Hygroscopicity of baru (Dipteryx alata Vogel) fruit

Daniel E. C. de Oliveira¹, Osvaldo Resende¹, Lilian M. Costa¹, Weder N. Ferreira Júnior¹ & Igor O. F. Silva¹

¹Instituto Federal Goiano/Diretoria de Pesquisa e Pós-Graduação/Campus Rio Verde. Rio Verde, GO. E-mail: oliveira.d.e.c@gmail.com (Corresponding author); osvresende@yahoo.com.br; lmctpg@yahoo.com.br; wedernunesiftm@gmail.com; igorolacirry95@gmail.com

Key words: equilibrium moisture content mathematical modeling desorption isotherms

ABSTRACT
With the knowledge on the hygroscopic equilibrium of the baru (Dipteryx alata Vogel) fruit, the product can be adequately handled to maintain the moisture content at the levels recommended for safe storage. Thus, this paper aimed to determine the water desorption isotherms of baru fruits at temperatures of 20, 25, 30 and 35 °C, and water activity between 0.14 and 0.80, and obtain the values of isosteric heat of desorption as a function of the equilibrium moisture content of the product. The equilibrium moisture content was obtained using the static-gravimetric method. Modified Halsey was the best model recommended to represent the hygroscopicity of baru fruits. The recommended moisture contents for safe storage of baru fruits are not more than 19.9, 19.3, 18.6 and 18.0 (%, d.b.) for the respective temperatures of 20, 25, 30 and 35 °C. The integral isosteric heat of desorption increases as the water content decreases, leading to an increment in the energy required to remove water from the product.

Higroscopicidade dos frutos de baru (Dipteryx alata Vogel)

Resumo
Com o conhecimento do equilíbrio higrosópico dos frutos de baru (Dipteryx alata Vogel), pode-se manusear adequadamente o produto visando à manutenção de seu teor de água nos níveis recomendados para o armazenamento seguro. Desta forma, objetivou-se determinar as isotermas de dessecação de água dos frutos de baru nas temperaturas de 20, 25, 30, 35 °C e atividades de água entre 0,14 e 0,80 e obter os valores do calor isostérico de dessecação em função do teor de água de equilíbrio do produto. Para obtenção do teor de água de equilíbrio foi utilizado o método estático-gravimétrico. O modelo de Halsey Modificado foi o melhor modelo recomendado para representar a higroscopicidade dos frutos de baru, cujos teores de água recomendados para o armazenamento seguro dos frutos de baru são de, no máximo, 19,9; 19,3; 18,6 e 18,0 (% b.s), para as respectivas temperaturas de 20, 25, 30 e 35 °C. O calor isostérico integral de dessecação aumenta com a redução do teor de água ocorrendo incremento da energia necessária para a remoção de água do produto.
Introduction

Baru (*Dipteryx alata* Vogel) is a plant typical of the Cerrado, containing one edible, elliptical, dark-brown seed, commonly called almond. This almond has great regional importance and has attracted scientific interest due to its nutritional composition, especially because of the levels of monounsaturated and saturated fatty acids (Bento et al., 2014).

Studies on the hygroscopicity of agricultural products aim to attenuate possible alterations in quality, since these products have the capacity to absorb and release water to the environment, tending to an equilibrium (Resende et al., 2006).

The study on the hygroscopicity of sorption is important to estimate changes in water contents under different conditions of the environment, as well as define the adequate water contents to avoid the beginning of the activity of microorganisms and the drying limits of the studied product (Ayranci & Duman, 2005).

Drying is indispensable to control and maintain the quality of vegetal products. The drying process reduces the water content and, consequently, water activity to levels that allow a safe storage. High contents of these two parameters can increase the number of microorganisms and, consequently, accelerate the deterioration. On the other hand, low values can lead to the excessive use of energy consumed during the drying and cause undesirable alterations in the product (Corrêa et al., 2010).

Thus, this study aimed to determine the water desorption isotherms of baru fruits at the temperatures of 20, 25, 30 and 35 °C, and water activity between 0.14 and 0.80, besides obtaining the values of isosteric heat of desorption as a function of the equilibrium moisture content of the product.

Material and Methods

The experiment 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, using baru fruits (*Dipteryx alata* Vogel) collected in the municipality of Santa Helena de Goiás, Goiás, Brazil (17° 48’ S; 50º 35’ W; 568 m), with water content of 43% (d.b.).

The fruits were manually cleaned, to remove the impurities and damaged fruits. The equilibrium moisture content was obtained using the static-gravimetric method, in three replicates for each condition of temperature and relative humidity. Each replicate used approximately 50 g of fruit involved in a permeable fabric (voile), to allow the passage of air through the product, and then placed in desiccators. Air temperature and relative humidity were monitored using a data logger (NOVUS), placed inside the desiccators.

The relative humidity in the desiccators was controlled using saturated solutions of different salts (Table 1). The desiccators were placed in BOD (Biochemical Oxygen Demand) incubating chambers (Marconi), regulated at the temperatures of 20, 25, 30 and 35 °C.

The samples were periodically weighed and the hygroscopic equilibrium of the fruits was achieved when the weight remained invariable for three consecutive readings. After reaching the hygroscopic equilibrium, the water content was determined in an oven at 105 ± 3 °C, during 24 h (Brasil, 2009).

The mathematical models frequently used to represent the hygroscopicity of vegetal products were fitted to the experimental data obtained at each temperature (Eqs. 1 to 12).

### Table 1. Values of relative humidity (%) established in the air inside the desiccators, obtained experimentally and used to determine the hygroscopic equilibrium

| Chemical compound | Relative humidity (%) |
|-------------------|-----------------------|
| LiCl | Lithium chloride | 15 ± 0.5 |
| CaCl<sub>2</sub> | Calcium chloride | 35 ± 2.0 |
| Ca(NO<sub>3</sub>)<sub>2</sub> | Calcium nitrate | 49 ± 3.0 |
| NaCl | Sodium chloride | 74 ± 0.5 |
| KBr | Potassium bromide | 80 ± 0.8 |

- Chung-Pfost
  \[ X_e = a - b \cdot \ln\left[-(T + c) \cdot \ln(a_w)\right] \]  

- Copace
  \[ X_e = \exp\left[a - (b \cdot T) + (c \cdot a_w)\right] \]  

- Oswin
  \[ X_e = \frac{a + b \cdot T}{\left[1 - a_w\right]/a_w} \]  

- GAB
  \[ X_e = \frac{a \cdot b \cdot c \cdot a_w}{(1 - c \cdot a_w) \cdot (1 - c \cdot a_w + b \cdot c \cdot a_w)} \]  

- Modified Halsey
  \[ X_e = \left[\exp(a - b \cdot T) - \ln(a_w)\right]^{1/3} \]  

- Henderson
  \[ X_e = \frac{\ln(1 - a_w)}{[-a \cdot (T + 273.16)]^{1/3}} \]  

- Sabbah
  \[ X_e = a \cdot \left(a_w^{b/c}\right) \]  

- Sigma Copace
  \[ X_e = \left[a - (b \cdot T) + [c \cdot \exp(a_w)]\right] \]  

- Modified Henderson
  \[ X_e = \left[\ln(1 - a_w)/[-a \cdot (T + b)]\right]^{1/2} \]
The values of water activity, temperature and equilibrium moisture content were obtained through desorption isotherms of ‘sucupira-branca’ fruits using the model of best fit to the observed data. The integral heat of sorption was obtained by adding the latent heat of vaporization of free water to the values of net isosteric heat of sorption, according to Eq. 15:

$$Q_a = \Delta h_a + L = a \cdot \exp (-b \cdot X_e) + c$$  \hspace{1cm} (15)

where:
- $Q_a$ - 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 $Q_a$, was obtained using the mean temperature ($T_{me}$) in the studied range, in °C, through Eq. 16.

$$L = 2502.2 - 2.39 \cdot T_{me}$$  \hspace{1cm} (16)

**Results and Discussion**

Table 2 shows the parameters of the hygroscopic equilibrium models for baru fruits obtained through desorption, for different conditions of temperature.

All parameters of the models Copace, Oswin, Modified Halsey, Henderson and Modified GAB were significant by t-test. The models Copace, Oswin, Modified Halsey, Sigma Copace and Modified GAB showed determination coefficient ($R^2$) higher than 99%, and the model Modified Halsey reached the highest value (99.46%).

As to the relative mean error (P), the models Copace and Modified Halsey showed the lowest values, while Chung-Pfost, Sabbah and BET exhibited values above 10%, which are not adequate to represent the phenomenon, according to Mohapatra & Rao (2005).

The Modified Halsey model showed the lowest value of estimated mean error (SE) and the capacity of a model to adequately represent certain physical process is inversely proportional to the value of this parameter (Draper & Smith, 1998).

Regarding the chi-square ($\chi^2$) test, all analyzed models are within the confidence interval of 95% and the models Modified Halsey, Oswin and Sigma Copace showed the lowest values. The lower the chi-square, the better the fit of the model to the experimental data (Günhan et al., 2005).

For a model to be considered as random, the distribution of residuals in the axis of the estimated values must be close to zero and these values should not form defined figures, which does not characterize bias in the residual values. If the analyzed model exhibits random distribution, it is considered as inadequate to represent the studied phenomenon (Goneli et al., 2010). Hence, the models Copace, Oswin, GAB, Modified Halsey and Sigma Copace showed random distribution of residuals, indicating adequate fit to the experimental data.

Therefore, among the evaluated models, Copace, Oswin, GAB, Modified Halsey and Sigma Copace can be recommended to represent the hygroscopicity of baru fruits. The Modified Halsey model showed higher determination coefficient, random distribution of residuals and lower values of relative mean error (P), which does not characterize bias in the residual values. If the analyzed model exhibits random distribution, it is considered as inadequate to represent the studied phenomenon (Goneli et al., 2010). Hence, the models Copace, Oswin, GAB, Modified Halsey and Sigma Copace showed random distribution of residuals, indicating adequate fit to the experimental data.
and estimated mean errors, as well as lower magnitude in the chi-square test. In addition, all parameters were significant at 0.01 probability level by t-test. Thus, this model was selected to predict the equilibrium moisture content of baru fruits.

Resende et al. (2006) studied the hygroscopicity of bean grains and observed that the Modified Halsey model showed the best fit to the experimental data. Caetano et al. (2012) and Costa et al. (2015) evaluated sorption isotherms of seeds of ‘caju-de-árvore-do-cerrado’ (Anacardium othonianum Rizz.) and ‘boca boa’ (Buchenavia capitata (Vahl) Eichler), species from the Cerrado, and observed that the models Chung-Pfost and Copace, respectively, showed the best fit to the experimental data.

Figure 1 shows the experimental values of equilibrium moisture content of baru fruits (Dipteryx alata Vogel), obtained through desorption, and their isotherms estimated by the Modified Halsey model. With the increase in temperature for a same water content, there was an increase in water activity and, for a constant water activity, the values of equilibrium moisture content decreased as temperature increased, following the same trend of most plants (Resende et al., 2006; Goneli et al., 2010; Caetano et al., 2012; Silva & Rodovalho, 2012; Corrêa et al., 2014; Hassini et al., 2015).

Table 2. Parameters of the models fitted to the hygroscopic equilibrium moisture contents of baru fruits (Dipteryx alata Vogel), with their respective determination coefficients ($R^2$, %), estimated mean errors (SE, decimal), relative mean errors (P, %), chi-square ($\chi^2$, decimal) and trend of distribution of residuals

| Models             | Parameters | $R^2$ (%) | P    | SE   | $\chi^2$ | Distribution of residuals |
|--------------------|------------|-----------|------|------|----------|--------------------------|
| Chung-Pfost        | a = 58.61948** | 0.9631    | 17.04| 1.875| 3.51     | Biased                  |
|                    | b = 10.71409** |           |      |      |          |                          |
|                    | c = 67.75428** |           |      |      |          |                          |
| Copace             | a = 1.313524** | 0.9890    | 4.32 | 1.022| 1.04     | Random                  |
|                    | b = 0.006959*  |           |      |      |          |                          |
|                    | c = 2.702833** |           |      |      |          |                          |
| Oswin              | a = 14.07099** | 0.9916    | 5.37 | 0.896| 0.80     | Random                  |
|                    | b = -0.08157** |           |      |      |          |                          |
|                    | c = -1.6688**  |           |      |      |          |                          |
| GAB                | a = 5.8226**   | 0.9910    | 6.41 | 0.926| 0.86     | Random                  |
|                    | b = 15.17599** |           |      |      |          |                          |
|                    | c = 0.99486**  |           |      |      |          |                          |
| Modified Halsey    | a = 2.870722** | 0.9946    | 4.44 | 0.720| 0.52     | Random                  |
|                    | b = 0.008399** |           |      |      |          |                          |
|                    | c = 1.248261** |           |      |      |          |                          |
| Henderson          | a = 0.00137**  | 0.9813    | 9.94 | 1.295| 1.68     | Biased                  |
|                    | b = 1.115249** |           |      |      |          |                          |
| Sabbah             | a = 65.89307** | 0.9654    | 15.26| 1.815| 3.30     | Biased                  |
|                    | b = 1.38607**  |           |      |      |          |                          |
|                    | c = 0.18912**  |           |      |      |          |                          |
| Sigma Copace       | a = 0.045796*  | 0.9912    | 6.05 | 0.917| 0.84     | Random                  |
|                    | b = 0.006838*  |           |      |      |          |                          |
|                    | c = 1.546895** |           |      |      |          |                          |
| Modified Henderson | a = 0.00032**  | 0.9829    | 9.86 | 1.279| 1.63     | Biased                  |
|                    | b = 99.51437** |           |      |      |          |                          |
|                    | c = 1.12358**  |           |      |      |          |                          |
| Cavalcanti Mata    | a = -0.020411* | 0.9828    | 9.89 | 1.281| 1.64     | Biased                  |
|                    | b = 0.206295** |           |      |      |          |                          |
|                    | c = 1.12346**  |           |      |      |          |                          |
| Modified GAB       | a = 6.1346**   | 0.9929    | 3.92 | 0.825| 0.68     | Biased                  |
|                    | b = 0.9815**   |           |      |      |          |                          |
|                    | c = 314.6193** |           |      |      |          |                          |
| BET                | a = -118.268** | 0.9825    | 11.69| 1.253| 1.57     | Biased                  |
|                    | b = 0.181**    |           |      |      |          |                          |

** Significant at 0.01 probability level by t-test; * Significant at 0.05 probability level by t-test; ns Not significant

Figure 1. Experimental values of equilibrium moisture content and desorption isotherms estimated by the Modified Halsey model for baru fruits (Dipteryx alata Vogel), under different conditions of temperature and water activity.
al. 2012), seeds of rice in husk (Oliveira et al., 2014) and seeds of pepper (Silva et al., 2015).

Considering that the development of fungi starts with water activity around 0.7 (Oliveira et al., 2005), the water contents recommended for safe storage of baru fruits are, at most, 19.9, 19.3, 18.6 and 18.0 (% d.b.), for the respective temperatures of 20, 25, 30 and 35 °C, and these values were estimated by the Modified Halsey model.

Figure 2 presents the integral isosteric heat of desorption as a function of the equilibrium moisture content (% d.b.) for baru fruits. The reduction of water content led to an increment in the energy necessary to remove water from the product, represented by the values of integral isosteric heat of desorption (Q_e), as observed by Caetano et al. (2012), studying seeds of 'caju-de-árvore-do-cerrado'.

The values of isosteric heat of baru fruits varied from 2,508.28 to 3,246.07 kJ kg⁻¹, for the respective water contents of 29.5 and 4.2% (d.b.). The necessity of higher expenditure of energy at lower water contents occurs because of the proximity between the water molecules of the monomolecular layer, and these layers are strongly linked to the molecules of dry matter, thus requiring large amounts of energy for removal (Al-Muhtaseb et al., 2012), seeds of rice in husk (Oliveira et al., 2014) and seeds of pepper (Silva et al., 2015).

In addition, according to Figure 2, the regression equation can be used to estimate the integral isosteric heat of desorption for baru fruits, because it has high determination coefficient (96.51%) and low relative mean error (1.41%).

![Figure 2. Experimental and estimated values of integral isosteric heat of desorption as a function of the equilibrium moisture contents for baru fruits (Dipteryx alata Vogel)](image)

**Conclusions**

1. Modified Halsey is the best model recommended to represent the hygroscopicity of baru fruits. The water contents recommended for safe storage of baru fruits are, at most, 19.9, 19.3, 18.6 and 18.0 (% d.b.), for the respective temperatures of 20, 25, 30 and 35 °C.

2. The integral isosteric heat of desorption increases as the water content decreases, leading to an increment in the energy necessary to remove water from the product.

**Literature Cited**

Al-Muhtaseb, A. H.; Mcminn, W. A. M.; Magee, T. R. A. Water sorption isotherms of starch powders. Part 2: Thermodynamic characteristics. Journal of Food Engineering, v.62, p.135-142, 2004. https://doi.org/10.1016/S0260-8774(03)00202-4

Anselmo, G. C. S.; Cavalcanti Mata, M. E. R. M.; Rodrigues, E. Comportamento higroscópico do extrato seco de urucum (Bixa orellana L.). Ciência e Agrotecnologia, v.32, p.1888-1892, 2008. https://doi.org/10.1590/S1413-70542008000600030

Ayranci, E.; Duman, O. Moisture sorption isotherms of cowpea (Vigna unguiculata L. Walp) and its protein isolate at 10, 20 and 30 °C. Journal of Food Engineering, v.70, p.83-91, 2005. https://doi.org/10.1016/j.foodeng.2004.08.044

Bento, A. P. N.; Cominetti, C.; Simões Filho, A.; Naves, M. M. V. Baru almond improves lipid profile in mildly hypercholesterolemic subjects: A randomized, controlled, crossover study. Nutrition, Metabolism & Cardiovascular Diseases, v.24, p.1330-1336, 2014. https://doi.org/10.1016/j.numecd.2014.07.002

Brasil. Ministério da Agricultura e Reforma Agrária. Secretaria Nacional de Defesa Agropecuária. Regras para análise de sementes. Brasília: MAPA/ACS, 2009. 399p.

Caetano, G. S.; Sousa, K. A.; Resende, O.; Sales, J. F.; Costa, L. M. Higroscopicidade de sementes de caju-de-arvore-do-cerrado. Pesquisa Agropecuária Tropical, v.42, p.437-445, 2012. https://doi.org/10.1590/S1983-40632012000600012

Corrêa, P. C.; Botelho, F. M.; Botelho, S. C. C.; Goneli, A. L. D. Isotermas de sorção de água de frutos de Coffea canephora. Revista Brasileira de Engenharia Agrícola e Ambiental, v.18, p.1047-1052, 2014. https://doi.org/10.1590/1807-1929/agriambi.v18n10p1047-1052

Corrêa, P. C.; Goneli, A. L. D.; Afonso [Junior, P. C.; Oliveira, G. H. H.; Valente, D. S. M. Moisture sorption isotherms and isosteric heat of sorption of coffee in different processing levels. International Journal of Food Science & Technology, v.45, p.2016-2022, 2010. https://doi.org/10.1111/j.1365-2621.2010.02373.x

Costa, L. M.; Resende, O.; Oliveira, D. E. C.; Sousa, K. A. Isotermas e calor isostérico de sementes de Buchenavia capitata (Vahl) Ehliert. Revista Ciência Agronômica, v.46, p.516-523, 2015. https://doi.org/10.5935/1806-6690.20150033

Draper, N. R.; Smith, H. Applied regression analysis. 3.ed. New York: John Wiley & Sons, 1998. 712p. https://doi.org/10.1002/9781118625590

Goneli, A. L. D.; Corrêa, P. C.; Oliveira, G. H. H.; Botelho, F. M. Water desorption and thermodynamic properties of okra seeds. Transactions of the ASAE, v.53, p.191-197, 2010. https://doi.org/10.13031/2031.29486

Günhan, T.; Demir, V.; Hancioglu, E.; Hepbaslı, A. Mathematical modelling of drying of bay leaves. Energy Conversion and Management, v.46, p.1667-1679, 2005. https://doi.org/10.1016/j.enconman.2004.10.001

Hassini, L.; Betaib, E.; Desmorieux, H.; Torres, S. S.; Touil, A. Desorption isotherms and thermodynamic properties of prickly pear seeds. Industrial Crops and Products, v.67, p.457-465, 2015. https://doi.org/10.1016/j.indcrop.2015.01.078

R. Bras. Eng. Agríc. Ambiental, v.21, n.4, p.279-284, 2017.
