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## Isotherms and isostatic heat of foam-mat dried yellow mombin pulp

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### Key words:

water activity  
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*Spondias mombin* L.

### ABSTRACT

Yellow mombin has high nutritional value but is very perishable. Foam mat drying is a method that has been widely used to preserve liquid and semi-solid powdered foods. In this context, the aim of this study was to determine desorption isotherms and isosteric heat of yellow mombin (*Spondias mombin* L.) foam for different conditions of temperature and water activity. Powdered yellow mombin pulp was obtained by drying in forced-air oven regulated to 60 °C. The indirect static method was used to determine the isotherms and isosteric heat, whereas water activity (*a<sub>w</sub>*) was determined using the Hygropalm-HP23AW-A analyzer. A B.O.D. incubator, set at 10, 20, 30 and 40 °C, was used to control the temperature, and the water activity for each temperature was between 0.220 and 0.832. The experimental data were fitted to mathematical models frequently used to represent the hygroscopicity of agricultural products, and the best model was the Modified Halsey. Integral isosteric heat of desorption of yellow mombin powder, within the water content range of 17.22 to 57.58 (% d.b.), ranged from 3198.56 to 2598.38 kJ kg<sup>-1</sup>. It was concluded that the equilibrium water content of yellow mombin pulp powder increased with the increment in water activity; desorption isotherms obtained for yellow mombin pulp powder showed sigmoid form and, with the reduction of water content, the isosteric heat increases.

### Palavras-chave:

atividade de água  
calor isostérico  
higroscopicidade  
modelagem matemática  
*Spondias mombin* L.

## Isotermas e calor isostérico da polpa do cajá seca em leito de espuma

### RESUMO

O cajá possui alto valor nutricional, porém é muito perecível. A secagem em leito de espuma é um método que tem sido muito utilizado para conservação de alimentos líquidos e semissólidos em pó. Nesse contexto, o intuito do trabalho foi determinar as isotermas de desorção e calor isostérico da espuma do cajazinho (*Spondias mombin* L.) para diferentes condições de temperatura e atividade de água. A polpa de cajá em pó foi obtida através do processo de secagem em estufa com ventilação forçada regulada para 60 °C. Utilizou-se o método estático indireto para determinação das isotermas e calor isostérico, sendo a atividade de água (*a<sub>w</sub>*) determinada por meio do equipamento Hygropalm Model Aw. Para controle da temperatura utilizou-se de uma incubadora B.O.D., regulada a 10, 20, 30 e 40 °C e a atividade de água para cada temperatura foi entre 0,220 a 0,832. Os dados experimentais foram ajustados a modelos matemáticos frequentemente utilizados para representação da higroscopicidade de produtos agrícolas, sendo o melhor modelo o de Halsey Modificado. O calor isostérico integral de desorção do pó de cajá, na faixa de teor de água 17,22 a 57,58 (% b.s), variaram de 3198,56 a 2598,38 kJ kg<sup>-1</sup>. Conclui-se que o teor de água de equilíbrio do pó da polpa de cajá cresce em função do aumento da atividade de água; as isotermas de desorção obtidas para polpa de cajá em pó apresentaram forma sigmóide e com a redução do teor de água ocorre aumento do calor isostérico.



## INTRODUCTION

Yellow mombin has sensory characteristics appreciated for fresh consumption and processed as ice creams, jellies and candies, thus adding economic and social importance. According to Mattietto et al. (2011), the post-harvest life is approximately three days, which hinders the distribution to markets in all regions of Brazil.

Foam mat drying consists in transforming liquid or semi-liquid foods into powder. The air exposure area in the foam layer promotes easier water removal, reducing the drying time. According to Rajkumar et al. (2007), this procedure is recommended for foods sensitive to heat, viscous and with high sugar content.

Compared with other types of drying, foam mat drying stands out for its quickness, low operational cost and for obtaining higher levels of nutritional and sensory conservation. The method of foam mat drying with different humidity conditions has been used to demonstrate the hygroscopic behavior that proves the optimal humidity value for storage conditions with microbiological and sensory safety (Baptestini et al., 2015). Isothermic heat contributes to estimating physical changes that occur on food surface and its microstructure, evaluating the energy required to remove the amount of water from the food (Costa et al., 2013).

Mathematical models allow to determine the relationship between water content and relative humidity, which are expressed by hygroscopic equilibrium curves and/or isotherms. Sorption isotherms are essential to define limits of dehydration, estimate changes in the moisture of the product when stored at certain temperature and relative humidity in the environment (Chaves et al., 2015).

Given this assumption, this study aimed to determine desorption isotherms and isosteric heat of yellow mombin (*Spondias mombin* L.), for different conditions of temperature and water activity.

## MATERIAL AND METHODS

Yellow mombin fruits were collected in January-February 2017 in the region of Montes Claros de Goiás, Goiás, Brazil (16° 06' 20" S; 51° 17' 11" W), placed in polyethylene bags (30 x 40 cm), stored in thermal boxes and taken to the Laboratory of Fruits and Vegetables of the Federal Institute of Goiás (IF Goiano) - Campus of Rio Verde.

At the laboratory, the fruits were selected according to size, absence of mechanical injuries and maturity stage, immediately sanitized in 150-ppm chlorinated water for 15 min and dried using paper towel. The selection aimed to homogenize the sample, which was subsequently pulped in a Tortugan® electric pulper. The pulp was packed in polyethylene plastic bags (25 x 35 cm) and stored in a freezer at -18 °C until the analyses.

Foam was formed using Emustab®, purchased at the local market, with proportion of 5% in mass. 300 g of yellow mombin pulp was added and subjected to agitation for 20 min in a food mixer. The emulsion, prepared in triplicate (pulp + Emustab®), was placed on aluminum trays to obtain different water contents, and subjected to drying in a forced-air oven,

regulated to 60 °C, until reaching water content between 16.96 and 57.43 (% d.b.).

Water activity ( $A_w$ ) was determined in triplicate for each water content using the Hygropalm HP23-AW-A analyser at temperatures of 10, 20, 30 and 40 °C, in a B.O.D chamber at the Laboratory of Post-Harvest of Plant Products of the IF Goiano - Campus of Rio Verde, until the samples came into equilibrium with the environment. Water content was determined by the oven method at  $105 \pm 3$  °C, for 24 h, until constant weight (Brasil, 2009), using subsamples in triplicate.

The experimental data of equilibrium water content were fitted to mathematical models frequently used to predict the hygroscopicity of plant products, as shown in Eqs. 1 to 9:

- Chung-Pfost

$$X_e = a - b \cdot \ln[-(T + c) \cdot \ln(a_w)] \quad (1)$$

- Copace

$$X_e = \exp[a - (b \cdot T) + (c \cdot a_w)] \quad (2)$$

- Modified Halsey

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

- Sabbah

$$X_e = a \cdot \left( a_w^{b/T^c} \right) \quad (4)$$

- Sigma-Copace

$$X_e = \exp\left\{ a - (b \cdot T) + \left[ c \cdot \exp(a_w) \right] \right\} \quad (5)$$

- Modified Oswin

$$X_e = \frac{(a + b \cdot T)}{\left[ \frac{a_w}{1 - a_w} \right]^{\frac{1}{c}}} \quad (6)$$

- Cavalcanti-Mata

$$X_e = \left\{ \frac{\ln(1 - a_w)}{\left[ a \cdot (T^b) \right]} \right\}^{\frac{1}{c}} \quad (7)$$

- Modified Henderson

$$X_e = \left\{ \frac{\ln(1 - a_w)}{\left[ -a \cdot (T + b) \right]} \right\}^{\frac{1}{c}} \quad (8)$$

- Henderson

$$X_e = \left\{ \frac{\ln(1 - a_w)}{\left[ -a \cdot (T + 273.16) \right]} \right\}^{\frac{1}{b}} \quad (9)$$

To fit the mathematical models, a nonlinear regression analysis was carried out by the Gauss-Newton method using the computer program Statistica 7.0<sup>®</sup>.

The model that best represented the process was selected considering the significance of the regression coefficient by t-test at 0.05 probability level, magnitude of the coefficient of determination (R<sup>2</sup>), mean relative error (P), mean estimated error (SE) and chi-squared test (χ<sup>2</sup>), with 95% confidence interval (p < 0.05).

Mean relative error, mean estimated error and chi-squared test were calculated for each mathematical model using the following expressions, respectively:

$$P = \frac{100}{n} \sum \frac{|Y - \hat{Y}|}{Y} \tag{10}$$

$$SE = \sqrt{\frac{(Y - \hat{Y})^2}{DF}} \tag{11}$$

$$\chi^2 = \sum \frac{|Y - \hat{Y}|^2}{DF} \tag{12}$$

where:

- Y - experimental value;
- Ŷ - value estimated by the model;
- n - number of experimental observations; and,
- DF - degrees of freedom of the model (number of observations minus the number of parameters).

Net isosteric heat of sorption and each equilibrium water content were calculated using the Clausius-Clayperon equation (Iglesias & Chirife, 1976):

$$\frac{\partial \ln(a_w)}{\partial T} = \frac{\Delta h_{st}}{RT_a^2} \tag{13}$$

where:

- a<sub>w</sub> - water activity, decimal;
- T<sub>a</sub> - absolute temperature, K;
- Δh<sub>st</sub> - differential enthalpy, kJ kg<sup>-1</sup>; and,
- R - universal gas constant, 0.287 kJ kg<sup>-1</sup>K<sup>-1</sup>; for water vapor, equal to = 0.4619 kJ kg<sup>-1</sup> K<sup>-1</sup>.

Integrating Eq. 13 and assuming that the net isosteric heat of sorption does not depend on temperature, the net isosteric heat of sorption was obtained for each equilibrium water content according to Eq. 14 (Wang & Brennan, 1991):

$$\ln(a_w) = -\left(\frac{\Delta h_{st}}{R}\right) \cdot \frac{1}{T_a} + C \tag{14}$$

where:

- C - coefficient of the model.

The integral isosteric heat of desorption was obtained by adding the latent heat of vaporization of free water to the values of net isosteric heat of sorption, as shown in Eq. 15.

$$Q_{st} = \Delta h_{st} + L = a \cdot \exp(-b \cdot X_e) + L \tag{15}$$

where:

- Q<sub>st</sub> - integral isosteric heat of sorption, kJ kg<sup>-1</sup>;
- L - latent heat of vaporization of free water, kJ kg<sup>-1</sup>;
- X<sub>e</sub> - equilibrium water content, % d.b.; and,
- a, b - coefficients of the model.

The latent heat of vaporization of free water (L), in kJ kg<sup>-1</sup>, used to calculate Q<sub>st</sub>, was obtained using the mean temperature (T) within the studied range, in °C, according to the following equation:

$$L = 2502.2 - 2.39 \cdot T \tag{16}$$

where:

- L - latent heat of vaporization of free water, kJ kg<sup>-1</sup>.

## RESULTS AND DISCUSSION

The mean values of hygroscopic equilibrium water content of yellow mombin powder obtained by desorption at temperatures of 10, 20, 30 and 40 °C and water activity between 0.220 and 0.832 (decimal) are presented in Table 1.

At each water activity, the equilibrium water content increased as temperature decreased. Campos et al. (2009) explain that this results from the increase in water vapor pressure on the product's surface, which leads to reduction of equilibrium water content with the increment in temperature.

When temperatures are constant, there is an increment in water activity along with equilibrium water content. Similar results were obtained by Alexandre et al. (2007) in 'pitanga' (*Eugenia uniflora* L.) powder at temperatures of 10, 20, 30 and 40 °C.

The parameters of the models fitted to the desorption isotherms by the static method for different conditions of temperature and relative air humidity, as well as the coefficient of determination (R<sup>2</sup>), mean relative error (P),

Table 1. Mean values equilibrium water content (d.b.) of yellow mombin (*Spondias mombin* L.) pulp powder obtained by desorption, as a function of temperature (°C) and water activity (decimal)

Water activity (decimal)	Temperature (°C)			
	10	20	30	40
0.220	17.83	-	-	-
0.236	-	17.63	-	-
0.242	-	-	17.26	-
0.297	-	-	-	16.96
0.368	22.15	-	-	-
0.388	-	20.62	-	-
0.404	-	-	19.68	-
0.416	-	-	-	18.45
0.697	40.05	-	-	-
0.711	-	39.48	-	-
0.712	-	-	38.43	-
0.733	57.43	-	-	-
0.745	-	-	-	38.05
0.764	-	55.64	-	-
0.785	-	-	54.89	-
0.832	-	-	-	54.21

mean estimated error (SE) and chi-squared test ( $\chi^2$ ) of yellow mombin pulp powder are presented in Table 2.

The models Copace, Modified Halsey, Sigma-Copace and Modified Oswin showed parameters with statistical significance by t-test and the best coefficients of determination ( $R^2$ ) among the mathematical models analysed. These models exhibited the lowest values of mean relative error (P), whereas the models Chung-Pfost, Sabbah, Cavalcanti-Mata and Modified Henderson showed values above 10% for this parameter, indicating low representativeness of the phenomenon, as described by Oliveira et al. (2017).

Nevertheless, the best mathematical model to describe the hygroscopic equilibrium of yellow mombin powder was the Modified Halsey model, which showed highest coefficient of determination ( $R^2$ ), 0.9606, and lowest mean relative error (P), 7.20%. In addition, Draper & Smith (1998) claimed that the mean estimated error (SE) indicates the capacity to represent a certain physical process, which is inversely proportional, and this model obtained the lowest value, 3.40 % d.b. According to Phoungchandang et al. (2008), the Modified Halsey model is the best one to describe the accuracy of equilibrium isotherms in tropical plants, such as yellow mombin, and medicinal plants with high contents of volatiles.

The Modified Halsey model was also representative for Teixeira et al. (2012), Costa et al. (2013), Oliveira et al. (2014, 2017) and Goneli et al. (2016) in the hygroscopic equilibrium of fruits of baru, castor bean, pineapple peel, rice seed and crambe fruits, respectively.

The b value, which characterizes the interaction between vapor and solid, observed in the Modified Halsey model was

Table 2. Parameters of the mathematical models fitted to the hygroscopic equilibrium water contents of yellow mombin (*Spondias Mombin* L.) pulp powder, with the respective coefficients of determination ( $R^2$ , % d.b.), mean estimated error (SE, decimal), mean relative error (P, %) and chi-square ( $\chi^2$ , decimal)

Models	Parameters	SE (decimal)	$\chi^2$	$R^2$	P (%)	
Chung-Pfost	a	112.4718**				
	b	20.6822**	4.87	23.71	0.9192	13.03
	c	57.1920 <sup>ns</sup>				
Copace	a	2.3140**				
	b	0.0075*	4.23	17.88	0.9391	9.91
	c	2.3255**				
Modified Halsey	a	4.6013**				
	b	0.0145**	3.40	11.58	0.9606	7.20
	c	1.4223**				
Sabbah	a	97.5961**				
	b	1.1443**	5.58	31.15	0.8939	15.61
	c	0.1252 <sup>ns</sup>				
Sigma-Copace	a	1.2356**				
	b	0.0087**	3.64	13.25	0.9549	7.44
	c	1.3464**				
Modified Oswin	a	32.8218**				
	b	-0.2430**	3.84	14.72	0.9499	9.43
	c	1.8964**				
Cavalcanti-Mata	a	-0.0047 <sup>ns</sup>				
	b	0.2037*	4.64	21.56	0.9266	12.19
	c	1.3073**				
Modified Henderson	a	0.0009 <sup>ns</sup>				
	b	78.7377 <sup>ns</sup>	4.58	20.94	0.9287	12.21
	c	1.3025**				
	b	1.3269**				

\*\* Significant at 0.01 probability level; \* Significant at 0.05 probability level; <sup>ns</sup> Not significant by t-test

low, 0.0145, which indicates that the predominant attraction forces are of the van der Waals-type and, therefore, they can act at large distances from the surface, which contributes to a more effective hygroscopicity during the process (Halsey, 1948).

Figure 1 presents the experimental values of equilibrium water content of yellow mombin powder obtained by desorption, and the isotherms estimated by the Modified Halsey model. For the same water content, the temperature increases as water activity increases, indicating proportionality, as described for various agricultural products: baru fruits (Oliveira et al., 2017), coffee (Corrêa et al., 2014), pear seeds (Hassini et al., 2015), ‘umbu-cajá’ (Silva et al., 2015).

Water content and water activity of dehydrated yellow mombin cannot be equal to zero, because the water present in the monolayer of a food is difficult to be extracted, due to the bond with other food components, such as proteins, lipids and carbohydrates.

The desorption isotherms analysed for yellow mombin pulp powder exhibited a sigmoid form, type II, obtained for soluble products (IUPAC, 1985). This type of curve indicates that the water is poorly bound to the product and usually present in small capillaries. Type-II isotherms are characteristic of agricultural products, according to Oliveira et al. (2017).

Similar curves were tested by Paglarini et al. (2013) in mango (*Mangifera indica* L.) and by Alexandre et al. (2007) in ‘pitanga’ powder. According to Medeiros & Lannes (2010), this is the most common form of isotherms in foods. Sorption isotherms can be used to predict the drying time and changes of moisture that may occur when the product is mixed with others or packed, indicating the final stability of the food (Henao et al., 2009).

Figure 2 shows the values of integral isosteric heat of desorption (Qst) as a function of equilibrium water content (d.b.).

The integral isosteric heat of desorption of yellow mombin powder varied from 3198.56 to 2598.38 kJ kg<sup>-1</sup> within the water content range from 17.22 to 57.58 (% d.b.). Consistent

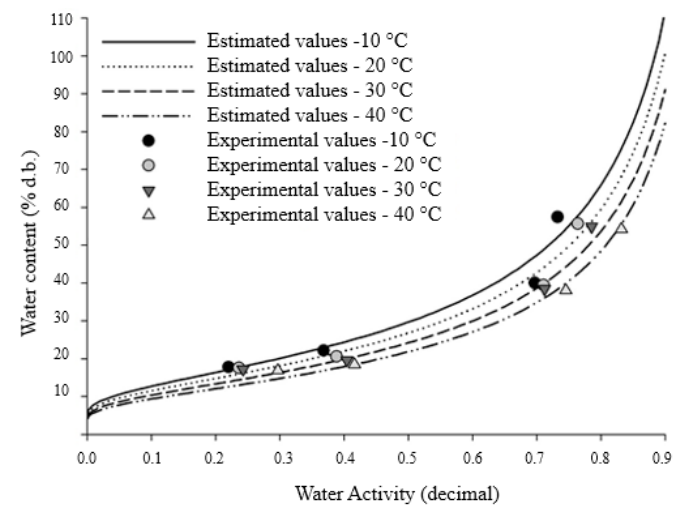


Figure 1. Experimental values of equilibrium water content and desorption isotherms estimated by the Modified Halsey model for yellow mombin (*Spondias mombin* L.) pulp powder, under different conditions of temperature and water activities

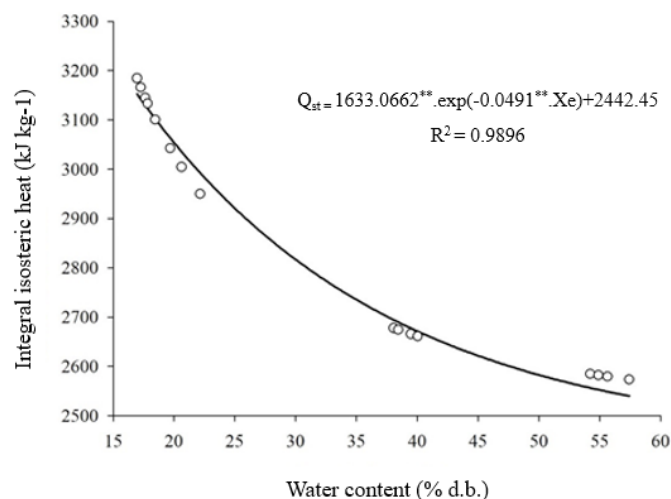


Figure 2. Experimental and estimated values of isosteric heat of desorption as a function of equilibrium water content of yellow mombin (*Spondias mombin* L.) pulp powder

values were found by Costa et al. (2015) in *B. capitata* seeds, varying from 2,667.93 to 2,819.56 kJ kg<sup>-1</sup>, with water content range from 13.31 to 7.21 (% d.b.). Caetano et al. (2012) found greater range for the isosteric heat of cashew seeds, 4,586.35 to 2,572.70 kJ kg<sup>-1</sup>.

According to the data, the  $Q_{st}$  decreased as water content increased, demonstrating that there is an increment in the energy required to remove water from the yellow mombin pulp powder, which had magnitudes of the isosteric heat. The reduction in water content leads to increment in the energy needed to remove water from the product, represented by the isosteric heat (Oliveira et al., 2017).

According to Resende et al. (2009), the difference in the values of isosteric heat of desorption can be explained because each product has specific characteristics. Despite the discrepant values, the isosteric heat estimates the energy required in the dehydration process and, therefore, is of great importance to estimate the variables needed for the dehydration of the products (Zhang et al., 1996).

Water activity described by mathematical models contributes to predicting phenomena and quality of yellow mombin pulp powder. In addition, studies on isotherms and isosteric heat for such drying helps understand industrial operations and develop methods that maintain the dehydrated pulp with microbiological and sensory quality.

## CONCLUSIONS

1. Equilibrium water content in yellow mombin pulp powder, at constant temperature, increases as water activity increases.
2. The Modified Halsey model was the most adequate to the data of desorption isotherms of yellow mombin pulp powder, at all temperatures evaluated.
3. Desorption isotherms obtained for yellow mombin pulp powder exhibit a sigmoid form.
4. As water content decreases, there is an increment in the isosteric heat.

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