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Kinetics and thermodynamic properties of the drying process of sorghum (*Sorghum bicolor* [L.] Moench) grains

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The goal of this work was to fit several mathematical models to the experimental data from the drying of sorghum (*Sorghum bicolor* [L.] Moench) grains of the AS4620 cultivar, to determine and evaluate the effective diffusion coefficient, to obtain the activation energy and to determine the thermodynamic properties of the drying process at different temperatures and air speeds. The initial moisture content of 0.228 ± 0.003 on a dry basis (d.b., decimal), were subjected to drying in an experimental dryer where the drying air speed was kept at either 0.5 or 1.0 m s^{-1}, and for each speed, the system was set to heat at 40, 50 and 60°C until the moisture contents reached 0.137 ± 0.004 (d.b.). The Page model was selected to represent the drying phenomenon. The effective diffusion coefficient of the sorghum grains increased as temperature and air speed increased, and the pattern can be described by the Arrhenius equation, which provides activation energy values for liquid diffusion in the sorghum drying process of 27.12 and 42.05 kJ mol^{-1} for air speeds of 0.5 and 1.0 m s^{-1}, respectively. When the drying temperature is increased, enthalpy and entropy decrease, whereas Gibbs free energy increases.

Key words: Mathematical modeling, activation energy, enthalpy, entropy, Gibbs free energy, *Sorghum bicolor* [L.] Moench, drying.

INTRODUCTION

Sorghum (*Sorghum bicolor* [L.] Moench) is a plant of African origin and is one of the main crops in the world's current agricultural scenario. Sorghum is the fifth most cultivated cereal in the world, only behind wheat, rice, corn and barley (EMBRAPA, 2011). Sorghum reaches physiological maturity with high moisture contents, in the 25 to 35% range, which can lead to product damage at the moment of drying. This challenge calls for studies of methods that prevent such damage to the grain (Vanderlip and Reeves, 1972)

Reducing the grain's moisture content after harvest allows the product to be safely stored. The drying method must be efficient while not affecting the grain's final quality because damage caused by inadequate drying is

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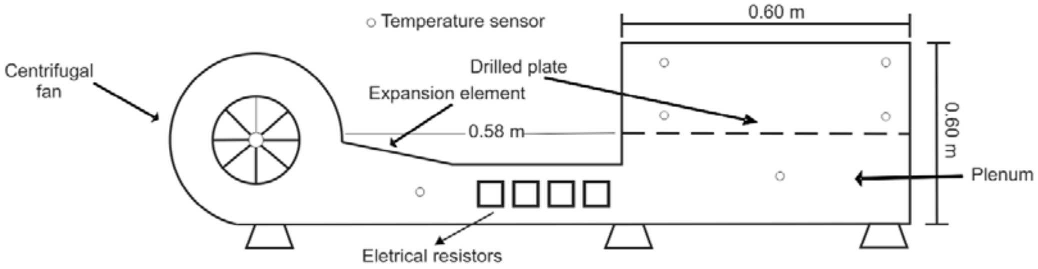

Figure 1. Side view of the experimental dryer.

notorious during the storage period. Agricultural product drying may be defined as a simultaneous process of heat and mass transfer between the product and the drying air, which consists of removing the excess moisture contained inside the grain through evaporation, usually promoted by forced convection of heated air, so that the product quality is maintained during a long storage period (Afonso Júnior and Corrêa, 1999).

The drying of hygroscopic products can be described using theoretical, semi-theoretical and empirical methods. In theoretical models, it is usual to take into consideration both the external conditions under which the operation takes place and the internal mechanisms of energy and mass transfer and their effects (Sousa et al., 2011). In semi-theoretical and empirical models, only the internal resistance, the temperature and the drying air's relative humidity are taken into consideration (Midilli et al., 2002).

Several authors have proposed that the main water-transport mechanism is liquid diffusion. This process is a complex mechanism due to the diversity of chemical composition and physical structure of grains. The data available in the literature present values that vary not only due to product diversity but also as a function of different estimation methods, type of material, moisture content, drying process and methodology used in obtaining the data (Corrêa et al., 2006). Knowledge of thermodynamic properties during the drying processes of agricultural products allows one to design drying equipment, to calculate the energy required in the process, to study the adsorbed water's properties, to evaluate the food microstructure and to study the physical phenomena that take place on the food surface (Corrêa et al., 2010). Because of the scarcity of studies in the literature that provide information on changes in sorghum moisture contents during drying, this work aimed to study the mathematical modeling of sorghum grains of the AS4620 cultivar and to obtain the diffusion coefficient, activation energy, enthalpy, entropy and Gibbs free energy under several temperatures and air speed conditions.

MATERIALS AND METHODS

Drying

The experiment was conducted in the Laboratory of Post-harvest Plant Products, Federal Institute of Education, Science and Technology of Goiás - Rio Verde Campus, using sorghum grains of the AS4620 cultivar originated from the Municipality of Rio Verde – Goiás, Brazil. Drying took place in a fixed-bed dryer built with a #16 gauge sheet metal. The drying chamber had the following dimensions: 0.60 x 0.60 x 0.60 m, for a total volume of 0.216 m^3, which contained a 25% perforation plate positioned at a 0.33 m height. The fan was a centrifugal type, powered by a 1.5 HP three-phase motor at 1,720 rpm, consisting of rotor, blades, volute and support. The drying chamber was connected to the fan by a 0.64 m long expansion element that transformed the fan's 0.20 x 0.20 m outlet into 0.57 x 0.03 m at the entrance of the drying chamber (Figure 1). Each drying unit was composed of 6 pendulum temperature sensors and four 1,500-watt electrical resistors, for a total of 6,000 watts. The sensors were positioned before and after the resistors and inside each tray. Four removable trays with perforated bottoms were placed inside the drying chamber, each measuring 0.28 x 0.28 x 0.15 m. The system also had an automated controller to manage the system and store the generated data.

The sorghum grains were wrapped in voile fabric and spread on the trays, forming a layer of approximately 0.06 m thickness. The drying air speed was set to either 0.5 or 1.0 m s^{-1}, and for each speed, the system was set to heat at 40 ± 2.3, 50 ± 1.4 and 60 ± 1.5°C. The relative humidity values inside the dryers for the 0.5 m s^{-1} air speed were 12.8, 8.3 and 5.3% at temperatures of 40, 50 and 60°C, respectively, whereas for the 1.0 m s^{-1} air speed, they were 15.0, 9.9 and 6.4% at temperatures of 40, 50 and 60°C, respectively.

The initial moisture content of the grains was 0.228 ± 0.003 on a dry basis (d.b., decimal). The drying process was only stopped when the grains' moisture content reached 0.137 ± 0.004 (d.b.), as assessed in a drying oven at 105 ± 1°C for 24 h, using three replicates (Brasil, 2009). The reduction of the moisture content throughout the drying process was monitored by the gravimetric method (mass loss), because the product's initial moisture contents were known, until the desired moisture contents were obtained, using a scale with 0.01 g precision.

The temperature and relative humidity of the environment outside the drying chamber were monitored using a psychrometer, using a thermometer with dry bulb and another with wet bulb, and the internal temperature was monitored using a thermometer installed inside the dryer. The relative humidity inside the dryer was obtained using basic psychrometric principles and the GRAPSI software. To compute the moisture content ratios of sorghum grains during the drying process, the following expression was used:

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

Where RX: Moisture content ratio of the product, dimensionless; X:

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

Model equation	Model name	Equation
$RX = a \cdot \exp(-k \cdot t) + (1-a) \cdot \exp(-k \cdot b \cdot t)$	Diffusion approximation	(2)
$RX = a \cdot \exp(-k_o \cdot t) + b \cdot \exp(-k_1 \cdot t)$	Two-term	(3)
$RX = a \cdot \exp(-k \cdot t) + (1-a)\exp(-k \cdot a \cdot t)$	Two-term exponential	(4)
$RX = a \cdot \exp(-k \cdot t)$	Henderson and Pabis	(5)
$RX = a \cdot \exp(-k \cdot t) + c$	Logarithmic	(6)
$RX = a \cdot \exp(-k \cdot t^n) + b \cdot t$	Midilli	(7)
$RX = \exp(-k \cdot t)$	Newton	(8)
$RX = \exp(-k \cdot t^n)$	Page	(9)
$RX = \exp\left(\left(-a - \left(a^2 + 4 \cdot b \cdot t\right)^{0.5}\right) / 2 \cdot b\right)$	Thompson	(10)
$RX = a \cdot \exp(-k \cdot t) + (1-a)\exp(-k_1 \cdot t)$	Verma	(11)
$RX = 1 + at + bt^2$	Wang and Sing	(12)

Where t: drying time, h; k, k_o, k_1: drying constants, h^{-1}; anda, b, c, n: model coefficients.

moisture content of the product (d.b., decimal); X_i: initial moisture content of the product (d.b., decimal); and X_e: equilibrium ratio content of the product (d.b., decimal).

To obtain the equilibrium moisture content of the sorghum grains for each drying condition, four replicates with 15 g each were used, each weighed until they reached a constant mass.

Mathematical modeling

The experimental data from drying sorghum grains were fitted to the mathematical models that are frequently used to represent the drying of agricultural products, as shown in Table 1 giving Equation (2) to (12). The mathematical models were fitted using the Gauss-Newton method for nonlinear regression analysis using a software Statistica 7.0. The models were selected based on the magnitudes of the coefficient of determination (R^2), the chi-squared test (χ^2), the mean relative error (MRE) and the standard error of the estimate (SEE). One of the criteria used in selecting the models was the mean relative error value being below 10%, in accordance with Mohapatra and Rao (2005).

$$MRE = \frac{100}{N} \sum \frac{\left|Y - \hat{Y}\right|}{Y} \tag{13}$$

$$SEE = \sqrt{\frac{\sum \left(Y - \hat{Y}\right)^2}{DF}} \tag{14}$$

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

Where Y: experimental value; Ŷ: value estimated by the model; N: number of experimental observations; DF: degrees of freedom of the model (number of experimental observations minus the number of model coefficients).

Drying kinetics

The liquid diffusion model for a spherical geometry, using an 8-term approximation (Equation 16), was fitted to the experimental data for sorghum grain drying using the following expression:

$$RX = \frac{X - X_e}{X_i - X_e} = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left[-\frac{n^2 \cdot \pi^2 \cdot D \cdot t}{{R_e}^2}\right] \tag{16}$$

Where RX: Moisture content ratio of the product, dimensionless; t: time, s; n: number of terms; π: pi, 3.14159; D: liquid diffusion coefficient, $m^2 s^{-1}$; and R_e: equivalent radius, m.

The equivalent radius is defined as the radius of a sphere of volume equivalent to that of the grain. The volume of each grain (V_g) was obtained by measuring the three orthogonal axes (length, width and thickness) of fifteen grains, after drying, using a digital caliper with 0.01 mm precision, according to the following expression:

$$V_g = \frac{\pi \cdot A \cdot B \cdot C}{6} \tag{17}$$

Where: V_g: grain volume, mm^{-3}; A: length, mm; B: width, mm; and C: thickness, mm.

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

$$D = D_o \cdot \exp\left(\frac{-E_a}{R \cdot T_{ab}}\right) \tag{18}$$

Table 2. Moisture content ratio (RX, decimal) for sorghum grains (*S. bicolor* [L.] Moench), AS4620 cultivar, over the drying time (h) under two air speed conditions (m s^{-1}) and three temperature conditions (°C).

0.5 m s^{-1}						1.0 m s^{-1}					
40°C		50°C		60°C		40°C		50°C		60°C	
Time	**RX**	**Time**	**RX**	**Time**	**RX**	**Time**	**RX**	**Time**	**RX**	**Time**	**RX**
0.00	1.00	0.00	1.00	0.00	1.00	0.00	1.00	0.00	1.00	0.00	1.00
0.32	0.93	0.32	0.91	0.32	0.89	0.17	0.92	0.10	0.88	0.10	0.86
0.48	0.88	0.48	0.84	0.48	0.81	0.33	0.87	0.27	0.80	0.27	0.77
0.65	0.84	0.65	0.77	0.65	0.77	0.50	0.80	0.43	0.71	0.43	0.65
0.82	0.81	0.82	0.73	0.82	0.68	0.67	0.74	0.60	0.64	0.57	0.59
0.98	0.77	0.98	0.67	0.98	0.61	0.92	0.67	0.77	0.57	0.67	0.56
1.15	0.73	1.15	0.62	1.15	0.55	1.07	0.64	0.93	0.52		
1.33	0.70	1.33	0.58	1.33	0.52	1.23	0.60				
1.48	0.67	1.48	0.54			1.40	0.57				
1.65	0.64	1.65	0.51			1.57	0.54				
1.90	0.61					1.90	0.51				
2.15	0.57										
2.40	0.54										
2.65	0.51										
2.90	0.48										

Where: D_o: 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, K.

Thermodynamic properties

The thermodynamic properties of the drying process of sorghum grains were obtained using the method described by Jideani and Mpotokwana (2009):

$$\Delta H = E_a - R \cdot T \tag{19}$$

$$\Delta S = R \cdot \left(\ln k - \ln \frac{k_B}{h_p} \right) - \ln T_{ab} \tag{20}$$

$$\Delta G = \Delta H - T_{ab} \cdot \Delta S \tag{21}$$

Where: ΔH = enthalpy, J mol^{-1}; ΔS = entropy, J mol^{-1}; ΔG = Gibbs free energy, J mol^{-1}; k_B = Boltzmann's constant, 1.38 x 10^{-23} J K^{-1}; and h_p = Planck's constant, 6.626 x 10^{-34} J s^{-1}.

RESULTS AND DISCUSSION

Mathematical modeling

Table 2 shows the mean moisture content ratios for sorghum grains of the AS4620 cultivar dried under different temperature and air speed conditions. The time taken for the moisture content of the grains to reach 0.137 ± 0.004 (d.b., decimal) was 2.90, 1.65 and 1.33 h for drying temperatures of 40, 50 and 60°C, respectively, and an air speed of 0.5 m s^{-1}. For the air speed of 1.0 m s^{-1}, the time taken for the moisture content to reach the same value was 1.90, 0.93 and 0.67 h at drying temperatures of 40, 50 and 60°C, respectively.

The results show that increasing temperature and air speed leads to reduced grain-drying time. Reductions in drying time are related to larger differences between the vapor pressures of the drying air and of the product due to increased temperature and air speed, causing water to be removed faster and more easily, a relation that has been observed by several authors in countless products (Babalis et al., 2006; Menges and Ertekin, 2006; Sousa et al., 2011; Oliveira et al., 2012; Vega-Gálvez et al., 2012).

Table 3 lists the values for the coefficient of determination (R²) and mean relative error (MRE) of the eleven models fitted to the drying of sorghum grains of the AS4620 cultivar at the different temperatures and air speeds.

According to Table 3, the values of the coefficients of determination (R²) were higher than 97% for all of the drying temperatures and air speeds in all of the models under evaluation. This result is indicative of a satisfactory representation of the studied phenomenon, according to Kashaninejad et al. (2007). Furthermore, the mean relative error (MRE) value was below 10% for all of the models and all six of the testing conditions, which indicates the models are adequate to represent the drying phenomenon, according to Mohapatra and Rao (2005). Table 4 shows the chi-squared (χ^2) and estimated mean error (SEE) values obtained for the various fitted models and drying conditions for sorghum grains of the

Table 3. Coefficient of determination (R², %) and mean relative error (MRE, %) for the analyzed models during drying of sorghum (*S. bicolor* [L.] Moench) grains of the AS4620 cultivar at two air speed conditions (m s^{-1}) and three temperature conditions (°C).

Models	0.5 m s^{-1}						1.0 m s^{-1}					
	40°C		50°C		60°C		40°C		50°C		60°C	
	R^2	MRE	R^2	MRE	R^2	MRE	R^2	MRE	R^2	MRE	R^2	MRE
2	99.92	0.46	99.11	1.03	99.39	1.65	99.84	0.73	99.95	0.42	98.84	0.97
3	99.93	0.45	99.97	0.69	98.87	1.90	99.96	0.35	99.95	0.42	99.71	0.97
4	99.91	0.50	99.86	1.03	99.60	1.36	99.70	1.06	99.65	0.66	97.13	2.75
5	99.87	0.72	99.58	0.75	98.87	1.90	98.94	1.86	98.92	1.58	98.19	2.24
6	99.93	0.46	99.84	0.69	99.43	1.64	99.85	0.75	99.36	1.13	99.14	1.28
7	99.95	0.41	99.97	0.42	99.73	0.96	99.92	0.54	99.88	0.67	99.63	1.11
8	99.87	0.72	99.11	1.03	98.43	2.29	98.59	2.15	97.93	2.26	97.13	2.75
9	99.89	0.58	99.95	0.55	99.63	1.29	99.54	1.35	99.68	0.91	99.54	1.00
10	99.91	0.51	99.86	1.03	98.43	2.29	99.72	1.01	99.40	1.26	99.34	1.17
11	99.92	0.46	99.97	0.72	99.68	1.12	99.96	0.35	99.95	0.42	99.71	0.97
12	99.93	0.45	99.62	0.67	99.39	1.65	99.95	0.42	98.84	1.45	98.72	1.47

Table 4. Values of the chi-squared test (χ^2, decimal x10^{-4}) and estimated mean error (decimal, SEE) computed for the ten models used in the kinetic representation of the drying process of sorghum (*S. bicolor* [L.] Moench) grains of the AS 4620 cultivar.

Models	0.5 m s^{-1}						1.0 m s^{-1}					
	40°C		50°C		60°C		40°C		50°C		60°C	
	SEE	χ^2	SEE	χ^2	SEE	χ^2	SEE	χ^2	SEE	χ^2	SEE	χ^2
2	0.0048	0.23	0.0124	1.55	0.0155	2.41	0.0073	0.53	0.0047	0.22	0.0119	1.41
3	0.0046	0.22	0.0088	0.78	0.0236	5.57	0.0039	0.16	0.0054	0.29	0.0145	2.11
4	0.0050	0.25	0.0116	1.35	0.0115	1.32	0.0096	0.92	0.0111	1.24	0.0321	10.33
5	0.0060	0.36	0.0090	0.81	0.0193	3.72	0.0179	3.20	0.0195	3.79	0.0255	6.51
6	0.0046	0.21	0.0082	0.68	0.0151	2.27	0.0071	0.51	0.0168	2.81	0.0203	4.11
7	0.0040	0.16	0.0045	0.20	0.0103	1.07	0.0051	0.26	0.0072	0.52	0.0133	1.76
8	0.0058	0.34	0.0110	1.20	0.0210	4.43	0.0196	3.83	0.0246	6.05	0.0287	8.26
9	0.0055	0.31	0.0065	0.42	0.0111	1.23	0.0118	1.38	0.0105	1.11	0.0129	1.67
10	0.0050	0.25	0.0116	1.35	0.0227	5.17	0.0092	0.84	0.0145	2.11	0.0154	2.38
11	0.0048	0.23	0.0090	0.80	0.0112	1.27	0.0038	0.15	0.0047	0.22	0.0119	1.41
12	0.0044	0.19	0.0081	0.65	0.0142	2.00	0.0039	0.15	0.0202	4.07	0.0215	4.60

AS4620 cultivar.

The eleven models analyzed herein yielded low estimated mean error (SEE) values, which is relevant in obtaining a good fit of the model to the experimental data. Regarding chi-squared values, all of the models displayed adequate values for representing the phenomenon being studied. However, Günhan et al. (2005) note that lower chi-squared values are associated to better goodness-of-fit. The chi-squared values were lower, in general, for the Midilli (7), Page (9) and Verma (11) models.

The models analyzed herein provide a satisfactory representation of the drying phenomenon for sorghum grains of the AS4620 cultivar. Among the models showed good fits to the experimental data, the Page model was selected to represent the phenomenon of drying the beans due to its simplicity of implementation and for being traditionally recommended and applied to predict the phenomenon of drying various agricultural products (Afonso Júnior and Corrêa, 1999; Resende et al., 2011; Siqueira et al., 2013).

Figure 2 shows the drying curves for sorghum grains of the AS4620 cultivar under the studied conditions, plotting Page model estimates over the experimental data. The figure indicates that the model satisfactorily fits the experimental values obtained throughout the drying of sorghum grains. Menges and Ertekin (2006) ascertained that the Midilli model satisfactorily represented apple drying using prototype drying at 60, 70 and 80°C temperatures and 1, 2 and 3 m s^{-1} air speeds. Table 5 shows the values for the "k" and "n" coefficients of the Page model fitted to the experimental data for sorghum

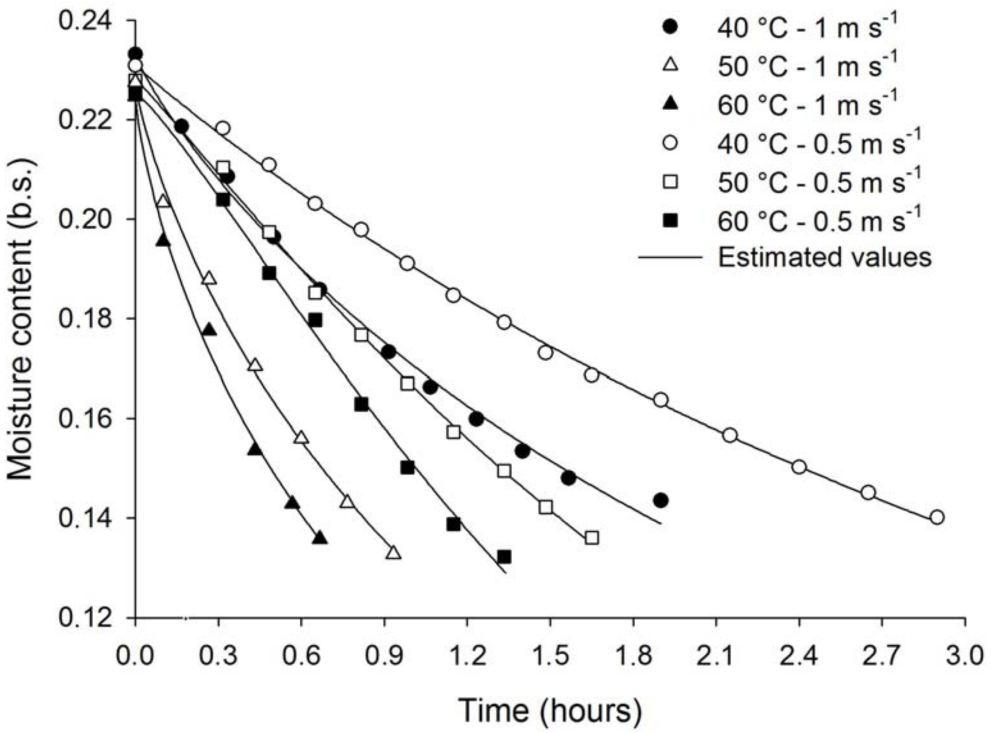

Figure 2. Drying curves, experimental values and Page model estimates for sorghum (*S. bicolor* [L.] Moench) grains of the AS4620 cultivar under two air speed conditions (0.5 and 1.0 m s^{-1}) and three drying temperatures (40, 50 and 60°C).

grain-drying kinetics at different temperatures and air speeds.

The magnitude of the Page model drying constant "k", which represents the effects of external drying conditions and tends to increase with increasing drying air temperature, increased as the drying temperature and air speed increased. Siqueira et al. (2013) studied the drying of fruits of *Jatropha curcas* L., found the same behavior. Also, the Page model coefficient "n" increased as the air temperature was increased at a speed of 0.5 m s^{-1}, but it decreased at a speed of 1.0 m s^{-1} (Table 3). According to Corrêa et al. (2007), this coefficient represents the internal resistance of the product to drying. Resende et al. (2011), while studying the drying of *Jatropha curcas* L. seeds, found that there was no well-defined trend for the "n" coefficient, a behavior also observed in its relation to the air speed of the drying process of sorghum grains. Thus, the drying of sorghum grains of the AS4620 cultivar can be estimated, within the temperature and air speed ranges studied herein, using the following expressions:

$$RX_{0.5} = \exp\left(-\left(-0.1631 + 0.0109T\right)\cdot t^{\left(0.5326+0.0112T\right)}\right) \tag{22}$$

$$RX_{1.0} = \exp\left(-\left(-0.3058 + 0.0186T\right)\cdot t^{\left(1.0834-0.0057T\right)}\right) \tag{23}$$

Where: T = drying temperature (°C), t = drying time (h).

Drying kinetics

Figure 3 shows the values for the effective diffusion coefficient of sorghum grains as a function of the drying air conditions.

The calculated equivalent radius was 1.69 x 10^{-3} m. The effective diffusion coefficient increased linearly with increasing drying temperature and air speed, and its values were 0.638 x 10^{-11}, 0.968 x 10^{-11} and 1.11 x 10^{-11} for the speed of 0.5 m s^{-1} at temperatures of 40, 50 and 60°C, respectively. For an air speed of 1.0 m s^{-1}, the effective diffusion coefficient values were 1.024 x 10^{-11}, 1.859 x 10^{-11} and 2.355 x 10^{-11} m^2 s^{-1} for temperatures of 40, 50 and 60°C, respectively, indicating greater intensity in water transport from the grain's interior to its periphery, as previously found by Sousa et al. (2011) and Resende et al. (2009). Madamba et al. (1996) stressed that effective diffusion coefficients have an order of magnitude of 10^{-11} to 10^{-9} m² s^{-1}.

Faria et al. (2012), in a study of the drying of crambe (*Crambe abyssinica*) seeds, found values different to those in the present work, on the order of 0.18 x 10^{-10} to 3.92 x 10^{-10} m^2 s^{-1} for temperatures between 30 and 70°C. Moreover, Oliveira et al. (2012) found effective diffusion coefficient values between 1.54 x 10^{-13} and 4.58 x 10^{-13} m^2 s^{-1} for maize grains of the AG 7088 cultivar. These differences in diffusivity may be due to the

Table 5. Coefficients of the Page model fitted for the various drying conditions of sorghum grains of the AS4620 cultivar.

Coefficients	0.5 m s^{-1}			Mean values	R^2 (%)
	40°C	50°C	60°C		
k	0.26432**	0.39832**	0.4822**	k = - 0.1631+0.0109T	98.27
n	0.97962**	1.09422**	1.20357**	n = 0.5326+0.0112T	99.98
	1.0 m s-1				
	40°C	50°C	60°C		
k	0.41531**	0.67531**	0.78812**	k = - 0.3058+0.0186T	95.06
n	0.8606**	0.79327**	0.74743**	n = 1.0834-0.0057T	98.81

**Significant at 1% based on a t-test.

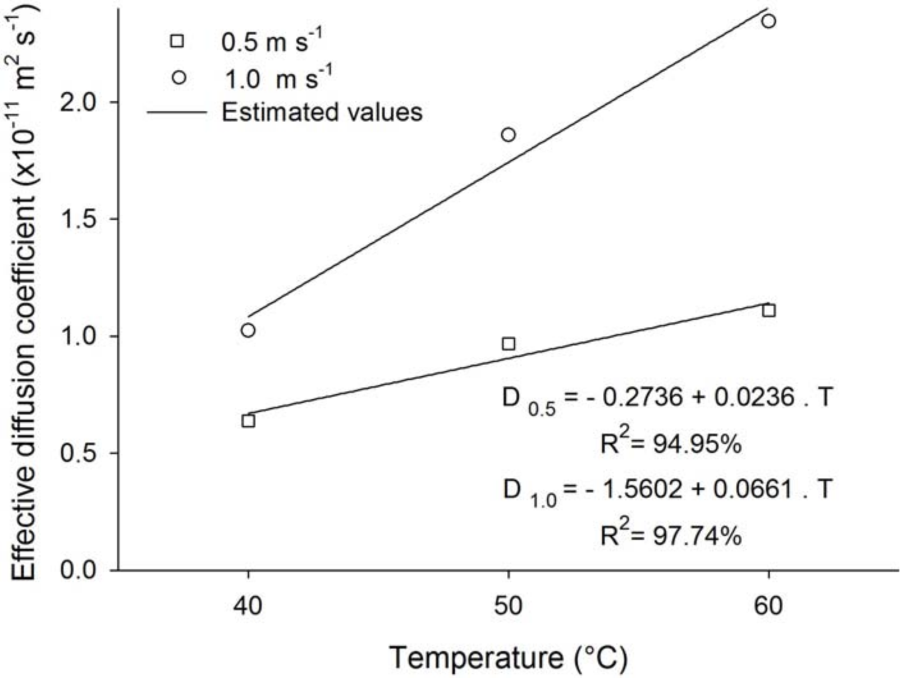

Figure 3. Mean values for the effective diffusion coefficient (m^2 s^{-1}) obtained for the drying of sorghum grains of the AS4620 cultivar under two air speed conditions (0.5 and 1.0 m s^{-1}) and three drying temperatures (40, 50 and 60°C).

chemical composition because maize and sorghum crops are rich in carbohydrates, while crambe is rich in lipids. For the product to dry, the water inside the grain must go through the layers of the various cellular tissues of which it is composed, that is, depending on the chemical composition of these layers, the product will display different characteristics. The dependency of the effective diffusion coefficient in sorghum grains of the AS4620 cultivar on the drying air temperature and speed was represented using an Arrhenius expression, as depicted in Figure 4.

Activation energy may be defined as the ease with which water molecules overcome the energy barrier while migrating from a product's interior to its exterior (Corrêa et al., 2005). The activation energy values for liquid diffusion in sorghum grains of the AS4620 cultivar were 27.12 and 42.05 kJ mol^{-1} at speeds of 0.5 and 1.0 m s^{-1}, respectively, for the temperature range from 40 to 60°C. According to Zogzas et al. (1996), the activation energy for agricultural products varies between 12.7 and 110 kJ.mol^{-1}, and the values obtained in the present study are within this range. Morais et al. (2013) found an activation energy value of 27.16 kJ mol^{-1} for cowpea grains drying at temperatures of 25, 35, 45 and 55°C, whereas Resende et al. (2011) and Oliveira et al. (2012), while evaluating the drying of *J. curcas* L. seeds and maize grains, observed activation energy values of 15.781 and 19.09 kJ.mol^{-1}, respectively.

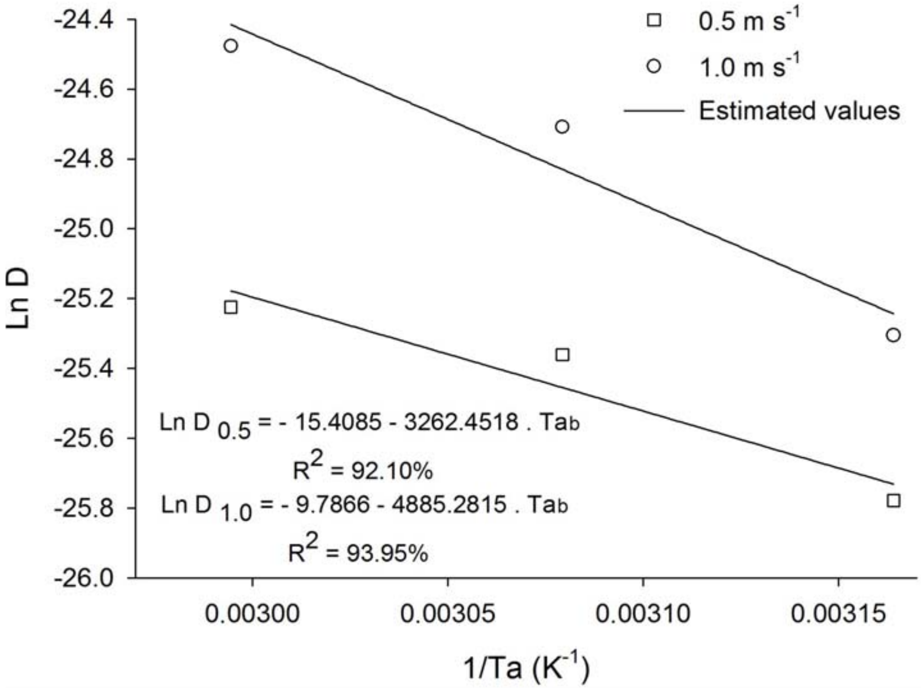

Figure 4. Arrhenius representation of the effective diffusion coefficient for the drying of sorghum (*S. bicolor* [L.] Moench) grains of the AS4620 cultivar under two air speed conditions (0.5 and 1.0 m s^{-1}) and three drying temperatures (40, 50 and 60°C).

Table 6. Enthalpy (ΔH, J mol^{-1}), entropy (ΔS, J mol^{-1} K^{-1}) and Gibbs free energy (ΔG, J mol^{-1}) values for the various air-drying conditions applied to sorghum (*S. bicolor* [L.] Moench) grains of the AS4620 cultivar.

Thermodynamic properties	Temperature (°C)					
	0.5 m s^{-1}			1.0 m s^{-1}		
	40	50	60	40	50	60
ΔH	24520.9	24437.8	24354.6	39450.4	39367.2	39284.1
ΔS	-256.4	-253.2	-251.9	-252.6	-248.8	-247.8
ΔG	104805.4	106268.7	108272.9	118558.4	119779.8	121841.6

Thermodynamic properties

Comparing the various drying conditions, the enthalpy and entropy decrease and Gibbs free energy increases as the drying temperature is increased (Table 6). Further, for sorghum grains of the AS4620 cultivar during moisture removal, the enthalpy value decreased as the drying temperature increased, showing that lower temperatures require larger amounts of energy. According to Goneli et al. (2010), entropy is a thermodynamic property that can be associated with the degree of disorder between the water and the product. The results showed that entropy, in absolute scale, decreased when the drying air temperature increased. According to Corrêa et al. (2010), this behavior was expected because a lower drying temperature means lower excitation of the water molecules in the product, thus increasing the order in the water-product system. The negative entropy values are related to the existence of chemical adsorption and / or structural changes of the adsorbent (Moreira et al., 2008).

Gibbs free energy is related to the work required to make sorption sites available (Nkolo Meze’e et al., 2008). This parameter can be positive for endogenous reactions, which require energy to be added from the environment in which the phenomenon takes place, or negative when the phenomenon spontaneously occurs without energy being added. The Gibbs free energy value for the sorghum grains was positive and increased as the drying temperature was increased. This behavior was also observed by Corrêa et al. (2011) while studying the thermodynamic properties of corn ears at temperatures of

45, 55 and 65°C.

Conclusion

The models analyzed herein provide a satisfactory representation of the drying of sorghum grains of the AS4620 cultivar at the various temperature and air-speed values assessed, and the Page model was selected from the different models due to its simplicity. The effective diffusion coefficient increases as the drying temperature and air speed increase, and the pattern can be described by the Arrhenius equation. The activation energy values of sorghum grains of the AS4620 cultivar were 27.12 and 42.05 kJ.mol^{-1} for air speeds of 0.5 and 1.0 m s^{-1}, respectively. Enthalpy and entropy decrease as the drying temperature is increased, and entropy was negative at all of the temperatures studied. Gibbs free energy values were positive at all of the temperatures analyzed, and these values increased when the drying temperature increased.

Conflict of Interest

The authors have not declared any conflict of interest.

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