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Hygroscopicity of 'sucupira-branca' (*Pterodon emarginatus* Vogel) fruits

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Key words:
equilibrium moisture content
isotherms
water activity
isosteric heat
Copace

A B S T R A C T

'Sucupira-branca' (*Pterodon emarginatus* Vogel) is a tree from 'Cerrado' and stands out mainly for its pharmacological properties; however, there are no technological information about its post-harvest operations. Thus, the aim of this study was to determine the sorption isotherms of 'sucupira-branca' fruits for different air conditions and obtain the values of desorption isosteric heat, depending on the equilibrium moisture content of the product. The equilibrium moisture content of 'sucupira-branca' fruits was determined by dynamic method for temperatures of 25, 30, 35 and 40 °C and water activities for each temperature between 0.270 and 0.775. The models Chung-Pfost, Copace, Modified Halsey, Oswin Modified and Sigma Copace obtained high coefficient of determination (R^2) and low chi-square (χ^2), relative mean error (P) and estimated mean error (SE), and the Copace model was selected to represent the desorption isotherms. The isosteric heat increases with the reduction of equilibrium moisture content and required more energy to remove water from the 'sucupira-branca' fruit.

Palavras-chave:
teor de água de equilíbrio
isotermas
atividade de água
calor isostérico
Copace

Higroscopicidade dos frutos de sucupira-branca (*Pterodon emarginatus* Vogel)

R E S U M O

A sucupira-branca (*Pterodon emarginatus* Vogel) é uma árvore do Cerrado e se destaca principalmente por suas propriedades farmacológicas; entretanto, inexistem informações tecnológicas sobre as operações de pós-colheita. Desta forma, objetivou-se, com este trabalho, determinar as isotermas de dessorção dos frutos de sucupira-branca para diferentes condições do ar, bem como obter os valores do calor isostérico de dessorção em função do teor de água de equilíbrio do produto. O teor de água de equilíbrio dos frutos de sucupira-branca foi determinado pelo método dinâmico para temperaturas de 25, 30, 35 e 40 °C e atividades de água para cada temperatura, entre 0,270 a 0,775. Os modelos Chung-Pfost, Copace, Halsey Modificado, Oswin Modificado e Sigma Copace obtiveram elevado coeficiente de determinação (R^2) e baixo Qui-quadrado (χ^2), erro médio relativo (P) e estimado (SE), sendo o modelo de Copace selecionado para representar as isotermas de dessorção. O calor isostérico aumenta com a redução do teor de água de equilíbrio, sendo relevante maior quantidade de energia para retirar a água dos frutos de sucupira-branca.

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Introduction

Pterodon emarginatus Vogel is a tree from the 'Cerrado' that belongs to the Fabaceae family, popularly known as 'sucupira-branca', 'fava-de-sucupira', 'sucupira' and 'sucupira lisa'. Its fruits are cryptosamaras, which have in their central structure an alveolus filled with bitter oil. These fruits occur in the states of Minas Gerais, São Paulo, Goiás and Mato Grosso do Sul (Lorenzi, 2008).

'Sucupira-branca' seeds are commercialized in popular markets, especially for its pharmacological properties. The Brazilian population uses extracts made from seeds as anti-rheumatic, anti-inflammatory, for spinal problems, as depurative and fortifier (Santos et al., 2010). However, there is no technological information on the post-harvest operations and their interactions with the qualitative aspects of the fruits for this species.

Important post-harvest steps include fruit drying and storage and, to correctly perform these operations, it is essential to know the relationships existing between the product and the surrounding air (Corrêa et al., 2015). The conservation of quality of the products depends on the environmental conditions of relative humidity and temperature under which they will be stored (Borges et al., 2009).

Agricultural products have the property of exchanging water in the form of vapor with the surrounding environment. These exchanges may occur through the gain or loss of water, phenomena respectively known as adsorption and desorption (Brooker et al., 1992).

Thus, this study aimed to determine sorption isotherms of 'sucupira-branca' fruits through the dynamic method for different psychrometric conditions of the air, and obtain the integral isosteric heat of desorption as a function of the equilibrium moisture content of the product.

Material and Methods

The present study was carried out at the Laboratory of Post-Harvest of Vegetal Products of the Federal Institute of Education, Science and Technology of Goiás - Campus of Rio Verde (IF Goiano - Campus Rio Verde), located in the municipality of Rio Verde-GO, Brazil.

The experiment was conducted using fruits of 'sucupira-branca' (*Pterodon emarginatus* Vogel) collected at the Bem Posta Farm, located in the municipality of Portelândia, Goiás, at 17° 15' S - 52° 40' W and altitude of 549 m, with initial water content of 10.6%, on dry basis (%, d.b.).

The desorption isotherms of 'sucupira-branca' fruits were obtained using the dynamic-gravimetric method. The desorption of the product in thin layer was performed for different controlled conditions of temperature (25, 30, 35 and 40 °C) and water activity between 0.27 and 0.775, until the product reached its moisture content in equilibrium with the specified air condition. In all, 13 conditions of temperature and water activity were used.

The environmental conditions for the hygroscopicity tests were provided by an atmosphere-conditioning chamber (Nova Ética, model 420 CLD). The samples, each one containing 10 g of product, were involved in a permeable fabric (voile) to allow the passage of air through the product and placed inside the device.

During the process, the samples were periodically weighed and the hygroscopic equilibrium was achieved when the weight remained virtually invariable during three consecutive weighings. After that, the water contents were determined in an oven at 105 ± 1 °C, during 24 h (Brasil, 2009).

The observed data of equilibrium moisture content were fitted to mathematical models frequently used to represent the hygroscopicity of agricultural products, whose expressions are presented to Eqs. 1 to 6:

- Chung Pfost

$$Xe^* = a - b \cdot \ln\left[-\left(T + c\right) \cdot \ln\left(a_w\right)\right] \quad (1)$$

- Copace

$$Xe^* = \exp\left[a - \left(b \cdot T\right) + \left(c \cdot a_w\right)\right] \quad (2)$$

- Modified Halsey

$$Xe^* = \left[\frac{\exp\left(a - b \cdot T\right)}{-\ln\left(a_w\right)}\right]^{\frac{1}{c}} \quad (3)$$

- Henderson

$$Xe^* = \left[\frac{\ln\left(1 - a_w\right)}{\left(-a \cdot T + 273.16\right)}\right]^{\frac{1}{c}} \quad (4)$$

- Modified Oswin

$$Xe^* = \frac{\left(a + bT\right)}{\left[a_w / \left(1 - a_w\right)\right]^{\frac{1}{c}}} \quad (5)$$

- Sigma Copace

$$Xe^* = \exp\left\{a - \left(b \cdot T\right) + \left[c \cdot \exp\left(a_w\right)\right]\right\} \quad (6)$$

where:

Xe^* - equilibrium moisture content, % d.b.;

a_w - water activity, decimal;

T - temperature, °C; and,

a, b, c - coefficients of the model.

For the fit of the mathematical models, nonlinear regression analysis was performed using the Gauss-Newton method. The degree of fit of each model was evaluated based on the significance of the regression coefficient by t-test, at 0.05 significance level, the magnitude of the determination coefficient (R^2), estimated mean error (SE), relative mean error (P) and chi-square test (χ^2), according to Sousa et al. (2016).

The values of net isosteric heat of sorption (or differential enthalpy), for each equilibrium moisture content, were obtained through the equation of Clausius-Clayperon (Iglesias & Chirife, 1976), as follows:

$$\frac{\partial \ln(a_w)}{\partial T} = \frac{\Delta h_{st}}{R T_a^2} \quad (7)$$

where:

T_a - absolute temperature, K;

Δh_{st} - net isosteric heat of sorption, kJ kg^{-1}; and,

R - universal gas constant, 8.314 J mol^{-1} K^{-1}.

The net isosteric heat of sorption, for each equilibrium moisture content, was obtained by integrating Eq. 7 and assuming that the net isosteric heat of sorption is independent of temperature.

$$\ln(a_w) = -\left(\frac{\Delta h_{st}}{R}\right) \cdot \frac{1}{T_a} + C \quad (8)$$

where:

C - coefficient of the model.

The values of water activity, temperature and equilibrium moisture content were obtained from the desorption isotherms of 'sucupira-branca' fruits using the model of best fit to the observed data. The integral isosteric heat of sorption was obtained by adding the value of latent heat of vaporization of free water to the values of net isosteric heat of sorption, according to Eq. 9:

$$Q_{st} = \Delta h_{st} + L = a \cdot \exp\left(-b \cdot Xe^{*}\right) + c \quad (9)$$

where:

Q_{st} - integral isosteric heat of sorption, kJ kg^{-1};

a, b and c - coefficients of the model; and,

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

The latent heat of vaporization of free water (L), in kJ kg^{-1}, necessary to calculate Q_{st}, was obtained using the mean temperature (T_m) in the studied range, in °C, using Eq. 10.

$$L = 2502.2 - 2.39 \cdot T_m \quad (10)$$

Results and Discussion

Table 1 shows the mean values of hygroscopic equilibrium moisture contents of 'sucupira-branca' fruits obtained through desorption for the temperatures of 25, 30, 35 and 40 °C and water activity between 0.270 and 0.775 (decimal). In general, for a constant water activity, there was an increase in the equilibrium moisture content with the reduction in temperature. In addition, there was an increment in the equilibrium moisture content for a same temperature with the increase in water activity for the 'sucupira-branca' fruits.

Table 1. Mean values of equilibrium moisture content (%, d.b.) of 'sucupira-branca' (*Pterodon emarginatus* Vogel) fruits obtained through desorption, as a function of temperature (°C) and water activity (decimal)

Water activity (decimal)	Temperature (°C)			
	25	30	35	40
0.270	-	-	-	4.7
0.300	5.7	-	-	-
0.375	-	5.8	-	-
0.405	-	-	-	6.2
0.450	7.4	-	-	6.1
0.525	-	8.2	7.6	-
0.600	9.0	-	-	-
0.675	-	-	8.1	-
0.700	10.4	9.9	-	-
0.775	-	-	10.2	-

These results corroborate those obtained by Corrêa et al. (2015), who observed increase in the equilibrium moisture content of coffee (*Coffea canephora*) fruits as a function of water activity for a specific temperature, and its reduction with the increase of temperature for a certain water activity, in both desorption and adsorption. The reduction in the equilibrium moisture content with the increase in temperature can be justified based on the increase of the water vapor pressure in the air and on the surface of the product (Campos et al., 2009).

The parameters of the models fitted to the values of hygroscopic equilibrium moisture content for 'sucupira-branca' fruits, obtained through desorption by the dynamic method for different conditions of temperature and water activity, are presented in Table 2.

The models showed high values of determination coefficient, above 0.95, except the model of Henderson. Madamba et al. (1996) indicate that the use of the determination coefficient as the only criterion of evaluation to select nonlinear models is not a consistent parameter to recommend the model.

Mohapatra & Rao (2005) highlight that, for a satisfactory representation of the model, the relative mean error (P) should be lower than 10%. The relative mean error was lower than 10% for all tested models and, therefore, they can be used to represent the hygroscopicity of 'sucupira-branca' fruits.

Table 2. Coefficients of the models fitted to the hygroscopic equilibrium moisture contents for 'sucupira-branca' (*Pterodon emarginatus* Vogel) fruits with the determination coefficients (R^2), estimated mean errors (SE), relative mean errors (P, %) and chi-square test (χ^2)

Models	Coefficients			R^2	SE	P	χ^2
	a	B	c				
Chung-Pfost	18.558**	3.341**	10.217^{ns}	0.9565	0.43	4.29	0.184
Copace	1.666**	0.012**	1.376**	0.9637	0.39	3.52	0.153
Modified Halsey	5.273**	0.031**	2.373**	0.9519	0.45	4.70	0.203
Henderson	3.7x10^{-5}**	2.061**	-	0.9175	0.56	5.77	0.316
Modified Oswin	10.086**	-0.089**	3.144**	0.9626	0.40	3.74	0.158
Sigma Copace	1.067**	0.012**	0.784**	0.9533	0.44	4.59	0.197

**Significant at 0.01 by t-test. *Significant at 0.05 by t-test. ^{ns}Not significant by t-test

For the estimated mean error (SE) and chi-square (χ^2), the model of Henderson showed the highest values in comparison to the others and the model of Copace showed the lowest values. Regarding the chi-square test (χ^2), all analyzed models are within the confidence interval of 95%.

The model of Henderson, under the conditions of the present study, did not fit satisfactorily to the hygroscopic equilibrium moisture contents of 'sucupira-branca' fruits. On the other hand, the models Chung-Pfost, Copace, Modified Halsey, Modified Oswin and Sigma Copace adequately fitted to the hygroscopic equilibrium moisture contents of 'sucupira-branca' fruits. Therefore, among the analyzed models, Copace was selected for exhibiting the highest determination coefficient and lowest values of relative and estimated mean errors and chi-square test. In addition, all coefficients of the model were significant at 0.01 probability level by t-test.

Costa et al. (2015) also observed that the Copace model showed the best fit for seeds of 'boca boa' (*Buchenavia capitata* (Vahl) Eichler), for the temperatures of 10, 20, 30 and 40 °C and water activity between 0.333 and 0.669. Sousa et al. (2013) evaluated two method of determination of hygroscopic equilibrium moisture contents, dynamic and static, for seeds of forage radish (*Raphanus sativus* L.) and observed that the Copace model obtained the best fit for the dynamic method.

Figure 1 shows the observed values of equilibrium moisture contents of 'sucupira-branca' fruits, obtained through desorption and their isotherms estimated by the Copace model.

Temperature influences the hygroscopicity of 'sucupira-branca' fruits and this behavior has been observed for most agricultural products (Goneli et al., 2013; Corrêa et al., 2014; Silva et al., 2015; Barbosa et al., 2016; Sousa et al., 2016). To obtain the same water activity, the equilibrium moisture content decreases with the increment in temperature or, similarly, for a same equilibrium moisture content, the increase of temperature requires an increase in water activity (Figure 1), i.e., for a safe storage in environments with high temperatures and water activity, it is necessary to reduce the water content of the 'sucupira-branca' fruits.

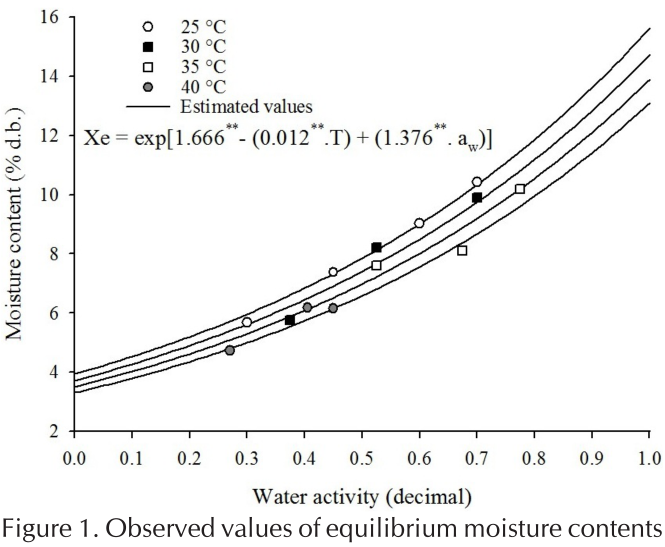


Figure 1. Observed values of equilibrium moisture contents and desorption isotherms estimated by the Copace model for 'sucupira-branca' (*Pterodon emarginatus* Vogel) fruits, under different conditions of temperature and water activity

The desorption isotherms of 'sucupira-branca' fruits estimated by the Copace model have an essentially exponential shape and, because of this, there was no inflection of the isotherm for the prediction of moisture contents when the water activity gets close to zero, thus leading to a limitation of this model in the estimate of equilibrium moisture contents. Corrêa et al. (2014), studying desorption and adsorption isotherms of coffee (*Coffea canephora*) fruits, observed the same limitation for the Sigma Copace model.

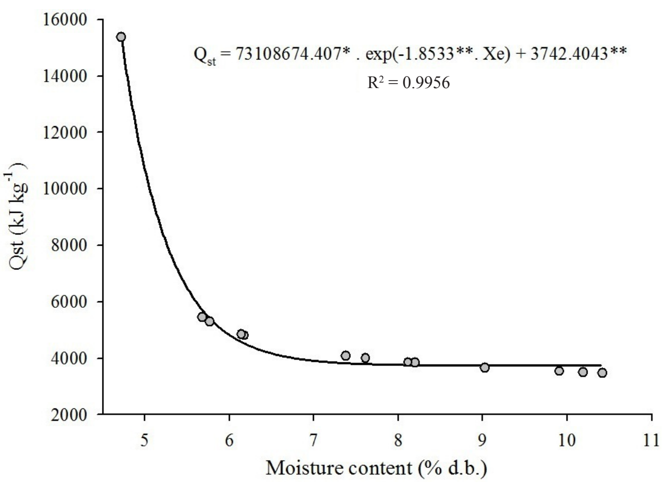
The desorption isotherms obtained for 'sucupira-branca' fruits are of type III. This behavior is related to the main constituents of the product, which in turn have low affinity for water molecules (Pena et al., 2010).

Microorganisms have a maximum limit of water activity to perform metabolic activities, which is around 0.7 for fungi, 0.9 for yeasts and 0.9 for bacteria (Oliveira et al., 2005). Thus, the moisture contents recommended for safe storage of 'sucupira-branca' fruits are at most 10.3, 9.7, 9.1 and 8.6 (%, d.b.), for the respective temperatures of 25, 30, 35 and 40 °C.

Figure 2 shows the values of integral isosteric heat of desorption (Q_{st}), as a function of the equilibrium moisture content (%, d.b.). It is noted that, with the reduction in moisture content, there is an increment in the energy necessary to remove water from the product.

The values of isosteric heat of 'sucupira-branca' fruits varied from 3,477.54 to 15,375.89 kJ kg^{-1} for the moisture contents of 10.4 to 4.7% (d.b.), respectively. Al-Muhtaseb et al. (2004) point out that the high values of integral isosteric heat for the lowest moisture contents are related to the binding forces of the water with the adsorbent surface of the product, i.e., the closer the water molecules are to the dry matter, the larger the amount of energy necessary for their removal. Thus, 'sucupira-branca' fruits should be stored with moisture contents close to the maximum recommended for each temperature, because the amount of energy necessary to reduce the moisture content is large. Caetano et al. (2012) and Barbosa et al. (2016) observed the same behavior for the seeds of 'caju-de-árvore-do-cerrado' and 'cajuzinho-do-cerrado', respectively.

The fitted exponential equation showed high determination coefficient and significance of the coefficients by t-test, and can



**Significant at 0.01 probability level by t-test. *Significant at 0.05 probability level by t-test

Figure 2. Integral isosteric heat of desorption for 'sucupira-branca' (*Pterodon emarginatus* Vogel) fruits

be used to determine the integral isosteric heat of 'sucupira-branca' fruits (Figure 2).

Conclusions

1. The equilibrium moisture content is directly proportional to the water activity and decreases with the increase in temperature, for a same value of water activity.

2. The models Chung-pfost, Copace, Modified Halsey, Modified Oswin and Sigma Copace fitted well to the observed data, while the Copace model was selected to represent the desorption isotherms of the fruits.

3. The isosteric heat increases with the reduction in the equilibrium moisture content, requiring a larger amount of energy to remove water from the 'sucupira-branca' fruits.

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