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Drying kinetics of 'gueroba' (*Syagrus oleracea*) fruit pulp[1]

Cinética de secagem da polpa dos frutos de gueroba (*Syagrus oleracea*)

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HIGHLIGHTS:

Midilli and Logarithmic models were the ones that obtained the best fit to the drying conditions.
The constant k of the Midilli model increases as a function of the drying air temperature for the pulp of 'gueroba' fruits.
The effective diffusion coefficient of 'gueroba' fruit pulp increases linearly with the increment in the drying air temperature.

ABSTRACT: The 'Gueroba' fruit can be used to produce flours with potential for the development of new products from the 'Cerrado' socio-biodiversity. The objective was to estimate the drying kinetics and determine the effective diffusion coefficient and activation energy for the pulp of 'gueroba' fruits subjected to different drying temperatures. 'Gueroba' fruits were manually pulped, removing the mesocarp with the epicarp, and this material was identified as the pulp. The material was subjected to oven drying at temperatures of 40, 50, 60 and 70 °C. Nonlinear regression models were fitted to the experimental data. The most adequate model was selected through the coefficient of determination, mean relative and estimated errors, Chi-square test, AIC and BIC. As the drying temperature increases, the processing time to achieve the same moisture content decreases, due to the increase in water diffusivity inside the product. The Midilli model showed the best fit to the experimental data obtained. The effective diffusion coefficients of the pulp of 'gueroba' fruits showed magnitudes between 3.11 x 10^{-9} to 5.84 x 10^{-9} m^2 s^{-1} for temperatures from 40 to 70 °C. The activation energy of the process was 18.34 kJ mol^{-1}.

Key words: mathematical modeling, AIC, BIC, Midilli

RESUMO: O fruto de gueroba pode ser utilizado na produção de farinhas com potencial para o desenvolvimento de novos produtos oriundos da sociobiodiversidade do Cerrado. Objetivou-se estimar a cinética de secagem, bem como determinar o coeficiente de difusão efetivo e a energia de ativação para a polpa dos frutos de gueroba submetida a diferentes temperaturas de secagem. Os frutos de gueroba foram despolpados manualmente, retirando o mesocarpo com o epicarpo, sendo esse material identificado como a polpa. O material foi submetido à secagem em estufa nas temperaturas de 40, 50, 60 e 70 °C. Aos dados experimentais foram ajustados modelos de regressão não linear. O modelo mais adequado foi selecionado com base no coeficiente de determinação, erro médio relativo e estimado, teste de Qui-quadrado, AIC e BIC. Com o aumento da temperatura de secagem, menor é o tempo do processamento para se atingir o mesmo teor de água, devido ao aumento da difusividade da água no interior do produto. O modelo de Midilli apresentou o melhor ajuste aos dados experimentais obtidos. Os coeficientes de difusão efetivos da polpa dos frutos de gueroba apresentaram magnitudes entre 3,11 x 10^{-9} a 5,84 x 10^{-9} m^2 s^{-1} para as temperaturas de 40 a 70 °C. A energia de ativação do processo foi de 18,34 kJ mol^{-1}.

Palavras-chave: modelagem matemática, AIC, BIC, Midilli

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Introduction

'Gueroba' (*Syagrus oleracea*) is a typical palm tree of the 'Cerrado' and is known in Goiás as 'gueroba' or 'guariroba', whereas in other regions of Brazil it is popularly known as 'guarirova', 'palmito amargoso' and 'catolé'. Its fruits have yellowish-green color with thick, fleshy, fibrous and sweetened mesocarp (Lorenzi et al., 2004).

The pulp of the fruits can be used for the extraction of oils and the by-product in the production of flours for food supplementation. The pulp of this fruit is rich in nutrients and sources of fats, besides having significant amounts of carbohydrates. The pulp oil is rich in unsaturated fatty acids (ISPN, 2013).

The fruits are harvested with high moisture content, which makes their storage difficult, so it is necessary to reduce the moisture content of the product. Therefore, the processing of pulp into flour by the drying method can be an efficient alternative to increase the shelf life of the fruits.

The drying process is extremely important in food technology, as it allows the handling of high-quality products, since it can preserve their physical and chemical properties and reduce the moisture content to adequate values for storage. Thus, the product can be used in periods with no availability of the fruit (Resende et al., 2018).

Drying can be estimated through curves fitted to experimental data by nonlinear regression models frequently used to estimate this process (Sousa et al., 2017; Souza et al., 2019). From this drying kinetics, many authors study the behavior of water inside the product, determining the water diffusivity and activation energy (Corrêa et al., 2007; Goneli et al., 2014; Guimarães et al., 2018).

The objective of this study was to estimate the drying kinetics and determine the effective diffusion coefficient and activation energy for the pulp of 'gueroba' fruits subjected to drying temperatures.

Material and Methods

'Gueroba' fruits were collected in the rural area of the municipality of Piracanjuba, Goiás, Brazil, at 17° 17' 47" S latitude, 49° 0' 38" W longitude and altitude of 752 m.

The fruits were harvested and sent to the Laboratory of Postharvest of Plant Products at the Instituto Federal Goiano, Campus of Rio Verde, Goiás, Brazil. Then, the fruits were selected and manually pulped using a stainless-steel knife, removing the mesocarp adhered to the epicarp, and the sum of these two structures was called the pulp of the 'gueroba' fruit. The initial moisture content was determined in an oven at 105 °C until constant mass was reached (Oliveira et al., 2018).

As the 'gueroba' pulp is a fibrous material, a spatula was used to homogenize it, turning the material without degrading its structure. Subsequently, the material was subjected to drying in a forced air ventilation oven (Marconi, MA-035), in three replicates, in perforated trays (25 cm in diameter) with a 2.5-cm-thick layer and 500 g of pulp, at temperatures of 40, 50, 60 and 70 °C, which promoted relative humidity of the drying air inside the oven of 27.15, 16.23, 10.05 and 7.07%, respectively.

Drying was performed up to the final moisture content of 0.125 ± 0.024 d.b., as it is an ideal moisture content for the processing of flour of this product, besides being an adequate value for storage. The reduction of moisture content was monitored by the gravimetric method (mass loss) (Resende et al., 2018), using a scale with resolution of 0.01 g.

The ambient temperature and the temperature inside the dryer were monitored using a thermometer, and the relative humidity of the air inside the oven was obtained through the basic principles of psychometry, with the computer program GRAPSI. The moisture contents of the product were determined in an oven at 105 °C up to constant mass (± 24 h).

To obtain the hygroscopic equilibrium, three replicates containing 20 g of pulp were maintained under the previously described drying conditions and periodically weighed until reaching constant mass. The moisture content ratios of the product were determined by Eq. 1:

$$RX = \frac{X - X_e}{X_i - X_e} \tag{1}$$

where:

RX - moisture content ratio, dimensionless;
X - moisture content of the product, d.b.;
X_i - initial moisture content of the product, d.b.; and,
X_e - equilibrium moisture content of the product, d.b.

'Gueroba' pulp drying was represented by the nonlinear regression models described in Table 1, which are commonly used for products of plant origin.

Table 1. Models used to predict the drying of 'gueroba' fruit pulp

Model	Model designation	Eq.
$RX = 1 + at + bt^2$	Wang and Singh	(2)
$RX = a\exp(-kt) + (1-a)\exp(-k_1t)$	Verma	(3)
$RX = \exp\{[-a-(a^2+4bt)^{0.5}]/2b\}$	Thompson	(4)
$RX = \exp(-kt^n)$	Page	(5)
$RX = \exp(-kt)$	Newton	(6)
$RX = a\exp(-kt^n) + bt$	Midilli	(7)
$RX = a\exp(-kt) + c$	Logarithmic	(8)
$RX = a\exp(-kt)$	Henderson and Pabis	(9)
$RX = a\exp(-kt) + (1-a)\exp(-kat)$	Two-Term Exponential	(10)
$RX = a\exp(-k_0t) + b\exp(-k_1t)$	Two Terms	(11)
$RX = a\exp(-kt) + (1-a)\exp(-kbt)$	Approximation of Diffusion	(12)

t - Drying time - h; k, k_o and k_1 - Drying constants - h^{-1}; a, b, c and n - Coefficients of the models

The models were fitted to the experimental drying data, by nonlinear regression analysis performed with the Gauss-Newton method using R software. The values reported in the literature for the modeling of other plant products were adopted as a criterion for the initial values of the coefficients of the models.

The degree of fit at each drying temperature was determined initially based on the magnitude of the coefficient of determination (R^2), the values of the mean estimated error (SE) and the mean relative error (P), as well as the Chi-square test (χ^2) at significance level of 5% and confidence interval at 95% (p < 5).

$$SE = \sqrt{\frac{\sum\left(Y - \hat{Y}\right)^2}{DF}} \tag{13}$$

$$P = \frac{100}{N} \sum \frac{\left|Y - \hat{Y}\right|}{Y} \quad (14)$$

$$\chi^2 = \frac{\sum\left(Y - \hat{Y}\right)^2}{DF} \quad (15)$$

where:

Y - value observed experimentally;
$\hat{Y}$ - value estimated by the model;
n - number of experimental observations; and,
DF - residual degrees of freedom (number of experimental observations minus the number of model parameters).

To choose a single regression model that best describes the drying process of the pulp of 'gueroba' fruits, additional criteria were used. For the models that obtained better fits according to the previously listed criteria, the Akaike Information Criterion (AIC) and the Schwarz's Bayesian Information Criterion (BIC) were calculated using Eqs. 16 and 17:

$$AIC = -2 \log like + 2p \quad (16)$$

$$BIC = -2 \log like + 2p \ln(n) \quad (17)$$

where:

p - number of parameters of the model;
n - total number of observations; and,
loglike - value of the logarithm of the likelihood function considering the estimates of the parameters.

The significance of the drying constants and the coefficients of the selected model to adjust the drying curves were evaluated by the t-test ($p \leq 0.01$). The variation of these parameters of the model was also evaluated as a function of the drying temperatures, in order to describe the possible trend using linear equations.

Liquid diffusion was determined by the liquid diffusion model used in the geometric shape of flat plate (Brooker et al., 1992), because it is the pulp of the fruit, with eight-term approximation (Afonso Júnior & Corrêa, 1999) (Eq. 18), being fitted to the experimental data of 'gueroba' fruit pulp drying.

$$RX = \frac{X - X_e}{X_i - X_e} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[-\frac{(2n+1)^2 \pi^2 Dt}{4}\left(\frac{S}{V}\right)^2\right] \quad (18)$$

where:

D - effective liquid diffusion coefficient, $m^2 s^{-1}$;
t - drying time, h;
n - number of terms;
S - pulp surface area, m^2; and,
V - pulp volume, m^3.

In the determination of the surface area of the pulp (epicarp and mesocarp), images of 15 pulps were taken and subjected to the computer program ImageJ®. Thickness measurements of 20 pulps were also taken in five different regions using digital caliper (Digimess) with a resolution of 0.01 mm. From the average data of pulp thickness and surface area, it was possible to calculate the volume, according to Eq. 19.

$$V = S\,T \quad (19)$$

where:

S - pulp surface area, m^2; and,
T - pulp thickness, m.

The relationship between the effective diffusion coefficient and the elevation of the drying air temperature was described using the Arrhenius equation (Eq. 20).

$$D = D_0 \exp\left(\frac{E_a}{RT_{abs}}\right) \quad (20)$$

where:

D_o - pre-exponential factor, $m^2 s^{-1}$;
E_a - Activation energy, kJ mol^{-1};
R - Universal constant of gases, 8.134 kJ $kmol^{-1} K^{-1}$; and,
T_{abs} - absolute temperature, K.

With application of the logarithm, the coefficients of the Arrhenius equation were linearized (Eq. 21).

$$LnD = LnD_0\left(\frac{-E_a}{RT_{abs}}\right) \quad (21)$$

Results and Discussion

Table 2 shows that, for all models used, at the four drying temperatures, the values of the mean estimated error (SE) were close to zero, indicating a good fit to the experimental data. According to Draper & Smith (1998), the closer the SE value is to zero, the better its ability to adequately represent a physical process, in this case the drying.

It is also verified that, for all models and drying conditions, except the Wang and Singh model for drying temperatures of 40 and 60 °C, the coefficients of determination (R^2) were greater than 99% (Table 2). Higher R^2 values indicate a better representation of the studied phenomenon by the model, but it cannot be taken as the main criterion for nonlinear estimates (Oliveira et al., 2018).

In relation to the mean relative error (P), Table 2 shows that the Midilli and Logarithmic models had lower values for all drying temperatures; in addition to these, the Henderson and Pabis, Two-Term Exponential and Two terms models had P values below 10%. For Mohapatra & Rao (2005), this is a condition that determines good fit of the model to the drying conditions. It can be noted that, for the Chi-square test (Table 2), all models had low values, and the lower this value, the better the fit of the model to the conditions, as reported by Günhan et al. (2005). Midilli and Logarithmic models were the ones that obtained the best fit to the drying conditions.

Table 2. Degrees of fit of the models for the drying of 'gueroba' (*Syagrus oleracea*) fruit pulp at four drying temperatures

Models	SE*	P (%)	χ^{2*}	R^2 (%)	SE*	P (%)	χ^{2*}	R^2 (%)
	40 °C				50 °C			
Wang and Sing	0.0443	12.57	0.00196	98.00	0.0326	13.07	0.00106	99.10
Verma	0.0310	9.39	0.00096	99.12	0.0132	5.29	0.00017	99.87
Thompson	0.0055	1.58	0.00003	99.97	0.0123	4.79	0.00015	99.87
Page	0.0118	3.67	0.00014	99.86	0.0124	5.43	0.00015	99.87
Newton	0.0280	9.39	0.00079	99.12	0.0118	5.29	0.00014	99.87
Midilli	0.0039	0.96	0.00002	99.99	0.0093	2.24	0.00009	99.94
Logarithmic	0.0052	1.26	0.00003	99.97	0.0113	3.28	0.00013	99.90
Henderson and Pabis	0.0249	7.80	0.00062	99.37	0.0122	5.37	0.00015	99.87
Two-Term Exponential	0.0080	2.64	0.00006	99.93	0.0122	4.66	0.00015	99.87
Two terms	0.0279	7.80	0.00078	99.37	0.0139	5.37	0.00019	99.87
Approximation of diffusion	0.0033	0.35	0.00001	99.99	0.0132	5.29	0.00017	99.87
	60 °C				70 °C			
Wang and Sing	0.0586	20.73	0.00343	96.92	0.0164	5.94	0.00027	99.78
Verma	0.0306	10.34	0.00094	99.25	0.0187	4.03	0.00035	99.76
Thompson	0.0224	5.14	0.00050	99.55	0.0230	5.57	0.00053	99.57
Page	0.0248	6.28	0.00061	99.45	0.0103	3.09	0.00011	99.91
Newton	0.0274	10.34	0.00075	99.25	0.0215	5.57	0.00046	99.57
Midilli	0.0246	4.13	0.00061	99.58	0.0081	2.05	0.00007	99.96
Logarithmic	0.0228	4.24	0.00052	99.59	0.0171	3.57	0.00029	99.80
Henderson and Pabis	0.0285	9.93	0.00081	99.27	0.0183	3.78	0.00033	99.73
Two-Term Exponential	0.0225	5.27	0.00050	99.55	0.0230	5.57	0.00053	99.57
Two terms	0.0241	4.38	0.00058	99.59	0.0216	3.78	0.00047	99.73
Approximation of diffusion	0.0306	10.34	0.00094	99.25	0.0187	4.03	0.00035	99.76

* - Decimal values; SE - Mean estimated error; P - Mean relative error; χ^2 - Chi-Square test; R^2 - Coefficient of determination

As shown in Table 3, these two models had similar values for AIC and BIC. According to results presented by Ferreira Junior et al. (2018), lower values for these criteria indicate better fit of the model to the data of the phenomenon.

The Midilli model showed lower values of both AIC and BIC under the drying conditions, so this was the model chosen to represent the drying of the pulp of 'gueroba' fruits. Gomes et al. (2018), working with the drying of jambu leaves, also used the AIC and BIC criteria to select the most adequate model.

It can be observed in Table 4 that the magnitude of the drying constant k for the Midilli model increased linearly with the increase in drying air temperature.

The constant k of the Midilli model increases as a function of the drying air temperature for the pulp of 'gueroba' fruits (Eq. 22). Similar behavior has been observed by Reis et al. (2018) for the drying of whole flour of 'baru' almonds and by Moscon et al. (2017) for the drying of quinoa grains.

$$k = 0.0098T - 0.1441 \quad \left(R^2 = 0.8968\right) \tag{22}$$

The drying constant k represents the external drying conditions, can be used as an approximation to characterize the effect of temperature, and is related to the effective diffusivity in the drying process in the falling rate period (Babalis & Belessiotis, 2004). The coefficients a, n and b (Table 4) showed no trend with the increase in drying temperature, showing different behavior from that of the constant k.

Table 4. Constant k and coefficients of the Midilli model fitted to estimate the drying of 'gueroba' (*Syagrus oleracea*) fruit pulp at different temperatures

Parameters	Temperature (°C)			
	40	50	60	70
a	1.017383**	0.990888**	1.002234**	0.993248**
k	0.272054**	0.339025**	0.387136**	0.585729**
n	1.190162**	1.067557**	1.134399**	1.085014**
b	0.004595**	-0.001192ns	0.000223ns	-0.005656*

**, *, ns - Significant at $p \leq 0.01$ and at $p \leq 0.05$ and not significant by t-test, respectively

Figure 1 shows the drying curves of the pulp of 'gueroba' fruits estimated by the Midilli model. The initial moisture content of the fruit pulp was 2.40 decimal on dry basis (d.b.). Through the correspondence between the experimental values and those estimated by the model, it can be observed that there was satisfactory fit of the model to the data obtained along the drying of 'gueroba' fruit pulp.

The Midilli model was also proposed to represent the drying of 'carambola' pulp at temperatures of 40, 50 and 60 °C and drying air speed of 1.0 m s^{-1} using a discontinuous tray dryer (Silva et al., 2016). Galdino et al. (2016), studying the drying kinetics of a suspension of whole 'atemoya' pulp, through the method of foam layer drying at different temperatures (60, 70 and 80 °C) and foam layer thicknesses (0.5, 1.0 and 1.5 cm), concluded that the Midilli model showed the best fits to the experimental data.

To reach the final moisture content of 0.125 ± 0.024, times of 6.25, 5.25, 5 and 3 h were necessary for the temperatures

Table 3. Akaike Information Criterion (AIC) and Schwartz's Bayesian Information Criterion (BIC) of the models fitted for curves of 'gueroba' (*Syagrus oleracea*) fruit pulp drying at different temperatures

Model	40 °C		50 °C		60 °C		70 °C	
	AIC	BIC	AIC	BIC	AIC	BIC	AIC	BIC
Midilli	-93.63	-91.21	-66.70	-64.71	-47.25	-45.26	-56.39	-55.40
Logarithmic	-87.49	-85.55	-62.91	-61.31	-45.46	-43.86	-43.32	-42.53

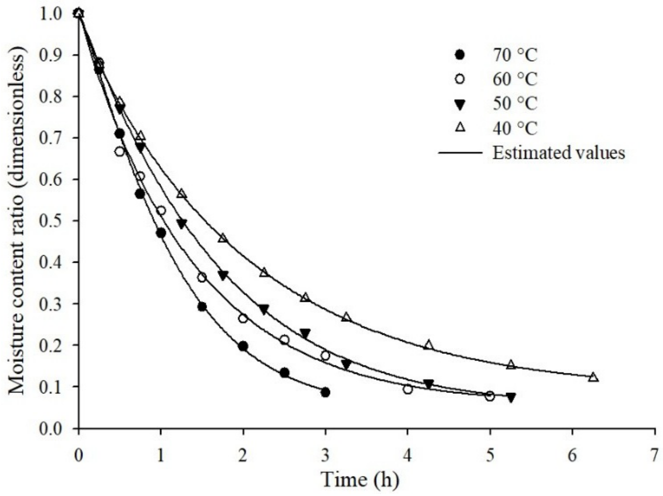


Figure 1. Values of moisture content ratio obtained experimentally and estimated by the Midilli model for the drying of 'gueroba' (*Syagrus oleracea*) fruit pulp during the drying period at different temperatures

of 40, 50, 60 and 70 °C, respectively (Figure 1). It was noted that the time spent is inversely proportional to the drying temperature, that is, the higher the temperature, the shorter the time over which the product will be subjected to drying.

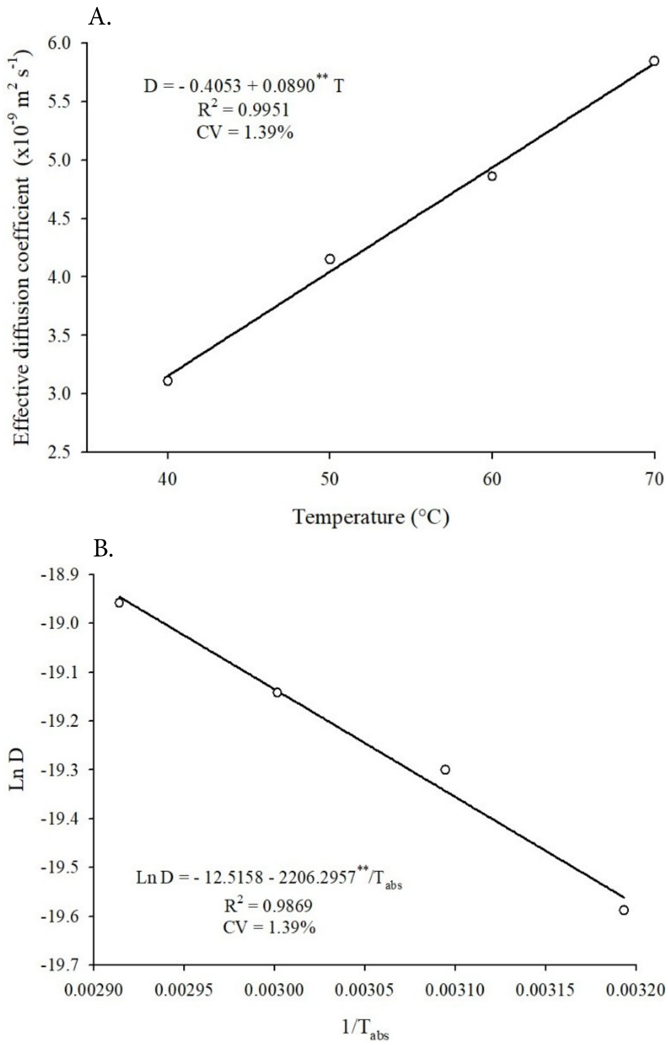
The behavior of drying time as a function of temperature has been observed by several researchers, studying the drying of cactus pear pulp (Madureira et al., 2011), sunflower grains (Smaniotto et al., 2017), and mesocarp of 'baru' fruits (Oliveira et al., 2018), because the higher the temperature, the higher the diffusivity of water under these conditions.

The effective diffusion coefficient of 'gueroba' fruit pulp (Figure 2A) increases linearly with the increment in the drying air temperature. This behavior corroborates the results obtained by other researchers, for the study of the drying kinetics of passion fruit peel (Bezerra et al., 2015) and drying of the sliced pulp of biofortified sweet potato (Souza et al., 2019).

The effective diffusion coefficients (Figure 2A) of 'gueroba' fruit pulp showed magnitudes from 3.11 x 10^{-9} to 5.84 x 10^{-9} m^2 s^{-1} for temperatures from 40 to 70 °C. The magnitudes of the effective diffusion coefficients of the drying of 'acuri' slices ranged from 3.28 (60 °C) to 5.53 x 10^{-10} m^2 s^{-1} (90 °C) (Santos et al., 2019). The values of the effective diffusivity of the drying of 'gueroba' fruits are below those found by Sousa et al. (2017) in the drying of pequi pulp, in which the effective diffusivity under the different drying conditions varied from 0.93 x 10^{-8} to 3.93 x 10^{-8} m^2 s^{-1}, for the temperature range from 50 to 80 °C, respectively.

Water diffusivity inside the product is dependent on drying air temperature, that is, the higher the drying air temperature, the higher the rate of vibration of the water molecules inside the product, resulting in a decrease in the resistance of the fluid to the flow (Goneli et al., 2014), promoted by the reduction in water viscosity.

The Arrhenius expression (Figure 2B) was used to represent the dependence of the effective diffusion coefficient of 'gueroba' fruit pulp on the drying temperature. The activation energy found for the drying kinetics was 18.34 kJ mol^{-1}. The activation energy for plant products is between 12.7 and 110 kJ mol^{-1}, so



** - Significant at p ≤ 0.01 by the F test

Figure 2. Effective diffusion coefficient for the drying of 'gueroba' (*Syagrus oleracea*) fruit pulp as a function of drying temperature (A). Arrhenius representation for the effective diffusion coefficient as a function of the inverse of the absolute temperature of the air in the drying of 'gueroba' (*Syagrus oleracea*) fruit pulp (B)

the value found in this study is within this range (Zogzas et al., 1996).

For slices of 'acuri' (*Attalea phalerata*), the activation energy of drying was 17.66 kJ mol^{-1} (Santos et al., 2019). For drying of okara (soybean residue) in the range from 40 to 70 °C, the activation energy was 28.15 kJ mol^{-1} (Guimarães et al., 2018). The difference between the activation energy values for the same temperature range can be explained by the difference in the composition of the products.

The activation energy represents the degree of difficulty encountered by water molecules to overcome the energy barrier in the migration inside the product (Corrêa et al., 2007). The higher the value of the activation energy, the lower the water diffusivity of the product, due to the low mobility of water inside the product. Thus, the pulp of 'gueroba' fruits is relatively easy to be dried, when compared to the mesocarp (pulp) of baru fruits, which has activation energy of 27.005 kJ mol^{-1} within the same temperature range used in this study (Oliveira et al., 2018).

Conclusions

1. Increase in drying temperature reduces the drying time from 6.25 to 3 h at drying temperatures of 40 °C and 70 °C, respectively.

2. The Midilli model showed the best fit to the experimental data of 'gueroba' fruit pulp drying at different temperatures.

3. The effective diffusion coefficients of the pulp of 'gueroba' fruits showed magnitudes from 3.11 x 10^{-9} to 5.84 x 10^{-9} m^2 s^{-1} at temperatures from 40 to 70 °C.

4. The Arrhenius equation confirmed the dependence of the effective diffusion coefficient on the drying temperature, in which the activation energy found for the drying phenomenon was 18.3434 kJ mol^{-1}.

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