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Drying kinetics of sunflower grains

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Key words:
mathematical modeling
Heliantus annus
liquid diffusivity

ABSTRACT

The objectives of this study were to fit different mathematical models to experimental data of drying of sunflower grains, determine and evaluate the effective diffusion coefficient and obtain the activation energy for the process during the drying under various conditions of air. The sunflower grains were collected with an initial moisture content of 0.5267 dry basis (d.b.) and dried in an oven with forced air ventilation under five temperature conditions: 35, 50, 65, 80 and 95 °C, until reaching the moisture content of 0.0934 ± 0.0061 (d.b.). Among the analyzed models, Wang and Singh showed the best fit to describe the drying phenomenon. The effective diffusion coefficient of sunflower grains increased with the increment in air temperature and has activation energy for liquid diffusion in the sunflower drying of 29.55 kJ mol^{-1}.

Palavras-chave:
modelagem matemática
Heliantus annus
difusividade líquida

Cinética de secagem dos grãos de girassol

RESUMO

Objetivou-se, neste trabalho, ajustar diferentes modelos matemáticos aos dados experimentais da secagem dos grãos de girassol, determinar e avaliar o coeficiente de difusão efetivo e obter a energia de ativação para o processo durante a secagem em diversas condições de ar. Os grãos de girassol foram colhidos com teor de água inicial de 0,5267 base seca (b.s) e submetidos à secagem em estufa com ventilação de ar forçada em cinco condições de temperatura: 35, 50, 65, 80 e 95 °C, até atingir o teor de água de 0,0934 ± 0,0061(b.s). Dentre os modelos analisados, o de Wang e Singh, apresentou os melhores ajustes e foi escolhido para descrever o fenômeno de secagem. O coeficiente de difusão efetivo aumenta com a elevação da temperatura do ar e apresenta uma energia de ativação para a difusão líquida na secagem do girassol de 29,55 kJ mol^{-1}.

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INTRODUCTION

Part of the production of sunflower grains is frequently harvested with high moisture content to obtain higher yields and maximum content of dry matter, because the grains have already reached physiological maturity. However, for an adequate processing and storage, it is necessary to reduce the moisture content to appropriate levels.

The drying of agricultural products is the most used process to ensure their quality and stability, because the decrease in the amount of water in the material reduces biological activity and the chemical and physical changes that occur during the storage (Resende et al., 2008). For this process to be fast, safe and economic, it is fundamental to know and monitor the physical phenomena occurring during the drying (Martinazzo et al., 2007).

The use of mathematical models in the simulations of drying operations has assisted the project, development, evaluation and optimization of dryers (Palacin et al., 2005). The simulation, whose principle is based on the drying of successive thin layers of the product, requires the use of a mathematical model that represents, with satisfactory limits of confidence, the loss of water during the drying period (Giner & Mascheroni, 2002). In the literature, there are various theoretical, semi-theoretical and empirical equations to describe the phenomenon of thin layer drying.

Considering the importance of the theoretical study of the drying process of agricultural products, this study aimed to fit different mathematical models to the experimental data of the drying kinetics of sunflower grains and determine and evaluate the effective diffusion coefficient, as well as obtain the activation energy for the process during the drying under various air conditions.

MATERIAL AND METHODS

The study was carried out at the Laboratory of Post-Harvest of Agricultural Products, of the Federal Institute of Education, Science and Technology of Goiás - Campus of Rio Verde, GO, Brazil, in July 2014, using sunflower grains with initial moisture content of 0.5267 (d.b.). The drying was conducted under different controlled conditions of temperature (35, 50, 65, 80 and 95 °C) and relative air humidity (37.15, 16.93, 8.35, 4.41 and 2.47). The grains were dried on 8-cm-long, 25-cm-wide trays, without perforations, containing 200 g of product, approximately 3 cm thick, in a completely randomized design, in four replicates.

For the determination of the drying curves and fits of the models, the final moisture content established was of 0.0934 ± 0.0061 (d.b.). The moisture content of the product was determined in an oven at 105 ± 3 °C, for 24 h, in three replicates, until constant weight (Brasil, 2009).

The hygroscopic equilibrium of sunflower was obtained using three replicates containing 10 g, maintained under the specific drying conditions and periodically weighed until constant weight. 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 at certain drying time (decimal, d.b.);

X_i - initial moisture content of the product (decimal, d.b.); and,

X_e - equilibrium moisture content of the product (decimal, d.b.).

The drying kinetics of sunflower grains was represented by models frequently used to describe the drying of agricultural products, according to Table 1.

The mathematical models were fitted using nonlinear regression analysis by the Gauss-Newton method. The models were selected considering the magnitude of the coefficient of determination (R^2), chi-square test (χ^2), relative error (P) and estimated mean error (SE).

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

$$SE = \sqrt{\frac{\sum \left(Y - \hat{Y}\right)^2}{DF}} \tag{15}$$

$$\chi^2 = \frac{\sum \left(Y - \hat{Y}\right)^2}{DF} \tag{16}$$

where:

Y - experimental value;

Table 1. Mathematical models used to predict the drying of agricultural products

Model	Model designation	Eq.
Wang and Singh	$RX = 1 + at + bt^2$	(2)
Verma	$RX = a . \exp(-k . t) + (1 - a) \exp(-k_1 . t)$	(3)
Thompson	$RX = \exp\{[-a - (a^2 + 4 . b . t)^{0.5}]/2 .b\}$	(4)
Page	$RX = \exp(-k . t^n)$	(5)
Newton	$RX = \exp(-k . t)$	(6)
Midilli	$RX = a . \exp(-k . t^n) + b . t$	(7)
Logarithmic	$RX = a . \exp(-k . t) + c$	(8)
Henderson and Pabis	$RX = a . \exp(-k . t)$	(9)
Modified Henderson and Pabis	$RX = a . \exp(-k . t) + b . \exp(-k_0 . t) + c . \exp(-k_1 . t)$	(10)
Two-term exponential	$RX = a . \exp(-k . t) + (1 - a) \exp(-k . a . t)$	(11)
Two-term	$RX = a . \exp(-k_0 . t) + b . \exp(-k_1 . t)$	(12)
Approximation of diffusion	$RX = a . \exp(-k . t) + (1 - a) \exp(-k . b . t)$	(13)

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

$\hat{Y}$ - value estimated by the model;
N - number of experimental observations; and,
DF - degrees of freedom of the model (number of experimental observations minus the number of coefficients of the model).

The liquid diffusion model for the geometric form of infinite cylinder, with approximation of eight terms (Eq. 17), was fitted to the experimental data of sunflower grain drying, considering the superficial area, volume and radius, according to Eq. 17:

$$RX = \frac{X - X_e}{X_i - X_e} = \sum_{n=1}^{\infty} \frac{4}{\lambda_n^2} \exp\left[-\frac{\lambda_n^2 \cdot D \cdot t}{4} \cdot \left(\frac{2}{r} \right)^2 \right] \qquad (17)$$

where:
D - liquid diffusion coefficient, $m^2 s^{-1}$;
n - number of terms;
r - equivalent radius, m; and,
λ_n - roots of the Bessel's equation of zero order.

The equivalent radius of the grains was determined by Eq. 18:

$$r = \sqrt[3]{\frac{3 \cdot V_g}{4\pi}} \qquad (18)$$

where:
V_g - volume of grains, mm^3.

The volume of each grain (V_g) was obtained through the measurement of the three orthogonal axes (length, width and thickness), in fifteen grains, at the end of the drying, using a digital caliper with resolution of 0.01 mm, according to Eq. 19:

$$V_g = \frac{\pi \cdot A \cdot B \cdot C}{6} \qquad (19)$$

where:
A - length, mm;
B - width, mm; and,
C - thickness, mm.

The relationship between the increase in the effective diffusion coefficient and the increment in drying air temperature was described by the Arrhenius equation.

$$D = D_o \cdot \exp\left(\frac{-E_a}{R \cdot T_{ab}} \right) \qquad (20)$$

where:
Do - pre-exponential factor;
E_a - activation energy, kJ mol^{-1};
R - universal gas constant, 8,134 kJ $kmol^{-1}$ K^{-1}; and,
T_{ab} - absolute temperature.

The coefficients of the Arrhenius expression were linearized with the application of the logarithm as follows:

$$LnD = LnD_o - \frac{E_a}{R} \cdot \frac{1}{T_{ab}} \qquad (21)$$

Results and Discussion

For the temperatures of 35, 50, 65, 80 and 95 °C, the times of grain drying were equal to 10.3, 6.0, 3.6, 2.0 and 1.8 h, respectively, considering the reduction in moisture content from 0.5267 to 0.0934 (decimal, d.b.) (Figure 1).

It is also observed the influence of temperature on the drying curves of sunflower grains. The increase in drying air temperature leads to a higher rate of water removal from the product, due to a higher water vapor pressure between the grain and the air, reducing the time necessary to decrease the moisture content to the desired value, a fact also observed by many researchers for various products, such as soybean (Oliveira et al., 2014), cowpea (Morais et al., 2013) and for the grains of jatropha (Siqueira et al., 2013).

The coefficients of determination (R^2) showed values higher than 0.95 for all drying temperatures (Table 2), which does not

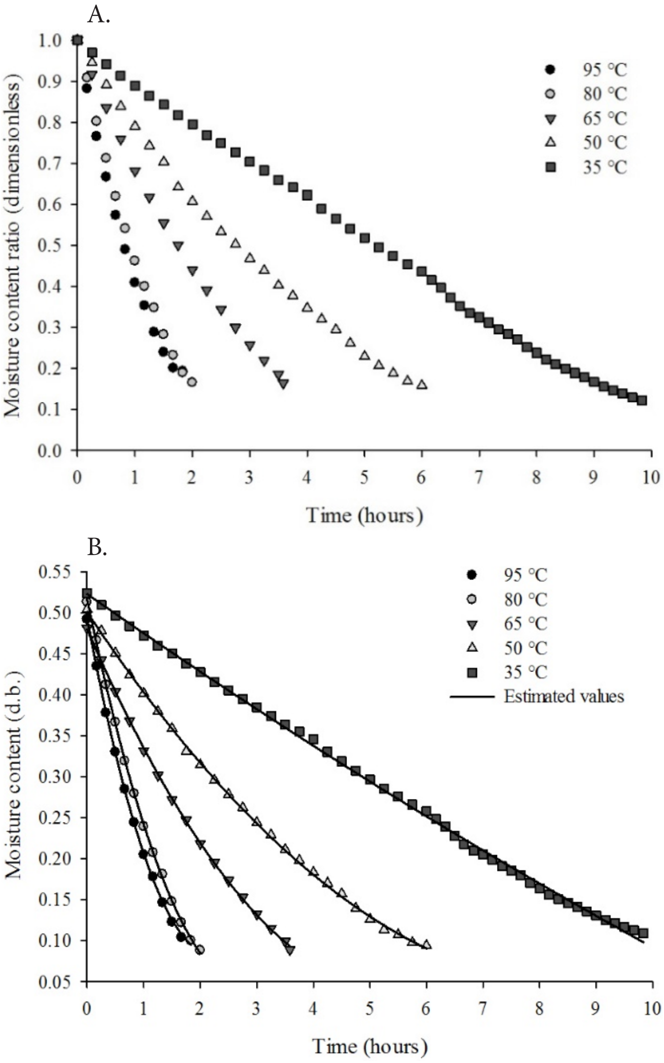

Figure 1. Experimental values of moisture content ratio (A) and drying curves with moisture contents obtained experimentally and estimated by the model Wang and Singh (B), for sunflower grains at temperatures of 35, 50, 65, 80 and 95 °C

indicate a satisfactory representation of the model, according to Madamba et al. (1996). For these researchers, the use of the coefficient of determination as the only criterion of evaluation for the selection of nonlinear models is not a good parameter to represent the drying phenomenon, which is the reason for the combined analysis of the other statistical parameters.

As observed in Table 2, the relative mean values for the models Wang and Singh, Verma, Page, Midilli, Logarithmic and Approximation of Diffusion were lower than 10% for all analyzed temperatures, which is considered as an adequate representation of the drying phenomenon by Mohapatra & Rao (2005).

In relation to the chi-square test (χ^2) (Table 3), the eleven models were within the confidence interval of 99%. However, comparing the magnitude of the values, only the models Wang and Singh, Verma, Page, Midilli, Logarithmic and Approximation of Diffusion exhibited lower values in comparison to the others, for all studied temperatures.

Based on the estimated mean error (SE) (Table 3), it is observed that the models Wang and Singh, Midilli and Logarithmic showed lower values in comparison to the others.

According to these statistical parameters, the models Wang and Singh, Midilli, Page Verma, Logarithmic and Approximation of Diffusion exhibited the best fits to the experimental data of sunflower drying.

The model Wang and Singh was used for the graphical representation of the drying curves (Figure 1B), because it is the simplest one, compared to others and also for the adjustment shown between the experimental and estimated values to describe the drying of sunflower grains.

Costa et al. (2011) fitted models to the experimental data of drying of crambe seeds at temperatures of 30, 40, 50, 60 and 70 ºC, and the equation of Wang and Singh showed the best fit among the evaluated models. Coradi et al. (2016) also found that the model of Wang and Singh proved to be adequate to describe the drying process of soybean grains at different temperatures (75, 90, 105 and 120 ºC).

Table 4 shows the coefficients of the Wang and Singh model fitted to the experimental data of sunflower drying kinetics at the different temperatures.

Figure 2A shows the effective diffusion coefficients for the sunflower grains, after drying under different air conditions. There was an increase in the effective diffusion coefficient of the sunflower grains with the increment in drying air temperature, which is consistent with the results obtained by other researchers (Goneli et al., 2007; Resende et al., 2008; Sousa et al. 2011).

The diffusivity is influenced by the drying air temperature, i.e., the higher the temperature, the lower the resistance of the grain to water removal, causing greater diffusivity. In addition, the linear model satisfactorily represented the experimental data.

The effective diffusion coefficients of sunflower grains showed magnitudes between 3.59 x 10^{-11} and 20.60 x 10^{-11} m^2 s^{-1}, which are close to the values observed by Sacilik (2007) in pumpkin seeds, 8.53 x 10^{-11} to 17.52 x 10^{-11} m^2 s^{-1} for the temperatures of 40, 50 and 60 °C.

This differs from the results of Almeida et al. (2009), who observed effective diffusion coefficients from 0.51 x 10^{-10} to 2.23 x 10^{-10} m^2 s^{-1} for the temperature range of 30 to 70 ºC, during

Table 2. Showed a better adjustment for the analyzed models, during the sunflower drying under various temperature (°C) conditions

Models	35 °C		50 °C		65 °C		80 °C		90 °C	
	P	R^2	P	R^2	P	R^2	P	R^2	P	R^2
Wang and Singh	2.70	0.9988	1.653	0.9992	1.01	0.9998	1.31	0.9996	1.55	0.9996
Verma	7.82	0.9897	1.275	0.9996	2.28	0.9989	1.85	0.9991	3.88	0.9955
Thompson	18.18	0.9512	6.847	0.9905	7.16	0.9894	7.30	0.9887	3.89	0.9955
Page	6.29	0.9915	3.343	0.9977	2.63	0.9984	1.56	0.9994	2.08	0.9992
Newton	18.18	0.9512	6.845	0.9905	7.16	0.9894	7.30	0.9887	3.88	0.9955
Midilli	2.46	0.9989	1.276	0.9996	0.61	0.9999	1.25	0.9997	2.06	0.9993
Logarithmic	2.78	0.9988	1.303	0.9996	0.65	0.9999	1.79	0.9993	2.59	0.9986
Henderson and Pabis	15.20	0.9639	5.781	0.9931	5.95	0.9925	5.92	0.9925	3.17	0.9969
Two-term exponential	18.18	0.9512	6.845	0.9905	7.16	0.9894	7.30	0.9887	3.88	0.9955
Two-term	15.20	0.9639	1.275	0.9996	5.95	0.9925	5.92	0.9925	1.97	0.9993
Approximation of diffusion	7.82	0.9897	1.275	0.9996	0.68	0.9999	7.30	0.9887	2.57	0.9986

Table 3. Estimated mean errors (SE) and Chi-square (χ^2) for the eleven models analyzed, during the sunflower drying under various temperature (°C) conditions

Models	35 °C		50 °C		65 °C		80 °C		90 °C	
	SE	χ^2 (10^{-3})	SE	χ^2 (10^{-3})	SE	χ^2 (10^{-3})	SE	χ^2 (10^{-3})	SE	χ^2 (10^{-3})
Wang and Singh	0.009	0.088	0.008	0.059	0.004	0.019	0.006	0.036	0.006	0.033
Verma	0.028	0.777	0.006	0.031	0.010	0.094	0.009	0.080	0.020	0.409
Thompson	0.060	3.606	0.026	0.662	0.029	0.817	0.031	0.958	0.019	0.368
Page	0.025	0.630	0.013	0.159	0.011	0.122	0.007	0.052	0.008	0.064
Newton	0.059	3.528	0.025	0.634	0.028	0.762	0.029	0.877	0.018	0.334
Midilli	0.009	0.084	0.006	0.032	0.003	0.008	0.005	0.028	0.009	0.076
Logarithmic	0.009	0.091	0.006	0.032	0.003	0.009	0.008	0.066	0.011	0.126
Henderson and Pabis	0.052	2.667	0.022	0.482	0.024	0.583	0.025	0.629	0.016	0.256
Two-term exponential	0.060	3.605	0.026	0.661	0.029	0.816	0.031	0.957	0.019	0.368
Two-term	0.053	2.788	0.006	0.032	0.026	0.680	0.028	0.769	0.009	0.073
Approximation of diffusion	0.028	0.777	0.006	0.031	0.003	0.009	0.032	1.053	0.011	0.128

Table 4. Coefficients of the Wang and Singh model fitted to sunflower drying under different conditions of air temperature with the respective equations

Coefficients	Temperature (°C)				
	35	50	65	80	95
a	-0.104642**	-0.216750**	-0.341480**	-0.641896**	-0.757550**
b	0.001388**	0.012765**	0.030975**	0.110398**	0.169871**

**Significant at 0.01by the t-test

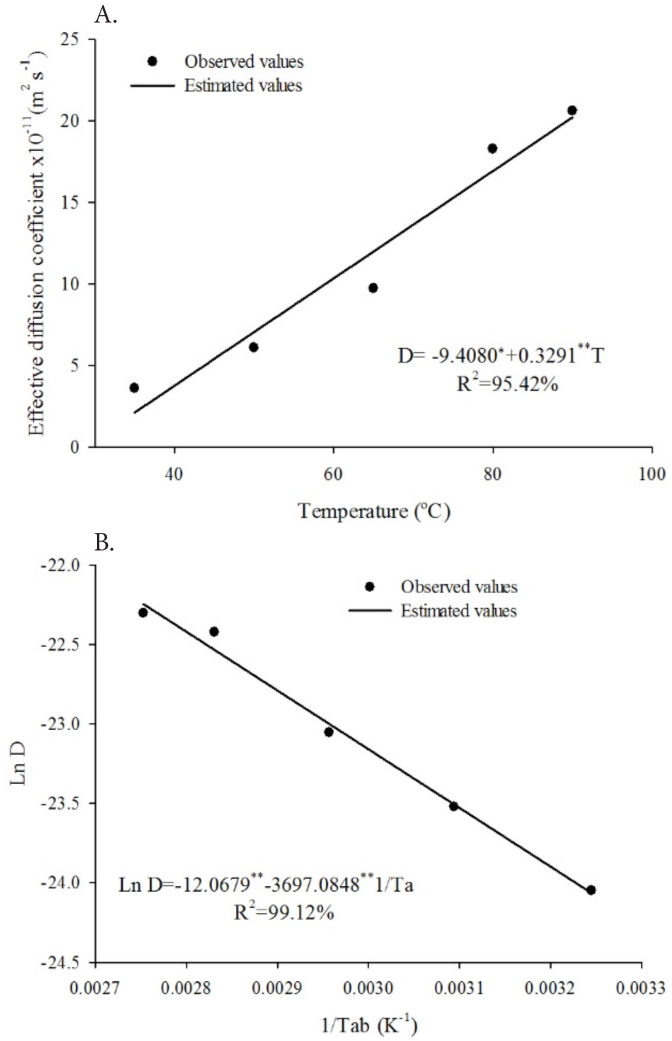

Figure 2. Effective diffusion coefficient and Arrhenius representation for the effective diffusion coefficient as a function of drying air temperature obtained during the drying of sunflower grains

the drying of adzuki beans. Such difference can be due to the difference of reserves found in the grains, because the higher the oil content in sunflower, the lower the energy required for water removal.

The dependence of the effective diffusion coefficient of sunflower grains in relation to the drying air temperature was represented by the expression of Ahrrenius, as illustrated in Figure 2B.

The activation energy for sunflower drying was 30.76 kJ mol^{-1} for the studied temperature range. According to Zogzas et al. (1996), the activation energy of agricultural products varies from 12.7 to 110 kJ mol^{-1}; thus, the observed value is within this range. The lower the activation energy, the higher the water diffusivity in the product, because the activation energy indicates the ease with which water molecules overcome the barrier of energy during their migration inside the product (Corrêa et al., 2007).

The values of activation energy vary for different agricultural products: wheat, 42.00 kJ mol^{-1} at temperatures from 25 to 55 °C (Goneli et al., 2007); adzuki beans, 31.16 kJ mol^{-1} at temperatures from 30 to 70 °C (Almeida et al., 2009); forage turnip, 24.78 kJ mol^{-1} at temperatures from 30 to 70 °C (Sousa et al., 2011).

It can be noted that the activation energy of sunflower grains is lower than that of wheat and adzuki beans, a behavior related to the more unstable bond of the water with the chemical compounds of the sunflower, since it is an oilseed crop, unlike wheat and beans, which are amylaceous and proteinaceous-amylaceous, respectively.

Conclusions

1. The drying time of sunflower grains decreased with the increase in drying temperature.

2. The Wang and Singh model was selected, for showing the best fits and being the simplest one to describe the phenomenon of drying of sunflower grains.

3. The effective diffusion coefficient for sunflower grains increases with the increment in air temperature during the drying and has activation energy of 29.55 kJ mol^{-1}.

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