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Full Length Research Paper

Drying kinetics of Baru almond (*Dipteryx alata Vog*) used for the production of biodiesel

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This study aimed to evaluate the drying kinetics of Baru (*Dipteryx alata Vog*), fit different mathematical models to the experimental values as a function of the water content, determine the diffusion coefficient and energy of Baru almonds during the drying process. Baru almonds were dried at 50, 60 and 70°C temperatures in a tray dryer until the water content reached 13% b.u. A non-linear regression analysis was performed to fit five mathematical models to the drying experimental data. The effective diffusion coefficient was obtained by fitting the mathematical model of the liquid diffusion. The diffusion coefficient variation, based on the drying temperature, was analyzed using the Arrhenius model, which made it possible to determine the activation energy. The drying process of the Baru was best represented by the two-term model. The diffusion coefficient showed values ranging from 18.15 × 10^{-11} to 27.62 × 10^{-11} m^2/s and 15.36 × 10^{-11} to 37.08 × 10^{-11} m^2/s. The ratio between the diffusion coefficient and the drying temperature may be described by the Arrhenius equation, with activation energy of 23.7 and 49.08 kJ/mol and velocities of 1.75 and 2.35 m/s, respectively.

Key words: Biotechnology, Fick's law, mathematical modeling.

INTRODUCTION

The Baru tree (*Dipteryx alata Vog*) belongs to the Leguminosae family and it is native to the Brazilian Cerrado (Queiroz and Firmino, 2014). A mature tree of this species produces about 150 kg of Baru fruit. It has only one seed per fruit, from which the endocarp, mesocarp and almonds can be used for several purposes (Cruz et al., 2011; Oliveira et al., 2011). The almond shelf life depends on the moisture content which directly influences the quality of the product during storage. The drying process is one of the conservation techniques applied to remove water from food.

Drying is a complex process involving heat phenomenon and mass transfer. It is often used in food processing industry (Costa et al., 2012; Martins et al., 2012). It is probably the main and most onerous step after harvest. The mathematical models and simulation of drying kinetic curves are applied in different ways. They are important for a better control of the unit operation and overall improvement of the quality of the final product.

The study and mathematical modeling of drying kinetic

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Table 1. Mathematical modeling.

Name	Modeling	Reference	Nº
Newton	$U_a = \exp(-kt)$	Westerman et al., 1973	(2)
Henderson and Pabis	$U_a = a.\exp(-kt)$	Sousa et. al., 2011	(3)
Two Term	$U_a = a.\exp(-kt) + bexp(-kt)$	Jittanit, 2011	(4)
Logarithmic	$U_a = a.\exp(-kt) + c$	Costa et. al., 2011	(5)
Page.	$U_a = \exp(-kt^n)$	Saccilik, 2007	(6)

U_a = moisture ratio (dimensionless); t = drying time (min); k, k_0, k_1 = drying constants (min^{-1}); a, *b* and *n* = model parameters.

have aroused the interest of many researchers in different types of grains and seeds, such as crambe seeds (Faria et al., 2012; Costa et al., 2011), beans (Sousa et al., 2011), peppermint and parsley leaves (Zaripour and Hamidi, 2011), seedless grapes (Çakmak and Yildizil, 2011), green beans and okra (Doymaz, 2011). Despite the great diversity of studies on almonds and grains, there are no available work on the effects of the drying temperature of Baru (*D. alata Vog*) almonds in the literature.

The models based on Fick's second law are not the exact representative of the different mechanisms used for the transportation of water in agricultural products, and the density varies as the drying conditions (temperature and air velocity) change. That is, it is not intrinsic to the material, and it is conventionally called effective diffusivity (Roca et al., 2008).

Energy values are usually used as indicators of influence of temperature on effective diffusivity. Kayacier and Singh (2004) reported that the activation energy of the product decreases with increase in the water content of the product. In the drying segments, the lower the activation energy, the higher is the diffusivity of water in the product. Costa et al. (2011) found activation energy of 37.07 kJ/mol for crambe seeds.

Thus, this study aimed to evaluate the drying kinetics of Baru almond (*D. alata Vog*), fit different mathematical models to the experimental values as a function of the water content, determine the diffusion coefficient and activation energy of the almonds, during drying at temperatures of 50, 60 and 70°C and velocities of 1.75 and 2.3 m/s.

MATERIALS AND METHODS

The experiment was conducted in the Laboratory for Separation of Biomolecules and Food Dehydration (LAPSDEA), of the Food Engineering Course, at the Federal University of Tocantins, Palmas, Brazil. The raw material was acquired in Palminha (Tocantins state, Brazil); then, it was transported and properly stored in the laboratory. The raw material was processed to obtain the baru almond used to perform the experiments.

A caliper was used to perform the axial measurements of the Baru almonds (length, width, and thickness). The baru almond moisture was determined by the gravimetric method, based on Instituto Adolfo Lutz (2008).

Drying curve

To determine the drying curve, a tray food dehydrator with air heating system and gas was used at 50, 60 and 70°C temperatures, and air flow velocities of 1.75 and 2.3 m/s. Each tray, initially with 2.4±0.04 g of Baru almond, was weighed and subjected to drying. The trays were weighed at 10-min intervals during the first fifty minutes (min); later, every 20 min for one hour and forty minutes, and every 30 min until constant weight was obtained. All dryings were done in triplicate.

Equation 1 was used to determine the moisture ratio of the baru almond, for the different drying conditions.

$$U_a = \frac{U - U_e}{U_i - U_e} \quad 1$$

Where, U_a = moisture ratio (dimensionany); U = mean water content at time t (% b.u.); Ue = equilibrium water content (% b.u.); and U_i = initial water content (% b.u.).

The mathematical models (Table 1) were fitted to the drying experimental data. An exponential non-linear regression analysis was used to fit the mathematical models, using the STATISTIC 7.0 software.

To evaluate the fitting of the models, we considered the significance of the regression coefficients, by t-test at 5% of significance level; the magnitude of the fitted determination coefficient (R^2), the relative error (P) and the estimated mean error (SE).

The effective diffusion coefficient was obtained by fitting the mathematical model of liquid diffusion, described by Equation 2, to the drying experimental data of the Baru almonds, which is an analytical solution to the equation of the Fick's second law. The product was considered as a spherical shape, disregarding the volumetric shrinkage of the Baru almonds and considering the condition of the boundary water content on the surface of the almonds.

$$U_a = \frac{U - U_e}{U_i - U_e} 6 \sum_{n=0}^{\infty} \frac{1}{n^2 \pi^2} exp\left[-n^2.\pi^2.\frac{D_{ef}.t}{r^2}\right] \quad 2$$

Where, D_{ef} = effective diffusion coefficient (m^2/s); r = Equivalent radius (m); and n = Number of terms.

The volume of each Baru almond (V), considered as a triaxial spheroid, was estimated using Equation 3 proposed by Mohsenin (1986).

$$V = \frac{\pi.a.b.c}{6} = \frac{4.\pi.r^3}{3} \quad 3$$

Where, V = volume of the almond (mm^3); *a* = almond larger axis (mm); *b* = almond mean axis (mm); and *c* = almond smaller axis (mm).

The radius of the equivalent sphere was calculated using Equation 4.

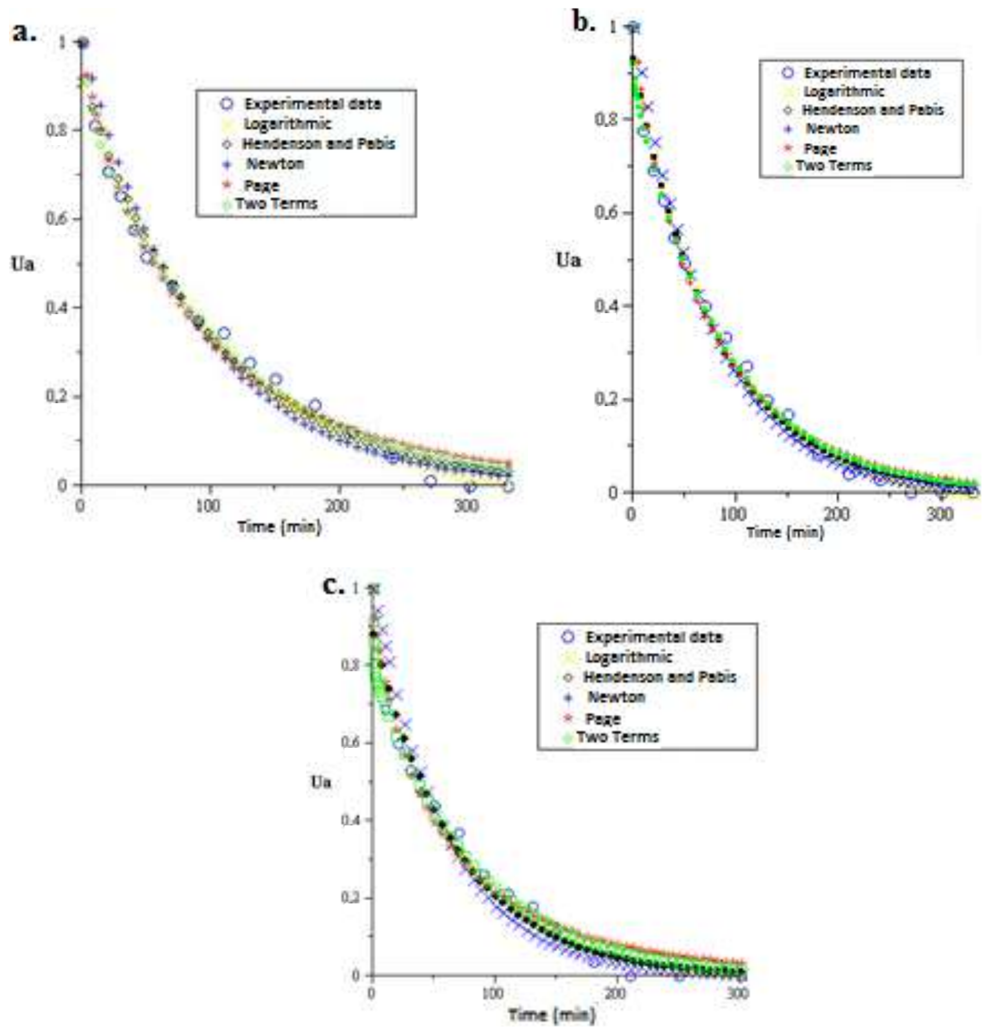

Figure 1. Experimental and mathematical model in the drying of 1.7 m/s: 50ºC (a), 60ºC (b) and 70°(c).

$$r = \frac{\sqrt[3]{a.b.c}}{2} \quad 4$$

The increased variation of the diffusion coefficient with the drying temperature was described by the Arrhenius model (Equation 5).

$$D = D_0.\exp\left(\frac{-E_a}{R.T_a}\right) \quad 5$$

Where, D_0 = pre-exponential factor, E_a = activation energy (kJ/mol), R = universal gas constant (8.134 kJ/mol) and T_a = absolute temperature (K).

RESULTS AND DISCUSSION

In the indication method of drying curves, the Baru almonds showed initial moisture of 31.7±0.04% b.s. The drying experimental values of the Baru almond, for the studied temperatures, are shown in Figure 1a to c, at a velocity of 1.7 m/s, and in Figure 2a to c, at a velocity of 2.3 m/s.

In all the studied temperatures, the moisture ratio for the drying curves of the Baru almonds rapidly decreased at the beginning and increased at the drying time. These results are in accordance with the theoretical data of the grain drying theory (Costa et al., 2011; Santos et al., 2013; Siqueira et al., 2012). Such results are in accordance with the results obtained by Iguaz et al. (2003); Calzetta et al. (2004); Sacilik (2007); Ruiz et al. (2008), Hii et al. (2009); Markowski et al. (2010), Gazor and Mohsenimanesh (2010) and Shen et al. (2011).

To reach constant weight, the Baru almond required 300, 270 and 210 min, at a velocity of 1.7 m/s; and 201, 120 and 110 min, at a velocity of 2.3 m/s. That is, with increased temperature, there was a higher removal of water from the product. In fact, it was observed for many agricultural products by several researchers (Doymaz, 2011; Promvonge et al., 2011).

The coefficients of determination (R^2), regarding the studied mathematical models showed the best values for

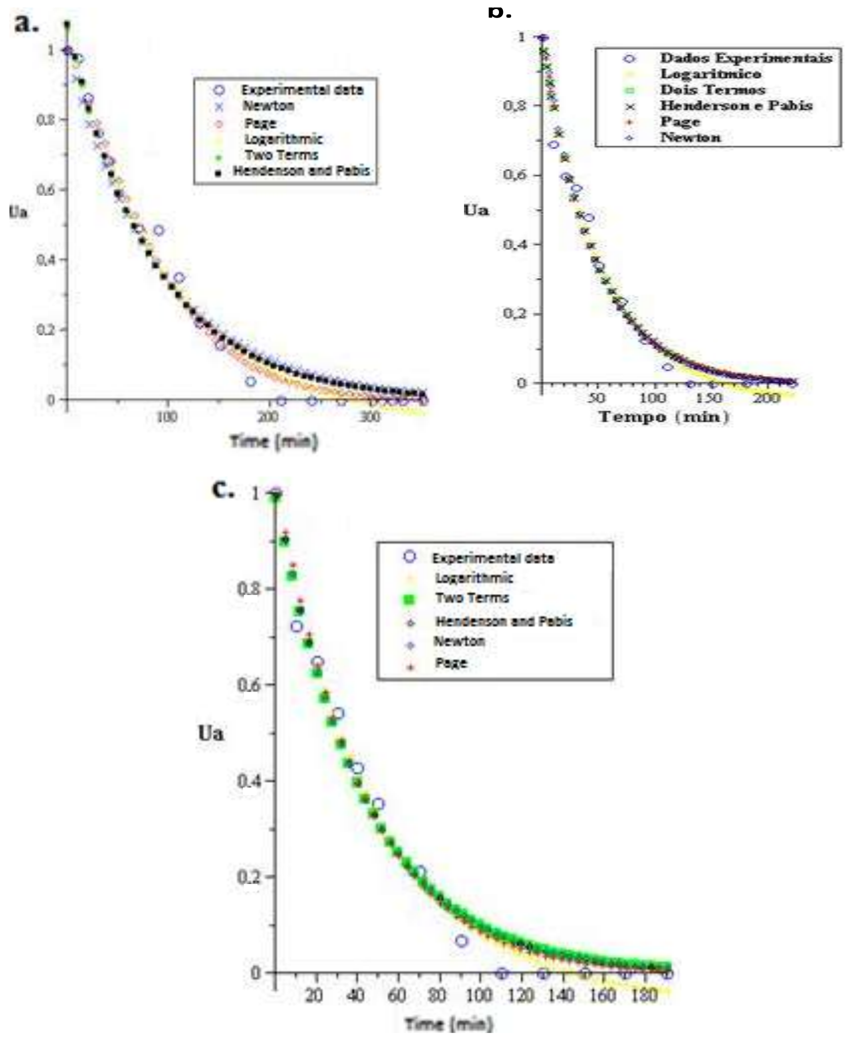

Figure 2. Experimental data and mathematical model in the drying of 2.3 m/s: 50ºC (a), 60ºC (b) and 70°C (c).

the statistical parameters at each studied temperature. The two-term model was the only one with values higher than 99%, at the three analyzed temperatures and velocity of 1.7 m/s. The logarithmic model showed values higher than 98%, at a velocity of 2.3 m/s, indicating according to Madamba et al. (1996), a satisfactory representation of the phenomenon under study. Regarding the estimated mean errors (SE), the two-term and logarithmic models showed lower values compared to the other models. The two-term and logarithmic models showed lower values of relative error (Table 2); and the logarithmic model showed lower relative values at the three studied temperatures (below 10%) (Table 2), which, according to Mohapatra and Rao (2005), indicated an adequate representation of the phenomenon.

The modeling aimed to fit a model or various models for the whole studied range of the variable in question: in this case, it is temperature. With this consideration and knowing that at the temperature of 70°C and velocity of 1.7 m/s, only the two-term model satisfies the relative error limit, which best represents the fitting of the Baru almond drying at all the analyzed temperatures. This model also obtained values of SE lower than 2% and values of R^2 higher than 99.51%. At the velocity of 2.3 m/s, only the logarithmic model showed the value of R^2 higher than 99.03, with SE lower than 3.4% and P equal to 7.1%, at 70°C.

The diffusion coefficient values at the different temperatures were obtained, using an equivalent radius of 0.00534 m (Table 3). The data were obtained by fitting Equation 2 to the experimental data of the Baru almond drying, with an approximation of eight terms. From this, it was observed that the D_{ef} value (which was constant K) denoted the eight terms.

There was an increase of the effective coefficient values with increased temperature. This result was

Table 2. Coefficients of determination (R^2%), estimated mean errors (SE%), and relative error (P%), of the Baru almond drying, for the studied temperatures and velocity of 1.75 m/s and 2.35 m/s.

Model	T°C	Coefficients					
		1.75 m/s	2.35 m/s	1.75 m/s	2.35 m/s	1.75 m/s	2.35 m/s
		R^2	R^2	P%	P%	SE%	SE%
Page	50	98.6927	98.2646	15.62	8.6	3.5	4.8
	60	99.0365	97.1250	14.32	11.39	3.1	5.7
	70	97.9183	97.7522	12.31	9.1	3.0	5.1
Newton	50	97.0906	96.6889	9.9	15.6	5.1	6.6
	60	98.1872	97.0432	9.6	9.11	4.2	5.7
	70	93.7996	97.6626	12.6	9.33	7.4	5.1
Henderson and Pabis	50	98.3380	97.3581	14.7	12.12	3.9	5.8
	60	98.9453	97.3207	16.5	10.7	3.2	5.4
	70	96.4469	97.6843	17.3	9.64	5.6	5.2
Two term	50	99.1897	97.3480	7.8	12.19	2.6	5.9
	60	99.5500	97.3208	7.1	10.6	2.1	5.5
	70	99.1068	97.6843	6.9	9.7	2.0	5.3
Logaríthmic	50	98.3772	99.0301	7.5	7.6	3.8	3.4
	60	99.0075	98.0414	7.3	7.4	3.1	4.7
	70	96.4538	99.0318	7.0	7.1	2.9	3.4

Table 3. Effective coefficient as a function of the temperature at a velocity of 1.75 and 2.35 m/s.

T (°C)	50°C	60ºC	70ºC
	D_{ef} (m^2/s)	D_{ef} (m^2/s)	D_{ef} (m^2/s)
1.75 m/s	18.15×10^{-11}	22.31×10^{-11}	27.62×10^{-11}
2.35 m/s	15.36×10^{-11}	28.85×10^{-11}	37.08×10^{-11}

expected because at higher temperatures, water removal is faster. The values obtained for the effective coefficient (D_{ef}) of the Baru almonds, are in the range of 18.15×10^{-11} to 37.08×10^{-11} m^2/s. The same was observed by Doymaz (2011), in this same array, 10^{-11}.

The effective coefficient values increased linearly, and their dependence on the drying air temperature was described by the Arrhenius equation (Figure 3).

The slope of the curve of the Arrhenius representation provides the ratio $E_a.R^{-1}$, whereas its intersection with the ordinate axis indicates the D_0 value. The coefficients of the Arrhenius expression fitted to the effective coefficient of the Baru almond are shown in Figure 3; 1.75 m/s velocity is presented in Equation 6, and 2.35 m/s velocity is shown in Equation 7.

$$D = 15.23\ exp\left(\frac{23.28}{R.T_a}\right) \quad 6$$

$$D = 7.35\ exp\left(\frac{49.08}{R.T_a}\right) \quad 7$$

As shown in Equations 6 and 7, the activation energy for the liquid diffusion in the Baru almond drying was 23.7 and 49.08 KJ/mol at 1.75 and 2.35 m/s velocities and temperature range of 50 to 70°C. These values correspond to those found for agricultural products, according to Zogzas et al. (1996), who highlighted that the activation energy for agricultural products ranges from 12.7 to 110 KJ/mol.

Conclusion

The drying of Baru almond in tray dryers is possible at the studied temperatures, and the drying time is inversely proportional to the expected temperature. The studied

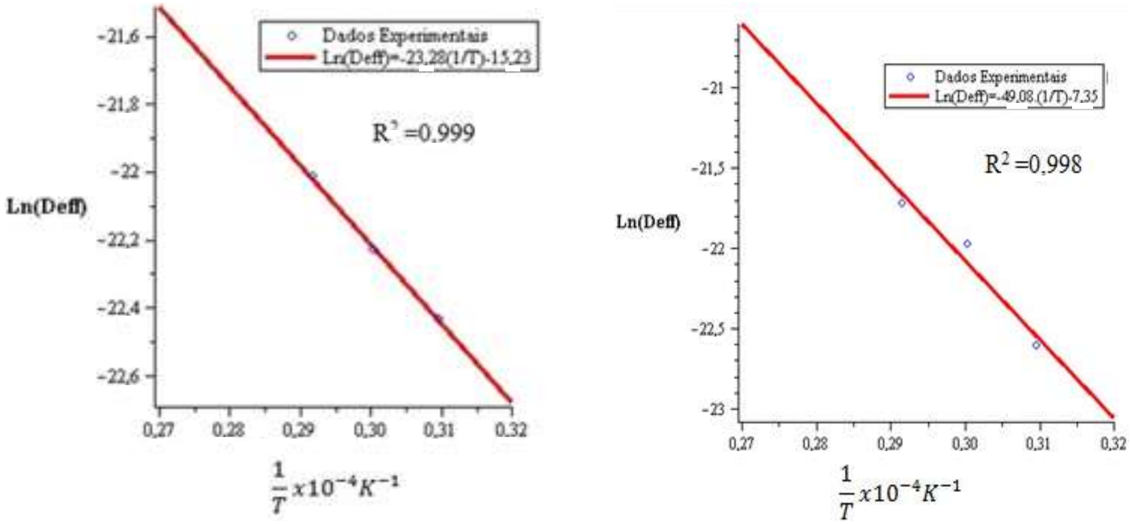

Figure 3. Arrhenius representation for the relation between the effective coefficient and the absolute temperature: Velocities 1.75 m/s (A) and velocities 2.35 m/s.

models fitted satisfactorily to the experimental data. However, the two-term model was the most suitable due to its higher coefficient of determination, lower estimated error and lower mean relative error values, at a temperature of 70°C and a velocity of 1.75 m/s. The effective diffusion coefficient increased with the air temperature, and therefore, the drying time decreased. It showed values ranging from 18.15×10^{-11} to 27.62×10^{-11} and 15.36×10^{-11} to 38.08×10^{-11} at a temperature range of 50 to 70°C and velocities of 1.75 and 1.35 m/s, respectively. The ratio between the diffusion coefficient and the drying temperature was described by the Arrhenius equation. For the activation energy, a value of 23.7 and 49.08 KJ/mol was found at velocities of 1.75 and 1.35 m/s, respectively for the liquid diffusion in the drying process of the Baru almonds. The information found in this study can be analyzed to obtain biodiesel and proteins to feed an energy industry.

Conflict of Interest

The authors have not declared any conflict of interests.

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