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# Drying kinetics and thermodynamic properties of 'baru' almond flours<sup>1</sup>

# Cinética de secagem e propriedades termodinâmicas de farinhas de amêndoas de baru

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#### HIGHLIGHTS:

The effect of temperature on drying properties of 'baru' almond flour oil concentration was studied.

The higher oil concentration in the flour provides faster drying, but this effect decreases with increasing temperature.

The thermodynamic properties were higher with higher oil concentration and smaller with increasing temperature.

**ABSTRACT:** The consumption of flour and oil of 'baru' (*Dipteryx alata* Vogel) has increased due to its nutritional characteristics; however, there are few studies on the processing of the flour of this almond. The aim of this research was to study the drying kinetics of the whole and partially defatted flours of 'baru' almond, the residue of the oil extraction, as well as its thermodynamic properties. The whole flour was obtained by the grinding of seeds and the partially defatted flour by chemical extraction. The products were dried with forced air circulation oven at 60, 70 and 80 °C. Ten models, commonly used for drying, were selected for fitting. Based on statistical criteria, the Midilli model was selected to represent the drying kinetics of 'baru' almond flour. The difference in the drying rate between the flours tended to attenuate with the elevation of the temperature. Activation energy was 39.24 kJ mol<sup>-1</sup> for the whole flour and 29.01 kJ mol<sup>-1</sup> for partially defatted flour. Enthalpy and entropy decreased with increasing temperature, whereas Gibbs free energy increased. For the flour with highest oil concentration, the thermodynamic properties were higher than for the one with lowest oil concentration.

Key words: Dipteryx alata Vogel, enthalpy, oil concentration

**RESUMO:** O consumo da farinha e do óleo de baru (*Dipteryx alata* Vogel) tem crescido em virtude de suas características nutricionais, contudo, são escassos os estudos a respeito do beneficiamento das farinhas desta amêndoa. O presente trabalho propôs-se estudar a cinética da secagem das farinhas integral e a parcialmente desengordurada de amêndoas de baru, resíduo da extração do óleo, bem como suas propriedades termodinâmicas. A farinha integral foi obtida pela trituração de sementes e a parcialmente desengordura por extração química. Os dois produtos foram submetidos à secagem em estufa com circulação forçada de ar a 60, 70 e 80 °C. Dez modelos, comumente utilizados para secagem, foram selecionados para o ajuste. Com base em critérios estatísticos, o modelo de Midilli foi selecionado para representação do fenômeno para as farinhas de amêndoas de baru. A diferença da taxa de secagem entre as farinhas tendeu a se atenuar com a elevação da temperatura. A energia de ativação foi de 39,24 kJ mol<sup>-1</sup> para a farinha integral e 29,01 kJ mol<sup>-1</sup> para parcialmente desengordurada. A entalpia e entropia decresceram com o aumento da temperatura, enquanto a energia livre de Gibbs aumentou. Para a farinha com maior teor de óleo, as propriedades termodinâmicas foram superiores à de menor teor de óleo.

Palavras-chave: Dipteryx alata Vogel, modelagem matemática, entalpia, teor de óleo



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## Introduction

'Baru' (*Dipteryx alata* Vog.) is a species native to the Brazilian 'Cerrado', and the consumption of its almond has been widespread due to its high nutritional value and medicinal properties. Various food products are produced from brown flour: peanuts, *rapaduras*, cereal bars and cakes (Zuchi et al., 2016). Almond oil is nutritionally rich and has wide industrial applicability, having partially defatted flour as its by-product (Vieira et al., 2016).

However, many difficulties are still encountered in establishing the cost price of flour, especially those related to processing, which include drying. Drying is the process by which the moisture content of food is reduced, decreasing the biological activity and physico-chemical changes inherent to postharvest activities (Oliveira et al., 2015).

Moisture reduction during drying can be represented by mathematical simulations through models that satisfactorily estimate the process. The behavior predicted by the models is employed in studies, designing and commercial viability of drying systems (Souza et al., 2019b).

In addition to the mechanisms of water loss, the thermodynamic study of drying is indispensable. This provides important information on the design of drying systems for agricultural products, such as the determination of energy changes, properties of adsorbed water, and the study of the physical phenomena that occur on the surface of these products (Araújo et al., 2017; Corrêa et al., 2010).

Thus, the present study was proposed to evaluate the influence of the oil concentration on the whole and partially defatted 'baru' almond flour during the drying kinetics, as well as fitting nonlinear regression models and determining their thermodynamic properties.

#### MATERIAL AND METHODS

The experiment was carried out in laboratories of the Universidade Federal de Rondonópolis, MT, Brazil, latitude 16° 27' 49" S, longitude 55° 34' 47" W and altitude of 286 m. The raw material came from a fragment of vegetation native to the 'Cerrado', in the city of Montes Claros, MG, Brazil, and was dried as established by Oliveira et al. (2016).

In order to obtain the whole 'baru' almond flour (WBF), the almonds were peeled off manually, ground in a domestic blender at maximum speed and subsequently homogenized in a sieve.

The extraction of the oil was carried out chemically by means of an extractor of oils and greases by immersion, in order to obtain a partially defatted flour of 'baru' almond (PDBF). Chemical extraction is common for obtaining vegetable oils and has been studied for 'baru' oil, in which the hexane solvent is the most used in research and industry (Souza et al., 2019a). Cartridges contained a portion of approximately 50 g of WBF, which were immersed in hexane solvent at 100 °C for 1 hour and 30 min, with PDBF as by-product. In order to remove the remaining Hexane in the PDBF, it was left exposed in the open air, in a laboratory environment, for about 2 hours, promoting the volatilization of the solvent.

In order to determine the reduction in lipid concentration, a test was performed to determine the lipid concentration of WBF and PDBF, in duplicate, following the methodology established by IAL (2008).

The WBF and PDBF flours were dried at three temperatures: 60, 70 and 80 °C, for 270 min, with 4.26% and 3.30% (d.b.) initial moisture contents, respectively. For this purpose, 15 g portions, arranged in glass crucibles, with 50 mL, in triplicate, for each type of flour, were allocated in a forced circulation oven, for each temperature studied.

Samples were weighed at intervals of 0, 5, 15, 30, 60, 90, 150, 210 and 270 min. After the time limit studied, the flours' moisture contents were determined after drying in an oven at  $105 \pm 3$  °C, until reaching constant mass, according to IAL (2008), determining the hygroscopic equilibrium moisture ( $M_e$ ) at the end of the dehydration process. With the periodic values of the masses, the moisture ratio (MR) was calculated at each established interval, based on the values of mass loss and equilibrium moisture ( $M_e$ ). The MR values are calculated by Eq. 1:

$$MR = \frac{M - M_e}{M_0 - M_e} \tag{1}$$

where:

M - product moisture in the interval t, percentage;

M<sub>0</sub> - moisture at time zero, percentage; and,

M<sub>a</sub> - equilibrium moisture of flours, percentage.

The numerator of the fraction represents the amount of free water that can be dried at a given time (t). The denominator refers to the total water that can be removed, given the conditions of the operation (Marcinkwoski, 2006). Ten nonlinear regression models (Table 1) were fitted to the experimental data, to predict the drying of the WBF and PDBF.

The described models were fitted to the experimental data of drying by non-linear regression analysis, using the Gauss-Newton method. The fit of the models to the WBF and PDBF moisture ratio data was done by Sigmaplot 14.0 software. The selection of the model most faithful to the prediction was performed using the statistical criteria of determination coefficient (R<sup>2</sup>), standard deviation of the estimate (SE) (Eq. 12), relative mean error (P) (Eq. 13), Akaike Information Criterion (AIC) (Eq. 14) and Bayesian Information Criterion

**Table 1.** Models fitted to the experimental data of whole 'baru' flour (WBF) and partially defatted 'baru' flour (PDBF) drying

Model name	Model	Eq.
Approximation of Diffusion	$MR = a \exp(-kt) + (1 - a)\exp(-kbt)$	(2)
Cavalcanti Mata	$MR = a \exp(-kt^n) + b \exp(-kt^m) + c$	(3)
Two Terms	$MR = a \exp(-kt) + b \exp(-ct)$	(4)
Two-Terms Exponential	$MR - a \exp(-kt) + (1 - a) \exp(-kat)$	(5)
Henderson and Pabis	$MR = a \exp(-kt)$	(6)
Logarithmic	$MR = a \exp(-kt) + b$	(7)
Midilli	$MR = a \exp(-kt^n) + bt$	(8)
Newton	MR = exp(-kt)	(9)
Page	$MR = exp(-kt^n)$	(10)
Verma	$MR = a \exp(-kt) + (1 - a) \exp(bt)$	(11)

a, b, c, m, n - Model's coefficients, dimensionless; k - Drying constant,  $min^{-1}$ ; t - Drying time, min

(BIC) (Eq. 15), these two parameter criteria according to Zhao et al. (2017) .

$$SE = \sqrt{\frac{\sum_{i=1}^{n} \left(MR_{exp} - MR_{theo}\right)^{2}}{RDF}}$$
 (12)

$$P = \frac{100}{n} \sum_{i=1}^{n} \left( \frac{MR_{exp} - MR_{theo}}{MR_{exp}} \right)$$
 (13)

$$AIC = n \ln \left( \frac{SE}{n} \right) + 2(N+1) + \frac{2(N+1)(N+2)}{n-N-2}$$
 (14)

$$BIC = n \ln \left( \frac{SSE}{n} \right) + (N+1) \ln (N)$$
 (15)

where:

MR<sub>exp</sub> - experimental moisture ratio, decimal;

 $\ensuremath{\mathsf{MR}}_{\ensuremath{\mathsf{theo}}}$  - estimated moisture ratio, decimal;

RDF - residual degrees of freedom of the model;

SSE - square sum error;

N - number of model parameters; and;

n - number of observed data.

The minimum energy required to start the drying phenomenon of WBF and PDBF, that is, the activation energy, was calculated by the Arrhenius equation (Eq. 16). It also relates the drying constant k of the model that best represented the process for the products, as established by Oliveira et al. (2015).

$$k = A_0 \exp\left(-\frac{E_a}{RT_{abs}}\right) \tag{16}$$

where:

A<sub>0</sub> - pre-exponential factor, min<sup>-1</sup>;

E<sub>a</sub> - activation energy, J mol<sup>-1</sup>;

R - universal gas constant, 8.314 J mol<sup>-1</sup> K<sup>-1</sup>; and,

 $T_{abs}$  - absolute temperature, K.

The thermodynamic properties of enthalpy, entropy and Gibbs free energy, related to the drying of 'baru' almond flour, were determined by Eqs. 17, 18 and 19, described by Jideani & Mpotokawana (2009).

$$\Delta h = E_a - RT_{abs} \tag{17}$$

$$\Delta s = R \left( \ln A_0 - \ln \frac{k_B}{k_p} - \ln T_{abs} \right)$$
 (18)

$$\Delta G = \Delta h - T_{abs} \Delta s \tag{19}$$

where:

Δh - enthalpy variation, J mol<sup>-1</sup>;

 $\Delta s$  - entropy variation, J mol<sup>-1</sup> K<sup>-1</sup>;

 $\Delta G$  - Gibbs free energy variation, J mol<sup>-1</sup>;

 $k_{\rm R}$  - Boltzmann's constant, 1.38 x 10<sup>-23</sup> J K<sup>-1</sup>; and,

 $k_{\rm p}$  - Plank constant, 6.626 x 10<sup>-34</sup> J s<sup>-1</sup>.

#### RESULTS AND DISCUSSION

The oil concentration values for WBF and PDBF were 45.60 and 30.16%, respectively. Therefore, the chemical extraction, with hexane, for 1 hour and 30 min, causes 15.4% less oil in comparison to the original raw material.

Table 2 shows the coefficients of determination  $(R^2)$ , standard deviation of the estimate (SE), relative mean error (P) and the Akaike and Bayesian Information Criteria for WBF and PDBF.

All models had  $R^2$  values above 0.99 for WBF and 0.96 for PDBF. For Cavalcanti Mata (3), the  $R^2$  values were above 0.999, in both flours analyzed, for the three temperatures.

According to Kashaninejad et al. (2007), models with determination coefficients above 0.95 indicate a satisfactory fit in the study of the drying processes. However, this statistical criterion alone is not recommended to select nonlinear models, regarding the drying process (Madamba et al., 1996).

The ability of a model to faithfully describe a physical process is inversely proportional to the standard deviation of the estimate (SE), characterizing a better fit (Oliveira et al., 2019). In the drying of 'baru' almond flour, the values of SE were lower than 0.0606 for all models, indicating a good fit, among which the lowest values of this parameter were calculated by Cavalcanti Mata (3).

Considering the relative mean error (P), the models with the best fit were the ones of Cavalcanti Mata (3) and Midilli (8), although they had values slightly above 10% for WBF, in the model (8) and PDBF, in the model (3) only at the temperature of 80 °C. The relative mean error represents how much the experimental data deviate from the curve of the estimated model (Kashaninejad et al., 2007).

Thus, Mohapatra & Rao (2005) describe models with P above 10% as unfit for predicting physical phenomena, that is, indicating the increase in the distance between the actual process and that predicted by the equation as it increases P. Some studies have slightly higher values, such as the study on the drying of coconut coir pith, carried out by Fernando & Amarasinghe (2016). The authors compared the Wang & Singh (1978) and Linear models to a new model proposed, evaluating drying at four speeds. Among the models fitted, the proposed model was the one indicated to describe the drying of the product, despite having relative mean error value above 10% at the speed of 1.7 m s<sup>-1</sup>.

The AIC and BIC parameters have been used in the literature as additional criteria for model selection. For these criteria, lower values indicate better fits, in which models that have a higher number of parameters are penalized (Quequeto et al., 2019).

From the previous statistical criteria, better fits were verified for Cavalcanti Mata and Midilli models. The Akaike and Bayesian Information Criteria showed lower values for Midilli compared to Cavalcanti Mata. This finding can be justified by the greater number of adjustable parameters in model (3).

**Table 2.** Statistical criteria (R<sup>2</sup> - Coefficient of determination, SE - Standard deviation of the estimate, P - Relative mean error, AIC - Akaike Information Criterion and BIC - Bayesian Information Criterion) for models fitted to the data of 'baru' almond flour

Eq./			WBF					PDBF		
Mod.	SE	P (%)	R <sup>2</sup>	AIC	BIC	SE	P (%)	R <sup>2</sup>	AIC	BIC
60 °C										
(2)	0.0234	3.6469	0.9969	-53.190	-66.795	0.0250	31.0833	0.9952	-29.071	-42.676
(3)	0.0152	1.8250	0.9993	41.352	-72.105	0.0149	1.4014	0.9991	42.221	-71.236
(4)	0.0237	3.8175	0.9973	-42.614	-65.683	0.0271	30.5609	0.9953	-17.136	-40.204
(5)	0.0261	6.6072	0.9954	-57.109	-65.829	0.0441	24.8757	0.9826	-36.951	-45.672
(6)	0.0262	8.3869	0.9954	-57.026	-65.747	0.0606	20.5183	0.9672	-36.881	-45.602
(7)	0.0217	3.8175	0.9973	-54.614	-68.220	0.0247	30.5609	0.9953	-29.136	-42.741
(8)	0.0141	2.8954	0.9990	-51.073	-74.141	0.0189	3.1789	0.9977	-46.498	-69.566
(9)	0.0256	8.2752	0.9950	-61.019	-67.019	0.0576	8.0464	0.9660	-60.999	-66.999
(10)	0.0273	8.4253	0.9950	-56.234	-64.955	0.0482	9.1190	0.9792	-46.064	-54.784
(11)	0.0234	3.5181	0.9969	-53.202	-66.807	0.0250	31.1251	0.9952	-29.045	-42.651
					70 °C					
(2)	0.0158	3.8848	0.9986	-59.703	-73.308	0.0101	26.2230	0.9994	-35.142	-48.747
(3)	0.0044	1.2595	0.9999	18.371	-95.086	0.0071	1.0141	0.9998	27.535	-85.922
(4)	0.0206	5.1402	0.9981	-45.131	-68.199	0.0174	25.3698	0.9984	-22.980	-46.049
(5)	0.0207	7.8625	0.9973	-61.283	-70.003	0.0215	7.8625	0.9966	-61.283	-70.003
(6)	0.0220	9.9039	0.9969	-60.163	-68.883	0.0293	17.9780	0.9937	-41.166	-49.887
(7)	0.0188	5.1402	0.9981	-57.131	-70.736	0.0159	25.3698	0.9984	-34.980	-48.586
(8)	0.0118	3.5117	0.9994	-52.761	-75.830	0.0104	2.0276	0.9994	-55.029	-78.098
(9)	0.0206	7.8625	0.9969	-66.083	-72.083	0.0285	7.8625	0.9931	-66.083	-72.083
(10)	0.0220	9.7301	0.9969	-60.195	-68.916	0.0250	7.3258	0.9954	-57.974	-66.694
(11)	0.0158	3.8104	0.9986	-59.754	-73.360	0.0101	26.5994	0.9994	-34.862	-48.467
					0° 08					
(2)	0.0289	29.2658	0.9960	-49.451	-63.057	0.0195	28.6813	0.9976	-40.741	-54.347
(3)	0.0065	2.8434	0.9999	25.454	<b>-</b> 88.004	0.0031	11.9634	1.0000	64.063	-49.394
(4)	0.0303	8.0181	0.9964	-38.218	-61.287	0.0213	28.7087	0.9982	-28.638	-51.707
(5)	0.0313	32.7244	0.9946	-53.813	-65.829	0.0223	31.4838	0.9972	-46.615	-55.335
(6)	0.0317	27.3706	0.9944	-53.588	-62.309	0.0230	27.5363	0.9971	-46.922	-55.643
(7)	0.0277	8.0181	0.9964	-50.218	-63.824	0.0216	17.7420	0.9978	-41.054	-54.659
(8)	0.0186	11.4430	0.9986	-46.955	-70.023	0.0109	9.6398	0.9995	-52.420	-75.488
(9)	0.0324	32.7244	0.9933	-58.613	-64.613	0.0244	31.4838	0.9962	-51.415	-57.415
(10)	0.0306	31.7446	0.9948	-54.224	-62.945	0.0214	24.6539	0.9975	-60.641	-69.362
(11)	0.0289	29.2661	0.9960	-49.451	-63.057	0.0195	28.6942	0.9982	-40.649	-54.255

Eq./Mod. – Equation/Model see Table 1: Nonlinear regression model; All models are significant at  $p \le 0.01$  by F test

Reis et al. (2018) studied the drying kinetics of the whole and defatted 'baru' almond flour, selecting the Midilli model for the description of the physical process of the whole and the Page model for the defatted at the temperatures of 40, 50 and 60 °C. Santos et al. (2013) determined the Two-Terms model as the best fit for the drying of residual annatto flours with and without oil, although the Midilli model was described as one of the models that satisfactorily represent moisture loss in the product. Souza et al. (2019b) determined that the Wang and Singh model best described the drying of pulp of biofortified sweet potato. These results point out that different models of drying suit different agricultural products.

No variation was observed in the parameters a, n and b of the Midilli model, according to the temperature variation, for WBF and PDBF (Table 3). The parameter k in turn increased with the elevation of the drying temperature, with higher values for WBF. This is an empirical variable, called a drying constant, that

associates the reduction of the moisture content of the product with time, relating the effective diffusivity and the net diffusion (Oliveira et al., 2015). This behavior occurs because, considering high temperatures, the drying rate is higher, increasing the rate of water loss, and subsequently its movement, agreeing with the results of Corrêa et al. (2010). The authors studied both the constant k and the diffusion coefficient, of Fick's Law, for drying of coffee beans, and noted that the two properties are directly proportional to the temperature, being related, which makes it possible to apply the k equation of Arrhenius.

It is also observed in the study of Reis et al. (2018) that the parameter k increases with increasing temperature, with higher values for whole 'baru' flour compared to defatted flour, agreeing with the present study. This indicates that the loss of water at high temperatures tends to be higher for 'baru' almond flour with higher lipid concentration, according to the drying rate k, implying consequences on the thermodynamic properties.

**Table 3.** Parameters of the Midilli model for whole 'baru' flour (WBF) and partially defatted 'baru' flour (PDBF) for different drying temperatures

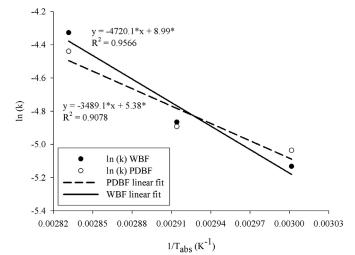
Tomporoturo	Parameters of the Midilli model								
Temperature - (°C) -	WBF				PDBF				
( 0) _	a	k	n	b	a	k	n	b	
60	1.0030	0.0063	1.1485	0.0003	1.0055	0.0061	1.1208	0.0003	
70	0.9888	0.0077	1.1260	0.0002	0.9881	0.0075	1.0915	0.0004	
80	1.0078	0.0132	1.1545	0.0002	1.0044	0.0118	1.1396	0.0001	

This finding can be observed by the drying curves estimated by the Midilli model for WBF (Figure 1A) and PDBF (Figure 1B). From the curves, at temperatures of 60 and 70 °C, WBF dried faster, demonstrating that a higher oil concentration interfered with the drying process, dehydrating more easily. The higher proportion of hydrophobic constituents (lipids) causes WBF to have less molecular interaction with water, drying faster. The difference tended to accentuate when the drying time increased. At 80 °C, the difference between the flours decreased, where the moisture loss values were closer during the process for the flours under study, which showed similar curves.

Figure 2 shows the Arrhenius diagram for the drying constant (k) of the Midilli model, as a function of temperature, obtained by linearization of Eq. 14. The graph relates  $\ln(k)$  to the inverse of the absolute temperature ( $K^{-1}$ ) of drying.

The tangent of the angle formed between the abscissa axis and the straight line in the Arrhenius diagram gives the Ea/R ratio and, since the universal gas constant is a known value, the activation energy (Ea) is calculated. Thus, for WBF the Ea is approximately 39.24 kJ mol<sup>-1</sup> and for PDBF, 29.01 kJ mol<sup>-1</sup>. The higher energy for the WBF can be justified by the higher oil concentration, which can act as a barrier to the exit of the water molecules from the sample, thus requiring greater energy for the beginning of the process.

The values of Ea for agricultural products vary between 12.7 and 110.0 kJ mol<sup>-1</sup>, according to Zogzas et al. (1996), which fit the flours under study. According to Baptestini et al. (2015), lower activation energy indicates a greater ease in the process of transforming liquid free water into steam. These values, compared to those found by Reis et al. (2018), indicate an inverse behavior between flours with increasing temperature.

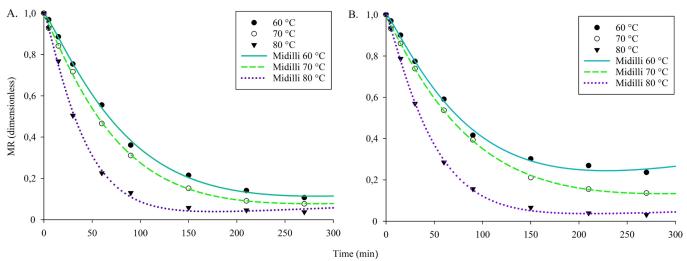


\* - Significant at  $p \le 0.05$  by F test

**Figure 2.** Arrhenius diagram for the drying constant, as a function of air temperature, during the drying of whole 'baru' flour (WBF) and partially defatted 'baru' flour (PDBF)

From the activation energy the thermodynamic properties can be obtained for the drying of the 'baru' almond flour (Table 4).

With respect to the enthalpy change ( $\Delta h$ ), there is a decrease with increasing temperature, characterizing them as inversely proportional. This behavior occurs because, considering the product as a thermodynamic system, the partial pressure of water vapor rises inside the flours, where the air remains constant, thus increasing the diffusivity to the surface (Araújo et al., 2017). The drying of the flours typified an endothermic process, by virtue of positive values, and the energy supply is necessary for the physico-chemical transformation to take place (Costa et al., 2016).



**Figure 1.** Moisture ratio (MR) of whole 'baru' flour (WBF) (A) and partially defatted 'baru' flour (PDBF) (B) as a function of drying time at three temperatures, fitted by the Midilli model

Table 4. Thermodynamic properties of the drying process of whole 'baru' flour (WBF) and partially defatted 'baru' flour (PDBF)

Temperature (°C)	Δh (J mol <sup>-1</sup> )	Δs (J mol <sup>-1</sup> K <sup>-1</sup> )	ΔG (J mol <sup>-1</sup> )	Δh (J mol <sup>-1</sup> )	Δs (mol <sup>-1</sup> K <sup>-1</sup> )	ΔG (J mol <sup>-1</sup> )
(0)		WBF			PDBF	
60	36,475.12	-229.16	112,819.24	26,240.02	-230.80	103,131.13
70	36,391.98	-229.40	115,112.06	26,156.88	-231.05	105,440.37
80	36,308.83	-229.64	117,407.30	26,073.73	-231.29	107,752.03

 $\Delta h$  - Enthalpy variation;  $\Delta s$  - Entropy variation;  $\Delta G$  - Gibbs free energy variation

Note also that  $\Delta h$  was higher for WBF compared to PDBF, at all temperatures. According to Oliveira et al. (2010), lower values of this property indicate less energy expenditure to break the intermolecular bond between water and product. Although WBF has a faster drying rate, the enthalpy property shows that there is higher energy expenditure for this product, in comparison to PDBF, as observed for Ea, showing an apparent contradiction. This difference can be justified by the fact that the enthalpy variation includes only temperature effects in its calculation. This situation indicates the need for further studies on the property, due to the chemical components of the product. The same conclusion was reached by Koukouch et al. (2017) when drying the whole and defatted olive waste.

As  $\Delta h$ , the entropy change ( $\Delta s$ ) decreased with the increase in temperature in the two flours studied. The negative values of this thermodynamic property are attributed to the existence of chemical adsorption or structural modifications of the adsorbent (Moreira et al., 2008). Entropy quantifies the energy lost in the physical phenomenon and that is not made available to the work, identified by the negativity of the attribute. This property is related to the spatial arrangement of the molecules of the water-product system (Corrêa et al., 2010).

It is observed that the entropy had smaller values with the increase of the temperature, which occurs because of the increase of the excitation of the molecules, reducing the degree of order of the molecular arrangement. Considering the flours, lower magnitudes of  $\Delta s$  were obtained for PDBF, indicating a lower order of the molecules and greater loss of energy compared to WBF. This can be attributed to the higher concentration of fatty acids in the whole flour, providing less interaction with water molecules.

For Gibbs free energy, it is possible to notice the spontaneity of the drying of the 'baru' almond flour, denoted when  $\Delta G$  is greater than zero. Thus, the reaction is endergonic, that is, it becomes necessary to add energy from the surrounding environment for the process to occur. The work performed by the physical phenomenon is also represented by  $\Delta G$ , so higher temperatures provide more work to make the adsorption sites available (Nkolo Meze'e et al., 2008). For the drying of the WBF a greater useful work was carried out; therefore, greater oil concentration requires more energy.

The results for the thermodynamic properties demonstrate the non-spontaneity of the process, according to Eq. 17, where, when the enthalpy variation is positive and entropy is negative, it illustrates one of the situations where  $\Delta G$  values are positive (Oliveira et al., 2015). Many studies have been conducted on the thermodynamic properties of agricultural products and the results have been similar (Oliveira et al., 2019; Santos et al., 2019; Araújo et al. 2017; Cagnin et al., 2017; Costa et al., 2016; Baptestini et al., 2015).

## Conclusions

- 1. The Midilli model showed satisfactory fit to the drying kinetics of 'baru' almond flours.
- 2. Reduction in oil concentration increased the drying time, but this effect decreases with increasing temperature.

- 3. Enthalpy and entropy decreased with increasing drying temperature, while Gibbs free energy increased in the two flours studied.
- 4. Activation energy, enthalpy, entropy and Gibbs free energy were higher for the whole flour, at the same temperature, compared to flour with lower lipid concentration.

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