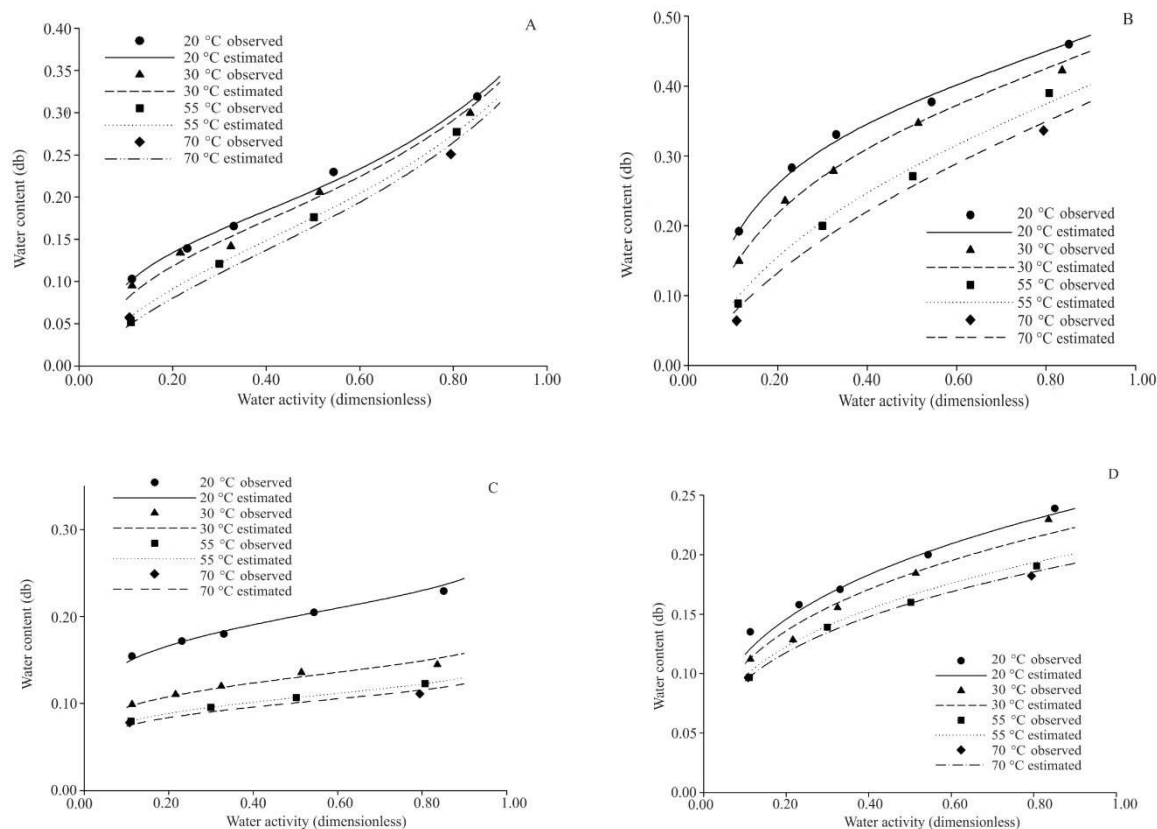
FIGURE 1. Estimated and observed sorption isotherms of exocarp + part of mesocarp (A), mesocarp (B), endocarp (C), and endosperm (D), at 20°C, 30°C, 55°C, and 70°C.

The figures show that the models fit the experimental data, in the range of water activity and equilibrium water content analyzed, at the four studied temperatures. Regardless of the coffee part, the temperature increase causes a decrease in the equilibrium water content. The equilibrium water content makes it possible to know the isosteric heat, which is essential in drying and storage studies of agricultural products, enabling one to estimate the energy needs of the drying process, as well as providing data on the water state in the product (Resende et al., 2006b).

An analysis of the sorption curve figures of coffee pericarp tissues and endosperm reveals that the equilibrium water content, in water activities of more than 0.50, increases more rapidly, resulting in a steeper sorption curve. According to Alves et al. (2015), this results from a weak water bond to food constituents in higher water contents, thus requiring energy close to that required for pure water vaporization. However, when the water activity decreases, the water in the product becomes increasingly bound.

For the same water activity, the equilibrium water content decreases as the temperature increases. According to Rizvi (2005) and Costa et al. (2015), at higher temperatures, the water molecules reach higher energy levels, and this enables them to break with their sorption sites, thus reducing the equilibrium water content. At constant temperatures, the water content increases with water activity values for the sorption isotherms of coffee pericarp tissues and endosperm.

The highest equilibrium water content was obtained by the mesocarp, followed by the exocarp + part of mesocarp, endocarp, and endosperm. This may be because the mesocarp's chemical composition has high levels of sugars, which result in higher water adsorption, unlike the endosperm, which has cellulose, lignin, and hemicellulose as the main chemical components.

The models that best represented the hygroscopicity phenomena were used for the determination of water activity values (a_w), in the analysis of isosteric sorption heat of coffee pericarp and endosperm tissues. From the calculation of $\ln(a_w)$ values, the curves of the natural logarithm of water activity of coffee pericarp and endosperm tissues were built as a function of inverse absolute temperature (1/T, K^{-1}). These curves are in Figures 2(A)–(D), for different equilibrium water contents (db), along with their respective linear equations.
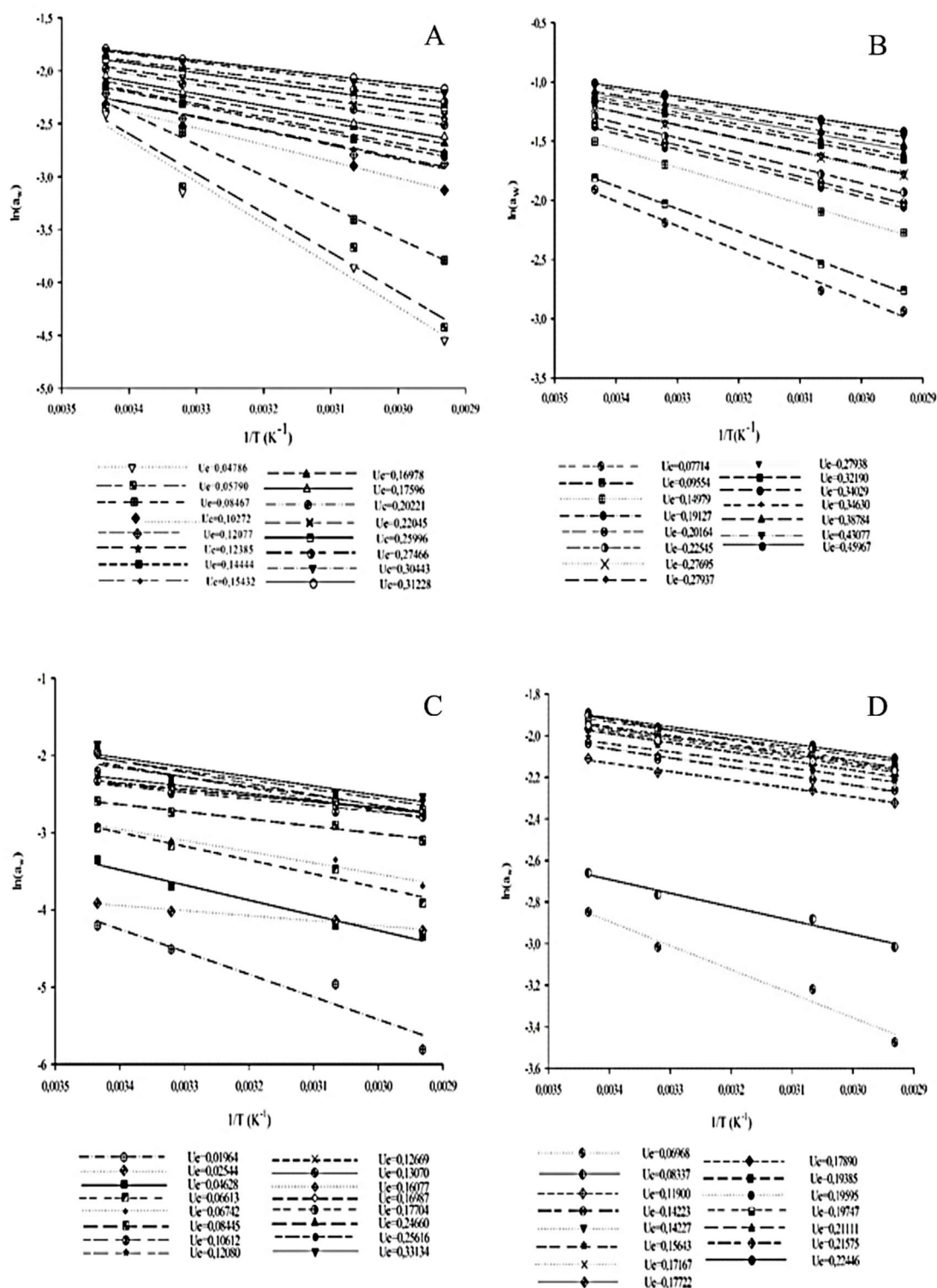
FIGURE 2. ln(a$_w$) values for different equilibrium water content (db), as a function of water activity (a$_w$) and temperature for exocarp + part of mesocarp (A), mesocarp (B), endocarp (C), and endosperm (D)

Net sorption isosteric heat (q$_{st}$) values were calculated as a function of the angular coefficient. For the determination of the integral isosteric sorption heat (Q$_{st}$), in kJ kg^{-1}, represented by Equation (11), the value of free water vaporization latent heat (L), which represents the minimum amount of energy required to evaporate water,

was also considered. This calculation considered the average working temperature, which was 43.75°C, resulting in a latent vaporization heat value of 2397.638 kJ kg^{-1}. The values of the liquid and integral sorption isosteric heat obtained, respectively, from the angular coefficient and the latent heat of vaporization are shown in Table 6.

TABLE 6. Liquid and integral sorption isosteric heat values for different equilibrium water contents (db).

Equilibrium water content (db)	Line equation	Angular coefficient	Liquid isosteric heat (kJkg^{-1})	Integral isosteric heat (kJkg^{-1})
EXOCARP + PART OF MESOCARP				
0.048	y = 728.454x – 16.076	728.454	336.473	2734.110
0.058	y = 708.968x – 15.283	708.968	327.472	2725.110
0.085	y = 621.514x – 14.485	621.514	287.077	2684.715
0.103	y = 594.741x – 7.756	594.741	274.711	2672.348
0.121	y = 555.642x – 6.778	555.642	256.651	2654.289
0.124	y = 551.039x – 6.665	551.039	254.525	2652.162
0.144	y = 508.478x – 6.597	508.478	234.866	2632.504
0.154	y = 492.816x – 6.433	492.816	227.632	2625.269
0.170	y = 462.404x – 6.125	462.404	213.584	2611.222
0.176	y = 452.558x – 5.978	452.558	209.037	2606.674
0.202	y = 413.016x – 5.530	413.016	190.772	2588.410
0.220	y = 383.344x – 5.219	383.344	177.067	2574.704
0.260	y = 339.411x – 5.010	339.411	156.774	2554.411
0.275	y = 302.011x – 4.729	302.011	139.499	2537.136
0.304	y = 279.529x – 4.492	279.529	129.115	2526.752
0.318	y = 269.461x – 4.334	269.461	124.464	2522.102
MESOCARP				
0.077	y = 2723.309x – 9.067	2723.309	1257.896	3655.534
0.096	y = 2518.968x – 8.389	2518.968	1163.511	3561.149
0.150	y = 2007.843x – 6.789	2007.843	927.423	3325.060
0.191	y = 1680.859x – 5.994	1680.859	776.389	3174.026
0.202	y = 1619.221x – 5.939	1619.221	747.918	3145.556
0.225	y = 1463.022x – 5.690	1463.022	675.770	3073.407
0.277	y = 1173.056x – 5.104	1173.056	541.835	2939.472
0.279	y = 1171.420x – 5.036	1171.420	541.079	2938.717
0.279	y = 1161.985x – 5.094	1161.985	536.721	2934.358
0.322	y = 968.410x – 4.627	968.410	447.309	2844.946
0.340	y = 907.796x – 4.502	907.796	419.311	2816.949
0.346	y = 872.267x – 4.552	872.267	402.900	2800.538
0.370	y = 793.666x – 4.351	793.666	366.594	2764.232
0.388	y = 733.775x – 4.193	733.775	338.931	2736.568
0.431	y = 613.267x – 3.938	613.267	283.268	2680.906
0.460	y = 547.814x – 3.808	547.814	253.035	2650.673
ENDOCARP				
0.020	y = 1756.154x – 14.190	1756.154	811.168	3208.805
0.025	y = 1704.841x – 6.184	1704.841	787.466	3185.104
0.046	y = 1595.913x – 10.168	1595.913	737.152	3134.790
0.066	y = 1474.935x – 9.081	1474.935	681.272	3078.910
0.067	y = 1471.449x – 7.889	1471.449	679.662	3077.300
0.084	y = 1378.355x – 5.838	1378.355	636.662	3034.300
0.106	y = 1273.902x – 6.486	1273.902	588.415	2986.053
0.121	y = 1199.788x – 6.231	1199.788	554.182	2951.819
0.127	y = 1182.413x – 6.393	1182.413	546.157	2943.794

Table 6 (continued)

0.131	y = 1173.547x – 6.254	1173.547	542.061	2939.699
0.161	y = 1037.323x – 6.287	1037.323	479.139	2876.777
0.170	y = 1002.387x – 6.295	1002.387	463.003	2860.640
0.177	y = 965.902x – 6.265	965.902	446.150	2843.788
0.247	y = 757.026x – 6.179	757.026	349.670	2747.308
0.256	y = 715.328x – 6.193	715.328	330.410	2728.047
0.331	y = 544.122x – 6.143	544.122	251.330	2648.968
ENDOSPERM				
0.070	y = 3978.029x – 6.823	3978.029	1837.452	4235.089
0.083	y = 3391.492x – 4.931	3391.492	1566.530	3964.168
0.119	y = 2259.659x – 3.509	2259.659	1043.737	3441.374
0.142	y = 1733.469x – 3.558	1733.469	800.689	3198.327
0.142	y = 1731.469x – 3.542	1731.210	799.646	3197.283
0.156	y = 1463.049x – 3.364	1463.049	675.783	3073.420
0.172	y = 1235.249x – 3.532	1235.249	570.561	2968.199
0.177	y = 1151.249x – 3.489	1151.146	531.714	2929.352
0.179	y = 1131.734x – 3.479	1131.734	522.748	2920.385
0.185	y = 1039.920x – 3.428	1039.920	480.339	2877.977
0.194	y = 942.330x – 3.415	942.330	435.262	2832.900
0.196	y = 923.726x – 3.356	923.726	426.669	2824.306
0.197	y = 907.381x – 3.376	907.381	419.119	2816.757
0.211	y = 778.826x – 3.307	778.826	359.740	2757.377
0.216	y = 739.480x – 3.592	739.480	341.566	2739.203
0.224	y = 677.764x – 3.320	677.764	313.059	2710.697

From these data, and using the STATISTICA version 5.0 program, the following equations were obtained that calculate the integral isosteric heat of sorption to the exocarp + part of the mesocarp in [eq. (15)], mesocarp in [eq. (16)], endocarp in [eq. (17)], and endosperm in [eq. (18)], as a function of the equilibrium water content (db) and 43.75°C average temperature.

$$Q_{st} = 401.838 \, x \exp(-3.716 \, x \, U_e) + 2397.638 \quad (15)$$

$$Q_{st} = 1740.206 \, x \exp(-4.205 \, x \, U_e) + 2397.638 \quad (16)$$

$$Q_{st} = 872.795 \, x \exp(-3.737 \, x \, U_e) + 2397.638 \quad (17)$$

$$Q_{st} = 4099.111 \, x \exp(-11.516 \, x \, U_e) + 2397.638 \quad (18)$$

The values of estimated parameters and the coefficient of determination were, respectively, a = 401.838, b = 3.716, and R^2 = 0.9948 (exocarp + part of mesocarp). a = 1740.206, b = 4.205, and R^2 = 0.9962 (mesocarp), a = 872.795, b = 3.737, and R^2 = 0.9996 (endocarp), and a = 4099.111, b = 11.516, and R^2 = 0.9994 (endosperm). Therefore, Figures 3(A)–(D) present the observed sorption isosteric heat and the sorption isosteric heat estimated by Equations (15)–(18), both as a function of the equilibrium water content (Ue), db.
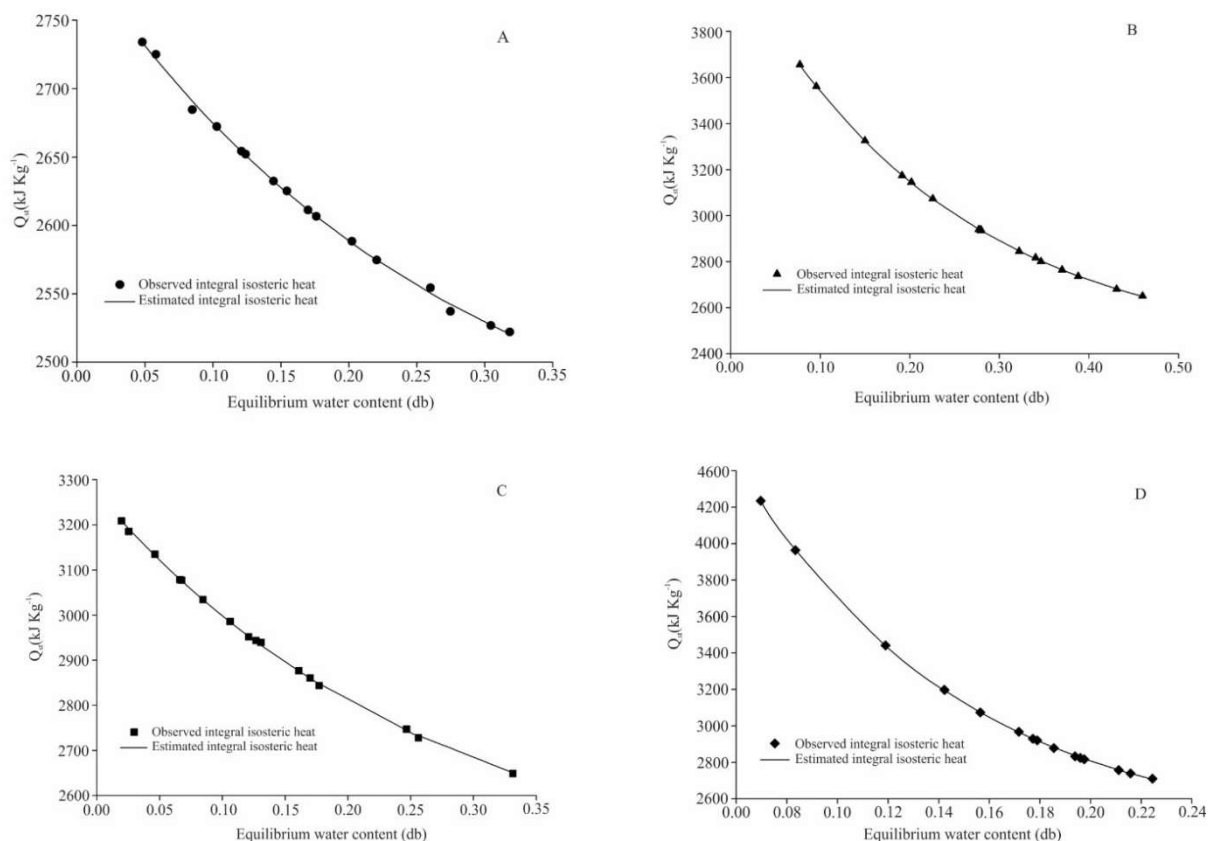
FIGURE 3. Integral isosteric sorption heat (Q_{st}) calculated values from angular coefficients and estimated values, as a function of equilibrium water content for exocarp + part of mesocarp (A), mesocarp (B), endocarp (C), and endosperm (D)

Regardless of pericarp tissue or coffee fruit endosperm, as the product water content decreases, more energy is required for water removal, as observed for various agricultural products, such as beans (Resende et al., 2006a), paddy rice (Resende et al., 2006b), wheat (Corrêa et al., 2005), pistachio nuts (Hayoglu & Gamli, 2007), chili peppers (Silva & Rodovalho, 2012), and sugarcane bagasse (Teixeira et al., 2015).

Integral isosteric heat values range from 2734 to 2522 kJkg^{-1} for the exocarp + part of mesocarp, in the equilibrium water content region between 0.04 and 032 (db), from 3655 to 2650 kJkg^{-1} for the mesocarp, in the equilibrium water content region between 0.07 and 0.45 (db), from 3208 to 2648 kJkg^{-1} for the endocarp, in the equilibrium water content region between 0.01 and 0.3 (db), and from 4235 to 2710 kJkg^{-1} for the endocarp, in the equilibrium water content region between 0.06 and 0.22 (db).

In the lowest range of water content, between 0.01 and 0.07 (db), the endosperm needs the highest amount of energy to adsorb water, compared with the other tissues of the arabica coffee pericarp. This is because the endosperm is mainly formed by cellulose and hemicellulose, which are water-insoluble compounds. Therefore, the amount of free water is smaller when compared with the pericarp tissues, and this gives the endosperm a barrier to product energy and mass exchange with air. The chemical composition of coffee endosperm is important in the drying process, because water exchange between the fruit and the environment depends on the predominance of one component or another, given the greater or lesser water affinity with each one of these compounds (Borém, 2013).

Polysaccharides in the coffee endosperm cell wall represent 50% of the coffee dry weight (15% cellulose, 25% to 30% arabinogalactan proteins, 50% mannan and galactomannan, and 5% pectin). Sucrose is the most abundant among the low-molecular-weight sugars (monosaccharides and disaccharides) and is found in concentrations up to 400 times the combined concentrations of other sugars. Lipids represent 12% to 18% of arabica coffee beans, and 75.2% of these lipids are triglycerides. Protein makes up 9.2% of the dry weight of arabica coffee beans (Borém et al., 2013).

The results obtained in this study make possible the development of drying technologies or methodologies that provide rapid dehydration without the use of high drying temperatures, especially in terms of reducing drying time.

CONCLUSIONS

The modified GAB model best described the sorption process for the exocarp + part of mesocarp and for the mesocarp; for the endocarp, the model that best describes the studied phenomenon was the modified Henderson model, and, for the endosperm, it was the Sabbab model.

Regardless of coffee pericarp or endosperm tissue, at the same temperature, increased water activity promoted increased equilibrium water content. For the same water activity, for all studied treatments, the temperature increase caused a lower equilibrium water content.

As the water content decreased, there was an increase in the energy required to remove water from the product for all pericarp tissues and the arabica coffee endosperm. Regardless of the treatment, increasing equilibrium water content resulted in integral isosteric heat decrease, and, because of the anatomical structure and chemical composition, the endosperm required the highest energy to reach the equilibrium water content.

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