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Drying kinetics of baru flours as function of temperature

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A B S T R A C T

Several types of seeds have been initially used in the food industry due to the great potential that vegetable proteins have. Baru is a fruit commonly found in the Cerrado biome, having a high nutritional value. This paper aimed to determine and analyze the drying kinetics of whole and defatted baru almond flours at different temperatures. The flour resulting from almond milling was defatted using petroleum ether. The drying processes were performed at temperatures of 40, 50 and 60 ºC. The mathematical models of Page, Henderson and Pabis, Midilli & Kucuk, Thompson and Approximation of Diffusion were fitted to the experimental data. The results showed a noticeable effect of air temperature on the drying kinetics of whole and defatted baru almond flours. According to the statistical parameters of analysis, the models Midilli & Kucuk and Page were the ones with the best fits to the experimental data. The effective diffusivity values found ranged from 8.02×10^{-10} to 19.90×10^{-10} $m^2 s^{-1}$ and for the activation energy were 22.39 and 39.37 KJ mol^{-1} for whole and defatted almonds, respectively.

Palavras-chave:
Dipteryx alata Vog.
castanha
proteínas vegetais
Midilli & Kucuk
Page

Cinética de secagem de farinha da amêndoa de baru em função da temperatura

R E S U M O

Vários tipos de sementes têm sido introduzidos em formulações na indústria de alimentos, graças ao grande potencial que as proteínas vegetais apresentam. O baru, fruto disseminado no bioma cerrado, apresenta em sua castanha um alto valor nutricional. O presente trabalho teve como objetivo determinar e analisar a cinética de secagem da farinha integral e desengordurada da amêndoa do baru em diferentes temperaturas. A farinha resultante da moagem das amêndoas foi desengordurada por éter de petróleo. As secagens foram realizadas nas temperaturas de 40, 50 e 60 °C. Os dados experimentais foram ajustados aos modelos matemáticos de Page, Henderson e Pabis, Midilli & Kucuk, Thompson e Aproximação da Difusão. Os resultados demonstraram notável efeito da temperatura do ar na cinética de secagem da farinha integral e desengordurada da amêndoa do baru. A farinha da amêndoa integral apresentou perdas de umidade mais lentas do que a farinha desengordurada. Segundo os parâmetros estatísticos de análises, os modelos de Midilli & Kucuk e Page foram os que obtiveram os melhores ajustes dos dados experimentais. Os valores de difusividade efetiva encontrados variaram de $8,02 \times 10^{-10}$ a $19,90 \times 10^{-10}$ $m^2 s^{-1}$ e para a energia de ativação foram de 22,39 e 39,37 KJ mol^{-1} para a amêndoa integral e desengordurada, respectivamente.

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Introduction

The Cerrado (Brazilian savanna) is known as the second largest biome in South America. It has a typically hot and semi-humid climate in which there are several species of trees flourishing in the native flora of the region (Sousa et al., 2011; Santos et al., 2016). In this context, the fruits of native plants from the Brazilian Cerrado, such as baru (*Dipteryx alata Vog.*), have been standing out because they have a nutritional potential with a great sensorial and economic appeal. In addition, baru is used as raw material for the formulation of new food products. Baru seed is also named as chestnut or almond. It is rich in lipids and proteins and it is usually processed and commercialized fresh, roasted or in the form of flour, generating income for several regional communities that live in the Cerrado area, being also very valued by the international market (Takemoto et al., 2001; Rocha & Santiago, 2009; Fernandes et al., 2010).

Taking into account the high lipid contents, baru almond defatting brings about an increase in the protein content, which can be used for the production of several products since the proteins contribute for increasing the nutritional and functional value and the technological properties of the food system (Wang et al., 1999; Ribeiro & Seravalli, 2007).

Another method that enables the concentration of these components is drying. This technique is a complex process in which heat and the mass transfer happen concurrently, reducing moisture and leading to a substantial reduction in mass and volume of the final product. Other benefits associated with food drying are the increase in product lifetime, easiness in transportation and commercialization (Fellows, 2009; Vega-Gálvez et al., 2010; Bettega et al., 2014).

The drying kinetics provides a physical view of the drying process and its principle is based on building a set of mathematical equations which are able to characterize properly the moisture loss as a function of time, in an accurate and simple way, being able to describe the drying process better (Barati & Esfahani, 2011; Rosa et al., 2015).

Until now, only a few papers about the drying kinetics of baru almond have been found in the literature (Teixeira et al., 2015); however, no study was found on the drying kinetics of whole and defatted baru almond flours, emphasizing its defatting. In this context, this paper aimed to determine and analyze the drying kinetics of whole and defatted baru almond flours at different temperatures.

Material and Methods

The experiments were performed in the Laboratory of Engineering and Agroindustrial Processing (LEPA) located at the university campus Deputado Estadual Renê Babour (Mato Grosso State University - UNEMAT), in Barra do Bugres, MT, Brazil. The raw material used was baru almond purchased at the local market from Mato Grosso Southwest region. The almonds were manually selected considering their physical integrity.

Almond milling was performed in a hammer-type food processor (Vieira MCO260) with a granulometric sieve of 0.7 mm. Then, the flour obtained was defatted based on the methodology of Boatright & Hettiarachchy (1995), adapted by substituting the hexane solvent by petroleum ether, because it is an organic solvent and volatilizes completely when exposed to ambient temperature without leaving residues.

The defatted flour and whole flour of baru chestnut were submitted to a washing process with distilled water aiming to remove the non-proteinaceous soluble fractions. Subsequently, a proteinaceous isolate was obtained from the baru almond, adapted from Carvalho et al. (2009).

Drying processes were performed under controlled air temperature conditions of 40, 50 and 60 °C, in triplicate. The samples were divided into 20-g portions and were uniformly placed in Petri dishes and then in a forced ventilation oven (Quimis Q314M242). During all the drying process, the samples were weighed periodically on an electronic scale (Bioprecisa FA2104n, 0.1 mg precision and four decimal places) until they reached a constant weight.

Moisture content at 105 °C and total lipids analyses were performed according to the Adolfo Lutz Institute (IAL, 2008) protocols.

The drying curves were obtained by converting the water loss data into the dimensionless parameter of moisture ratio (RU), Eq. 1 was used.

$$RU = \frac{U - Ue}{Ui - Ue} \qquad (1)$$

where:

U - moisture content of the product, decimal d.b.;

Ui - initial moisture content of the product, decimal d.b.; and,

Ue - equilibrium moisture content of the product, decimal d.b.

Different mathematical models were used to describe the drying rate of the process. Aiming at obtaining information about the drying kinetics of the baru almond whole and defatted flours, the curves of the moisture ratio as a function of time, were constructed for different drying air temperatures.

The drying curves of the baru almond whole and defatted flours were shown through five mathematical models (Table 1) fitted by non-linear regression using the statistical program XLSTAT (Addinsoft, 2016).

The models were fitted through non-linear regression analyses by using the Quasi-Newton method. The degree

Table 1. Mathematical models used to describe the drying process

Model designation	Model	
Page (Page, 1949)	$RU = e^{-Kt^n}$	(2)
Henderson & Pabis (Henderson & Pabis, 1961)	$RU = a\,e^{-Kt}$	(3)
Midilli & Kucuk (Midilli & Kucuk, 2003)	$RU = a\,e^{-Kt} + b\,t$	(4)
Thompson (Thompson et al., 1968)	$RU = e^{(-a-(a^2+(4.b.t)^{0.5}).(2.b))}$	(5)
Approximation of diffusion (Ertekin & Yaldiz, 2001)	$RU = a\,e^{-Kt} + (1-a)e^{-Kbt}$	(6)

RU - Moisture ratio of the product, dimensionless; t - Drying time, h; K - Drying coefficients; a, b, n - Constants of the models of fit of each model took into account the magnitude of the determination coefficient (R^2) and the estimated average error (SE).

$$SE = \sqrt{\frac{\sum \left(RU_{pre} - RU_{exp} \right)^2}{N}} \quad (7)$$

where:

RU_{pre} - moisture ratio predicted by the model;
RU_{exp} - experimental moisture ratio; and,
N - number of observations made during the experiment.

The values of average effective moisture diffusivity were determined by analytical solution of Fick's law for liquid water diffusion in on solid, taking into account the conditions of the material in question. The activation energy (Ea) was obtained from the dependence of effective diffusivity (D_{ef}) on temperature, analyzed by an Arrhenius-type equation, Eq. 8.

$$Def = D_o \exp\left(-\frac{Ea}{RT} \right) \quad (8)$$

where:

D_o - pre-exponential factor, $m^2\ s^{-1}$;
E_a - activation energy, $J\ mol^{-1}$;
R - universal gas constant, 8.314 $J\ mol^{-1}\ K^{-1}$; and,
T - absolute temperature, K.

Results and Discussion

The curves shown in Figure 1 (A, B) indicate the effect caused by the increase in air temperature through the drying kinetics, facilitating the energy transfer in the form of heat to the samples, which consequently increases the moisture removal rate of the product. This trend can be usually observed in drying experiments. These results are in accordance with other studies, such as Andrade et al. (2006), who worked with drying kinetics in bean seeds; Costa et al. (2011) with crambe seeds; Santos et al. (2013) with urucum flour; and Teixeira et al. (2015) with drying of whole baru almonds.

The initial moisture values found for the whole and defatted baru almond flours were 3.22 and 3.51%, which are within the range found by Vera et al. (2009) from 2.93 to 5.07%, Lima et al. (2010) (3.23%) and Fernandes et al. (2010) (from 3.20 to 4.00%). After washing with distilled water, the moisture was around 68% for the whole flour and 70% for the defatted flour.

Analyzing the drying curves in Figure 1 (C, D, E), there is an evident difference between both flours at the three evaluated temperatures, where the defatted flour reached equilibrium in less time compared with the whole flour. This effect was attributed to higher lipid content in the whole flour (45.55% dry basis) comparing to the defatted flour (4.97% dry basis); therefore, it became more difficult for the water to break the hydrophobic barrier formed by the lipids, which increased the drying time. These results are in accordance with those found by Cyprian et al. (2015) for the Capelin (*Mallotus villossus*) drying, where the moisture loss was slower for the samples with higher lipid contents.

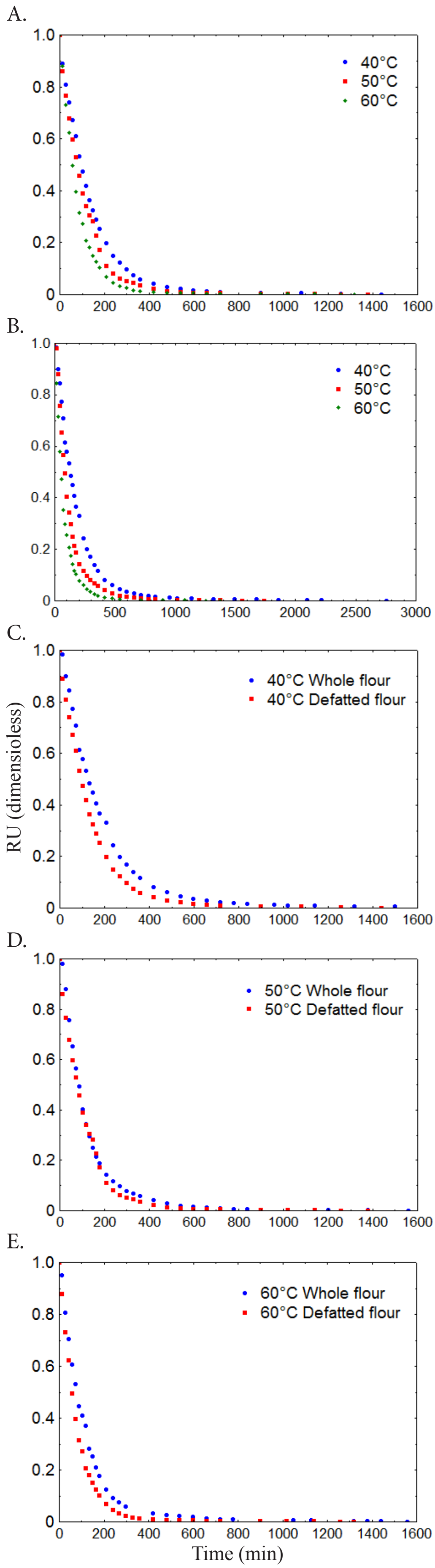

Figure 1. Drying curves of whole (A) and defatted (B) baru almond flours at 40, 50, 60 °C and a comparison of the two drying curves under temperatures of 40 (C), 50 (D) and 60 °C (E)

In this way, the lipid content works as a limiting factor during the drying process, acting as a physical barrier to heat transfer, which is responsible for water evaporation as well as its diffusivity from the interior to the surface of the food.

Using the dimensionless moisture data from Figure 1 (A, B), it is possible to fit them with the mathematical models shown in Table 1, as well as determine the coefficient of determination (R^2), estimated average error (SE) and verify which model is the best to represent adequately the drying process of the baru almond samples.

Table 2 shows the parameters of the mathematical models fitted to the experimental data of whole and defatted almond flours through non-linear regression at the three temperatures, as well as their coefficients of determination (R^2) and estimated average error (SE).

It is possible to identify that, for the analyzed models, the estimated average error (SE) of the moisture ratio, which describes the value of the standard deviation for the estimate, has relatively low values. It is also possible to observe that high determination coefficients (R^2) were obtained, higher than 90%, indicating a successful representation of the drying process in the studied conditions (Table 2).

As noted in Table 2, the value of the drying constant k increased with the temperature rise in almost all samples, which occurs because higher temperatures result in higher drying rates, reaching the equilibrium content in a shorter process time. These results were also observed by Corrêa et al. (2010) with coffee drying.

All models fitted well to the experimental data, mainly the Midilli & Kucuk model for the whole flour and Page model for the defatted flour, since both had R^2 values closer to 100% of the curve fitting and lower SE value for the samples.

The Figure 2 shows a graphical representation of the mathematical models which fitted best to the data for both types of samples at the three temperatures.

Based on the parameters found through the best data fits with the mathematical models, an analytical procedure was done and it was possible to represent graphically the moisture variation rate in relation to time in both raw materials, shown in Figure 3.

The curves in Figure 3 (A, C, E) describe the moisture loss rate in relation to time, highlighting a meaningful difference in the drying kinetics of the whole flour compared to the defatted flour. The comparison of moisture loss between both raw materials is represented in Figure 3 (B, D, F). This difference is related to the lipid content of the sample, since the whole flour showed a lipid content of 45.55% (dry basis) and the defatted flour of 4.97% (dry basis). These aspects are in accordance with the experiment done by Cyprian et al. (2015).

Using the Fick's law equation (Eq. 8) for products with a flat plate geometric shape, the values of the effective diffusivity were calculated from the experimental data. The effective diffusion coefficient values increased when the drying air temperature increased, which demonstrates a reduction of the internal resistances to the drying processes. They were 11.90×10^{-10} and 8.02×10^{-10} (40 °C), 15.30×10^{-10} and 12.90×10^{-10} (50 °C); and 19.90×10^{-10} and 19.50×10^{-10} (60 °C) for WBF and DBF, respectively.

Table 2. Mathematical models fitted to the experimental data at drying temperatures of 40, 50 and 60 °C for whole and defatted baru almond flours

Model	T	Sample	A	b	K	n	R^2	SE
Henderson & Pabis (1961)	40	WBF	1.0171	-	0.0075	-	99.926	0.0122
	40	DBF	1.0771	-	0.0059	-	99.877	0.0165
	50	WBF	1.0050	-	0.0090	-	99.901	0.0135
	50	DBF	1.1285	-	0.5681	-	97.636	0.4841
	60	WBF	1.0384	-	0.0126	-	99.901	0.0129
	60	DBF	1.0151	-	0.0130	-	99.908	0.0124
Approximation of Diffusion (2001)	40	WBF	0.0615	0.99844	0.0075	-	99.926	0.2647
	40	DBF	1.0745	-0.00003	0.0059	-	99.881	0.0162
	50	WBF	-0.1999	0.56652	1.0401	-	99.928	0.1848
	50	DBF	-0.6382	0.49000	1.4646	-	99.857	0.3693
	60	WBF	-0.9141	0.76206	1.1902	-	99.931	0.2036
	60	DBF	-1.0933	0.93918	0.8812	-	99.910	0.3873
Midilli & Kucuk (2003)	40	WBF	0.9888	0.000005	0.0045	1.09	99.972	0.0075
	40	DBF	1.0462	0.000017	0.3192	1.08	99.940	0.2885
	50	WBF	0.9895	0.000002	0.0071	1.04	99.964	0.0126
	50	DBF	1.4893	-0.000005	0.0473	0.71	95.617	0.0976
	60	WBF	1.0107	0.000004	0.0076	1.10	99.961	0.0084
	60	DBF	1.4424	0.00035	0.7341	1.04	99.640	0.0383
Page (1949)	40	WBF	-	-	0.0047	1.05	99.959	0.0091
	40	DBF	-	-	0.0036	1.07	99.880	0.0161
	50	WBF	-	-	0.0076	1.03	99.917	0.0124
	50	DBF	-	-	0.0039	1.15	99.730	0.0236
	60	WBF	-	-	0.0087	1.07	99.936	0.0104
	60	DBF	-	-	0.0112	1.02	99.909	0.0123
Thompson (1968)	40	WBF	-140.541	-3.42910	-	-	99.940	0.0110
	40	DBF	-94.4188	78.73540	-	-	97.592	0.0728
	50	WBF	-114.771	-1.89411	-	-	99.916	0.0125
	50	DBF	-52.7379	43.73245	-	-	96.549	0.2036
	60	WBF	-80.1935	-0.38929	-	-	99.830	0.0170
	60	DBF	-72.2937	3.386105	-	-	99.868	0.0149

WBF - Whole baru flour; DBF - Defatted baru flour; K - Drying coefficients; A, b, n - Constants of the models; R^2 - Magnitude of the coefficient of determination; SE - Estimated average error; T - Temperature °C

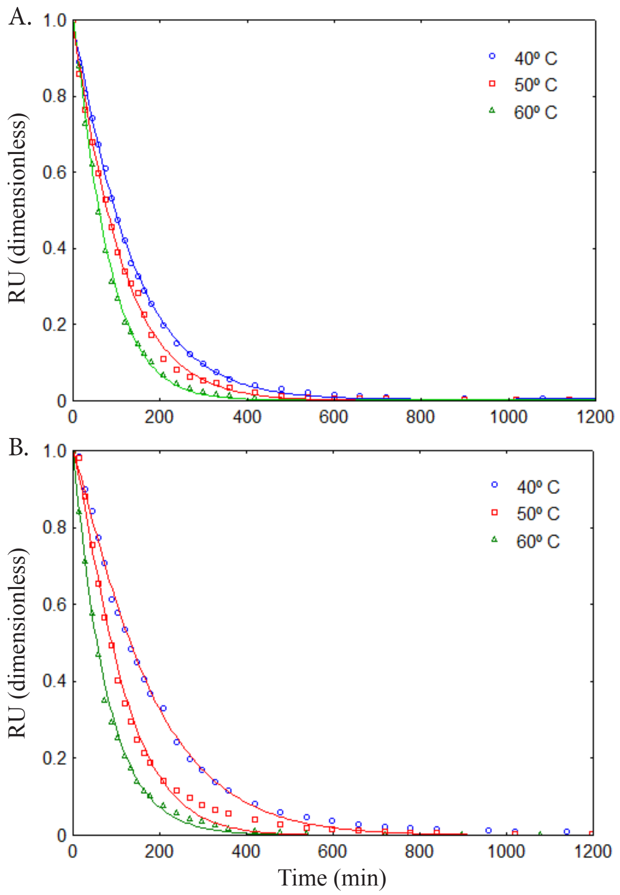

Figure 2. Adjustment moisture ratio (RU) to the Midilli & Kucuk model for drying of whole baru almond flour (A) and to the Page model for drying of defatted baru almond flour (B) at the three temperatures evaluated

Teixeira et al. (2015) evaluated the whole baru almond drying kinetics and obtained diffusivity values from 18.15 x 10^{-11} to 37.08 x 10^{-11} $m^2 s^{-1}$ for the temperatures of 50, 60 and 70 °C, showing that the diffusivity values also increased when the drying temperature increased. Almeida et al. (2009) dried beans of the adzuki variety in the temperature range from 30 to 70 °C and obtained diffusion coefficients from 0.510 x 10^{-10} to 2.230 x 10^{-10} $m^2 s^{-1}$ for 30 and 70 °C, respectively. For Jittanit (2011), the effective diffusion coefficient is dependent on the drying air temperature as well as factors such as variety and composition of materials. Gazor & Mohsenimanesh (2010) studying canola beans drying, found effective diffusivity values ranging from 3.76 x 10^{-11} to 8.46 x 10^{-11} $m^2 s^{-1}$ for the temperature range from 30 to 100 °C.

Figure 4A shows a graphical representation for the effective diffusivity (D_{ef} x10^{-10}) as a function of air temperature. After obtaining the effective moisture diffusivity values, it was possible to calculate the activation energy values using Arrhenius representation (Figure 4B).

It is noticeable in Figure 4A a higher difference between the samples at the temperatures of 40 and 50 °C; consequently, when the drying temperature increases the D_{ef} values of both flours tend to be similar.

For Kashaninejad et al. (2007), the activation energy is a barrier that needs to be crossed, so the diffusion process can occur in the product. In this paper, the activation energies found for the drying process were 22.39 and 39.37 KJ mol^{-1} and the coefficients of determination were of 99.95 and 99.98% for the whole and defatted almond flours. These values were close to that found by Silva et al. (2008) for cowpea, of 26.90 KJ mol^{-1}. Doymaz (2005) working with green beans and Corrêa et al. (2006) with beans of the red group obtained the values of 35.43 and 40.08 KJ mol^{-1}, respectively.

In the drying processes the lower activation energy, the higher the water diffusivity in the product. Therefore, the activation energy obtained is within the range shown by Zogzas et al. (1996) for agricultural products, ranging from

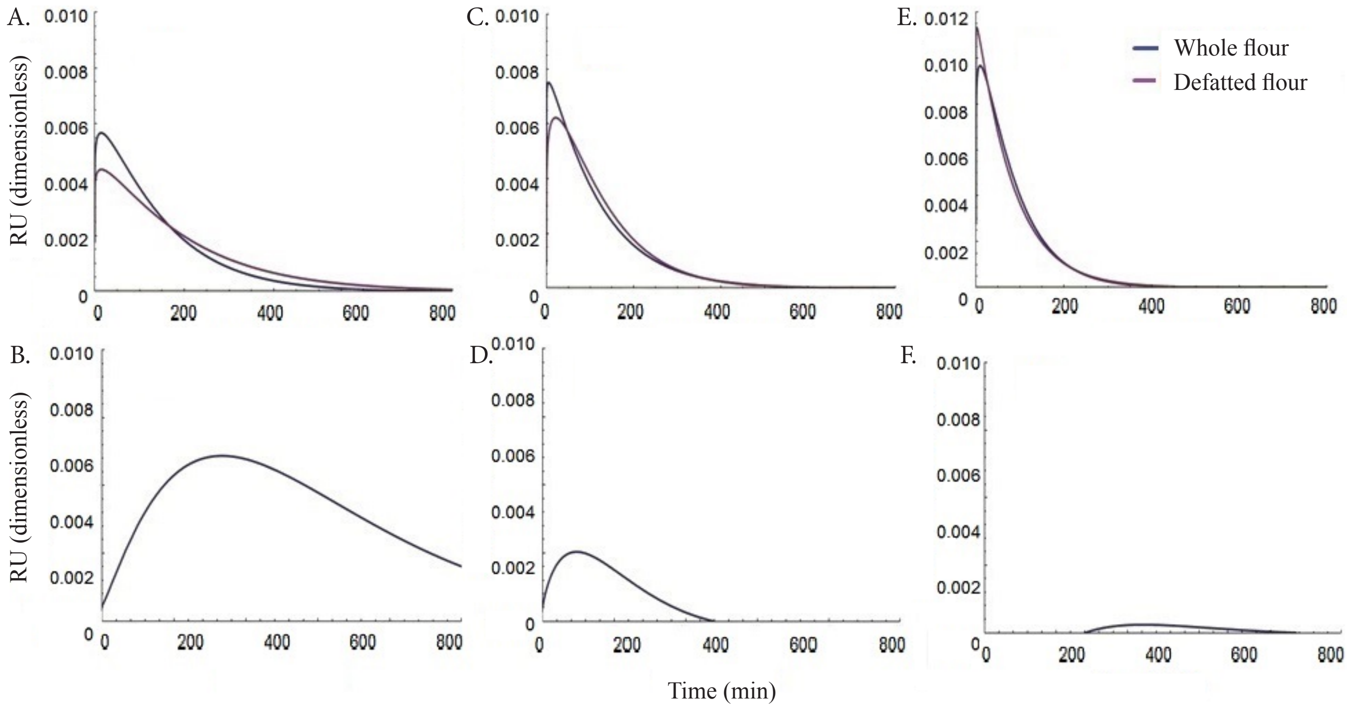

Figure 3. Moisture ratio (RU) variation rate with respect to time of whole and defatted baru almond flours, at 40 (A, B), 50 (C, D) and 60 °C (E, F)

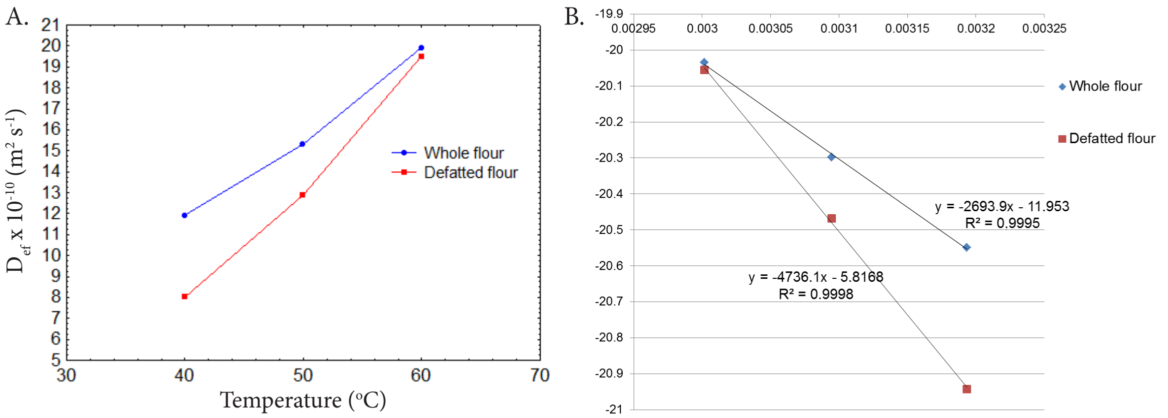

Figure 4. Graphic representation for the effective diffusivity (D_{ef} x 10^{-10}) as a function of the drying air temperature (A) and Arrhenius representation for the effective diffusion coefficient (B) for both baru flours

12.70 to 110 KJ mol^{-1}. In general, it is possible to say that the higher the temperature, the faster the activation energy will be overcome and, consequently, the food begins to lose its moisture more quickly.

Conclusions

1. The increase in the drying temperature led to higher water removal rates of the product.

2. The flour of whole almond showed slower moisture loss than the defatted flour and the lipid content acted as a limiting factor during the drying process.

3. The Midilli & Kucuk model had the best results for the whole flour and Page model had the best fits for the defatted flour.

4. The defatting contributed to the reduction of the drying time of the samples, being the most indicated process to be executed industrially.

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