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Influência das propriedades físicas e químicas de grãos de soja no processo de secagem

Influence of physical and chemical properties of soybean grains on drying process

Influencia de las propiedades físicas y químicas de la soja en el proceso de secado

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Thiago Aurélio Arruda Silva
ORCID: https://orcid.org/0000-0001-8280-7454
Universidade Federal do Mato Grosso, Brasil
E-mail: thiagoarruda@ufmt.br
Nahyara Batista Caires Galle
ORCID: https://orcid.org/0000-0003-2821-7183
Universidade Federal do Mato Grosso, Brasil
E-mail: nahyarac@hotmail.com
Carlos Caneppele
ORCID: https://orcid.org/0000-0002-6678-371X
Universidade Federal do Mato Grosso, Brasil
E-mail: thiagoarruda@ufmt.br
Niédja Marizze Cezar Alves
ORCID: https://orcid.org/0000-0003-0677-590X
Universidade Federal do Mato Grosso, Brasil
E-mail: niedjamarizze@yahoo.com.br

Resumo

A secagem de grãos pode ser influenciada por muitos fatores e o conhecimento enérgico desse processo é essencial. O objetivo foi avaliar a influência das propriedades de grãos de soja na cinética de secagem e propriedades termodinâmicas. Procedeu-se o estudo de quatro cultivares de soja, através da esfericidade, circularidade, volume, teor de óleo, proteína total e umidade inicial, em delineamento inteiramente casualizado. A secagem foi realiza para as temperaturas de 40 e 60 °C, ajustando-se seis modelos matemáticos. Pelos critérios estatísticos diferentes modelos foram selecionados às cultivares, os quais foram empregados nos cálculos das propriedades termodinâmicas. A cultivar C, de menor volume, apresentou maior taxa de secagem e maior constante k, que apresentou menor energia de ativação 23,81 kJ mol-1. As propriedades termodinâmicas de entalpia, entropia e energia livre de Gibbs foram influenciadas principalmente pelo volume, sendo menores para cultivar C.

Palavras-chave: *Glycine max*; Page; Entalpia; Entropia; Volume de grãos; Energia.

Abstract

Grain drying can be influenced by many factors and energetic knowledge of this process is essential. The objective was to evaluate the influence of soybean grain properties on drying kinetics and thermodynamic properties. Four soybean cultivars were studied through sphericity, circularity, volume, oil content, total protein and initial moisture in a completely randomized design. Drying was performed at temperatures of 40 and 60 °C, adjusting six mathematical models. By the statistical criteria different models were selected to the cultivars, which were used in the thermodynamic properties' calculations. The cultivar C with lower volume presented higher drying rate and higher constant k, which presented lower activation energy 23.81 kJ mol-1. The thermodynamic properties of Gibbs enthalpy, entropy and free energy were mainly influenced by volume, being lower for cultivar C.

Keywords: *Glycine max*; Page; Enthalpy; Entropy; Grain volume; Energy.

Resumen

El secado de los granos puede estar influenciado por muchos factores y el conocimiento energético de este proceso es esencial. El objetivo fue evaluar la influencia de las propiedades de la soya en la cinética de secado y las propiedades termodinámicas. Se estudiaron cuatro cultivares de soja utilizando esfericidad, redondez, volumen, contenido de aceite, proteína total y humedad inicial, en un diseño completamente al azar. El secado se realizó a temperaturas de 40 y 60 °C, ajustando seis modelos matemáticos. Por criterios estadísticos, se seleccionaron diferentes modelos para los cultivares, que se utilizaron en los cálculos de las propiedades termodinámicas. El cultivar C, de menor volumen, mostró una tasa de secado más alta y una constante k más alta, que mostró una energía de activación más baja 23.81 kJ mol-1. Las propiedades termodinámicas de entalpía, entropía y energía libre de Gibbs fueron influenciadas principalmente por el volumen, siendo menor para el cultivar C.

Palabras clave: *Glycine max*; Page; Entalpía; Entropía; Volumen de grano; Energía.

1. Introduction

Soy (*Glycine max* L. Merrill) is among the major cereals produced in the world, along with corn, wheat and rice (Borges et al., 2018). Grains are processed by agribusiness as raw material for vegetable oil production, biofuel, animal feed, chemical and food industries (Botelho et al., 2018). The projected production for the 2019/20 crop is 347.04 million tons of which 30.15% in the United States and 35.44% in Brazil, making them the largest soybean countries (United States Department of Agriculture, 2019).

The harvest of this crop is concentrated in a period of the year, so that there is the temporal spacing of the grains, storage is necessary. However, as the harvest water content is usually between 16 and 18%, the product must be dried prior to storage (Coradi et al., 2016). Drying is a thermodynamic, heat and mass transfer process that removes water from grains, reducing the action of storage degrading agents such as microorganisms and chemical reactions (Darvishi et al., 2015).

Drying behavior is influenced by numerous factors. Among those that are inherent to the material to be dried, one can mention the structure, chemical constituents, porosity, diameter, etc. (Yogendrasasidhar & Pydi Setty, 2018). Given these factors, sizing, planning and optimization of drying systems is essential for commercial viability. One tool for this study is the use of mathematical simulations (Correa et al., 2010).

Another important aspect of drying today is energy (Yogendrasasidhar & Pydi Setty, 2018). One source of information regarding the energy required in the process is thermodynamic properties, which further describe properties such as adsorbed water, product microstructure and the physical phenomena that occur in the surface area of the product (Oliveira et al., 2014).

The objective of this research was to evaluate the influence of physical and chemical properties of soybean on the drying kinetics curves for five hours, as well as the energetic characteristics through thermodynamic properties.

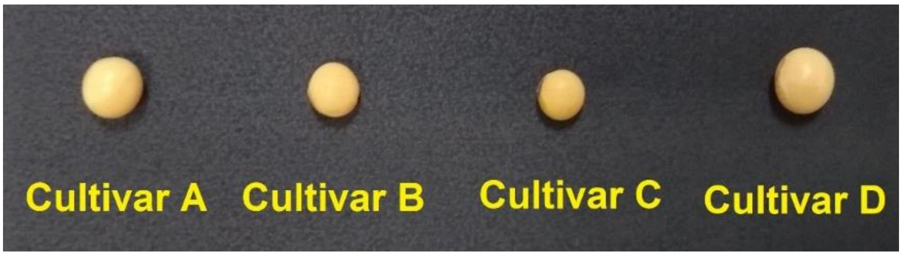
2. Materials and Methods

The present study is a quantitative investigation regarding the influence that physical properties (size, shape, volume, etc.) and chemical (nutritional constituents) have on the process of removing water from soybeans, which is a essential technique and widely used in agro-industries and farms.

The experiment was conducted in a laboratory of the Center for Storage Technology, Faculty of Agronomy and Zootechnics, Federal University of Mato Grosso, Campus Cuiabá-MT. The soybeans were provided by Tropical Genetic Improvement, coming from the Bela Vista do Paraíso Experimental Farm, located in the municipality of Rondonópolis-MT, latitude 16 ° 23'30 "S, longitude 54 ° 29 '59" W.

The cultivars employed were: TMG 7067 IPRO, TMG 7058 IPRO, TMG 2185 IPRO and TMG 7370 IPRO, in the present work denominated cultivar A, Cultivar B, Cultivar C and Cultivar D, respectively (Figure 1).

Figure 1. Grains of soybean cultivars A, B, C and D.



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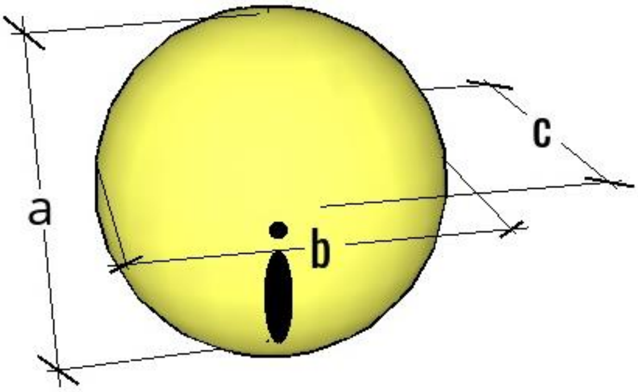
From Figure 1, one can notice the physical differences in soybeans from different cultivars. For physical characterization of grains, size and shape were analyzed by measuring the three grain size axes (a, b and c) using a digital caliper (Figure 2). For this analysis, the measurements were determined in 30 repetitions for each cultivar.

Figure 2. Schematic representation of the characteristic axes of soybean seeds used in size and shape calculations.



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The Figure 2 demonstrate the three basic measures measured in each soybean grain, in order to obtain its physical properties. From the measurements, the volume (Vg), sphericity (Es) and Circularity (Cr) measurements were calculated using Equations 1, 2 and 3, respectively, according to Mohsenin (1986) methodology.

$$V_g = \frac{\pi \cdot a \cdot b \cdot c}{6} \tag{1}$$

$$E_s = \left[\frac{(a \cdot b \cdot c)^{1/3}}{a} \right] \cdot 100 \tag{2}$$

$$C_r = \frac{c}{a} \cdot 100 \tag{3}$$

Where: Vg: grain volume, mm^3; a: largest grain axis, mm; b: average grain axis, mm; c: smallest grain axis, mm; E_s: sphericity, %; C_r: circularity, %.

To determine the chemical composition, lipid content and total protein - nutritional analysis - four replications were performed using the Spectra Alyser Premium analytical equipment (Zeutec GmbH, Germany) using Near Infrared (NIR).

In order to verify significant differences in the cultivars characterization data, a completely randomized design (CRD) statistical analysis was performed. First, the normality of the data was studied through the Shapiro-Wilk test. Data that presented normality were submitted to the Tuckey test. Nonparametric variables were evaluated by Kruskal-Wallis tests. All analyzes were studied at 5% significance in Assistat 7.7 software (Silva & Azevedo, 2016).

Drying was performed in a thin layer in a forced circulation oven with four replications at 40 and 60 ° C. Water loss was monitored at times 0, 10, 30, 60, 90, 120, 150, 210, 270 and 300 minutes by weighing the repetitions on an analytical balance, accurate to 0.001 g. After that, the humidity was determined by submitting the samples at 105 ° C for 24 h. Drying curves were plotted by converting mass loss data in terms of moisture ratio (Equation 4).

$$MR = \frac{M - M_e}{M_0 - M_e} \tag{4}$$

Where: M: product moisture at time t, dry basis, %; M_0: moisture at time zero, dry basis, %; M_e: equilibrium moisture, dry basis,%.

Experimental moisture ratio values, as a function of time, were adjusted to six mathematical models to predict drying in agricultural products (Table 1). The adjustments were made using Sigmaplot 14.0 software.

Table 1. Description of the models employed in adjusting the drying kinetics of soybeans.

Model Name	Model	Equation
Diffusion Approximation	$MR = a\exp(-kt) + (1-a)\exp(-kbt)$	(5)
Cavalcanti Mata	$MR = a\exp(-k\,t^{n}) + b\exp(-k\,t^{m}) + c$	(6)
Two Terms	$MR = a\exp(-k\,t) + b\exp(-c\,t)$	(7)
Henderson and Pabis	$MR = a\exp(-k\,t)$	(8)
Midilli	$MR = a\exp(-k\,t^{n}) + b\,t$	(9)
Page	$MR = \exp(-k\,t^{n})$	(10)

a, b, c, m, n: model coefficients, dimensionless; k: drying constant, min^{-1}; t: drying time, min. Source: Leite (2019), Gusmão (2016).

Numerous models are proposed in the literature to describe or predict the behavior of different agricultural products during drying. Each model has its specification, with better adjustment according to its properties, according to the number of adjustment parameters. Thus, given the different characteristics of the grains, some of the main models studied so far were selected and exposed at Table 1. The best fit model was selected considering the statistical criteria of coefficient of determination (R^2), root mean square error (RMSE), Equation 11, estimate standard deviation (SE), Equation 12, as well as the analysis of the distribution of residuals.

$$RMSE = \sqrt{\frac{\sum_{i=1}^{n}(MR_{exp} - MR_{teor})^2}{n}} \tag{11}$$

$$SE = \sqrt{\frac{\sum_{i=1}^{n}(MR_{exp} - MR_{teor})^2}{DF}} \tag{12}$$

Where: MR_{exp}: experimentally obtained moisture ratio; MR_{teor}: moisture ratio predicted by the model; n: number of observations in the experiment; DF: degree of freedom of the model residue.

The activation energy for the beginning of seed drying was determined by the relationship of the Arrhenius equation (Equation 13) with the drying constant k of the selected model, according to the best representation of the process, according to Oliveira et al. (2015).

$$k = A_0 \exp\left(-\frac{E_a}{R\,T_{abs}}\right) \tag{13}$$

Where: A_0: pre-exponential factor, min^{-1}; E_a: activation energy, J mol^{-1}; R: universal gas constant, 8,314 J mol^{-1} K^{-1}; T_{abs}: absolute temperature, K.

The thermodynamic properties of enthalpy, entropy and Gibbs energy variation, referring to the drying data of soybean cultivars, were determined by equations 14, 15 and 16, according to Jideani & Mpotokawana (2009).

$$\Delta h = E_a - R\,T_{abs} \tag{14}$$

$$\Delta s = R\left(\ln A_0 - \ln\frac{k_B}{h_p} - \ln T_{abs}\right) \tag{15}$$

$$\Delta G = \Delta h - T_{abs}\,\Delta s \tag{16}$$

Where: Δh: enthalpy variation, J mol^{-1}; Δs: entropy variation, J mol^{-1} K^{-1}; ΔG: Gibbs energy variation, J mol^{-1}; k_B: Boltzmann constant, 1.38 x 10^{-23} J K^{-1}; h_p: Plank constant, 6.626 x 10^{-34} J s^{-1}.

3. Results and Discussion

Measurements of the characteristic axes of soybean cultivars A, B, C and D are shown in Table 2, as well as the properties of volume, sphericity, circularity, oil content, total protein and moisture.

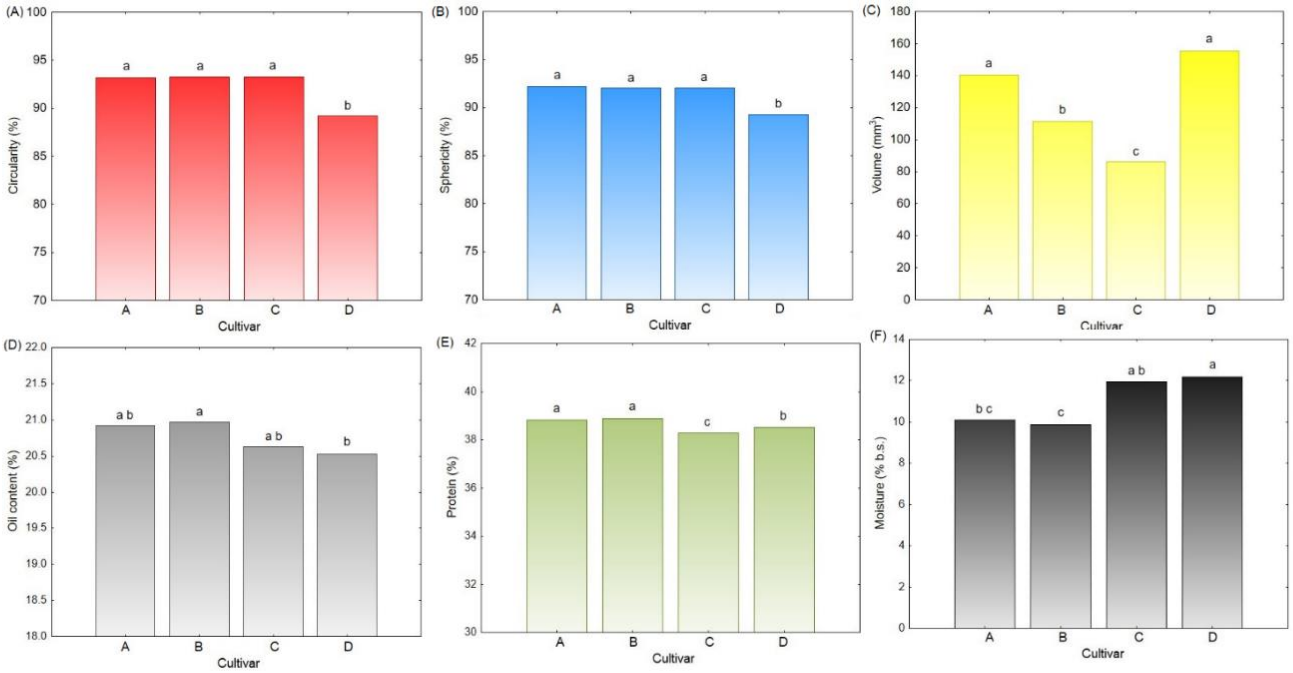
Table 2. Average data for characterization of soybean cultivars A, B, C and D according to dimensions (c, a and b), volume (V_g), sphericity (E_s), roundness (C_r), oil content (OC), total protein (TP) and initial moisture (M), on dry basis.

Cultivar	c (mm)	a (mm)	b (mm)	V_g (mm³)	E_s (%)	C_r (%)	OC (%)	TP (%)	M (%)
A	5,87	6,98	6,49	140,52	92,21	93,20	20,92	38,83	10,09
B	5,42	6,48	6,04	111,29	92,02	93,28	20,97	38,89	9,88
C	4,98	5,94	5,54	86,11	92,02	93,28	20,63	38,28	11,95
D	5,96	7,45	6,64	155,44	89,24	89,20	20,53	38,50	12,18

Source: The authors.

The results of the Shapiro-Wilk test demonstrated the normality of data (p> 0.05) only for the total protein studied by the Tuckey test. The other parameters evaluated were not normal and were studied by nonparametric statistics. Figure 3 presents the results for the multiple comparisons, according to the applied analysis methodology.

Figure 3. Graphical representation for the evaluated properties, where means followed by the same letters for circularity (A), sphericity (B), volume (C), oil content (D) and humidity (F) do not differ statistically from each other by the Kruskal-Wallis test, and protein (E) by Tukey test, at 5% significance.



Source: The authors.

The highest values for water content were observed for cultivars C and D. The water content in cultivar A did not differ from C and B. However, cultivar B was different from C and D. Although the moisture of cultivar B was inferior to those of C and D, the circularity and sphericity characteristics were statistically the same, where only cultivar D differed statistically. Even with the difference, the cultivars can be classified as spheroid and circular (E_s and C_r greater than 80%) (Araújo et al., 2014).

Resende et al. (2005), when studying the effect of drying on bean size and shape property, found that moisture was inversely proportional to circularity and sphericity. This is because, when the moisture is reduced, the beans come out of an ellipsoid shape, assuming a spherical shape (Rath et al., 2017). This fact can be observed in the results for cultivar D, which contained higher humidity and lower values for C_r and E_s. However, the difference in moisture between cultivars B and C and D was not enough to influence size and shape comparing the three. It is also noted that although C and D had the same water content, statistically, there was a difference between them, considering the variables C_r and E_s. Araújo et al. (2014) found a low relationship between these properties and humidity by studying peanut grains.

Regarding the volume, the cultivars A and D presented the highest volumes, statistically equal, while the B and C were different from each other. Higher water contents are expected to imply higher volumes of plant material, including grains (Araújo et al., 2014; Gomes et al., 2018). However, this fact was not observed, since cultivar C with higher humidity obtained the lowest volume, suggesting that not only the water content can influence, but other characteristics as chemical constituents and genetic factors, as well as climatic conditions in the environment seed maturation period.

The lowest oil percentage (20.53%) was obtained for cultivar B, which was also statistically equal to A and C, differing only from cultivar D. The highest protein levels were for cultivars A and B, 38.83% and 38.89%, respectively, which were not statistically different. Protein levels for cultivar C and D were different from each other and from grains A and B. Many studies have been conducted on the proportions of chemical constituents of soybeans, in which a wide range of values is observed (Finoto et al., 2017, Faria et al., 2018). This fact is justified because this variation occurs due to factors, mainly climatic and genetic, which influence the biosynthesis of reserve tissues (Faria et al., 2018).

The statistical parameters of each adjusted model, coefficients of determination (R^2), estimate standard deviation (SE), root mean square error (RMSE) and the distribution of residues are presented in Table 3, depending on the cultivars studied.

It is observed that most adjustments obtained R^2 above 0.95, considered adequate for drying processes (Kashaninejad et al., 2007), however, this parameter alone is not enough to evaluate nonlinear models.

Regarding the standard deviation of the estimate and the mean square deviation, it is noted that, in general, all models presented satisfactory values, among which the highest values found for the parameters were 0.0541 and 0.0485, respectively, for the adjustment of the Henderson and Pabis equation to cultivar D. The ability of a model to safely describe a physical phenomenon occurs the lower the SE (Oliveira et al., 2019) and the lower the RMSE (Silva et al., 2014).

Since the biased distribution of waste demonstrates an underestimation or overestimation of the phenomenon, a randomization of waste is sought (Corrêa et al., 2014). Different residue distributions were observed according to cultivar.

Table 3. Statistical criteria applied to mathematical model adjustments in soybean drying kinetics (R^2 - coefficient of determination; SE - standard deviation of estimate; RMSE - root mean square error; distribution of residues).

Mod.	**40 °C**							
	SE	**RMSE**	**R^2**	**Residue**	**SE**	**RMSE**	**R^2**	**Residue**
	Cultivar A				**Cultivar B**			
(5)	0.0122	0.0184	0.9972**	TD	0.0142	0.0119	0.9960**	RD
(6)	0.0146	0.0103	0.9977**	TD	0.0150	0.0094	0.9974**	TD
(7)	0.0129	0.0100	0.9973**	TD	0.0153	0.0119	0.9960**	TD
(8)	0.0148	0.0133	0.9953**	TD	0.0146	0.0132	0.9951**	TD
(9)	0.0134	0.0104	0.9971**	RD	0.0163	0.0127	0.9954**	TD
(10)	0.0118	0.0106	0.9970**	TD	0.0142	0.0128	0.9954**	RD
	Cultivar C				**Cultivar D**			
(5)	0.0112	0.0094	0.9977**	RD	0.0075	0.0063	0.9988**	TD
(6)	0.0141	0.0095	0.9980**	TD	0.0025	0.0071	0.9999**	RD
(7)	0.0120	0.0100	0.9978**	RD	0.0076	0.0068	0.9990**	TD
(8)	0.0175	0.0158	0.9937**	TD	0.0193	0.0173	0.9912**	TD
(9)	0.0124	0.0096	0.9976**	TD	0.0103	0.0081	0.9991**	TD
(10)	0.0112	0.0102	0.9974**	TD	0.0091	0.0083	0.9980**	RD
	60 °C							
	Cultivar A				**Cultivar B**			
(5)	0.0041	0.0355	0.9997**	TD	0.0052	0.0046	0.9995**	RD
(6)	0.0053	0.0035	0.9993**	TD	0.0066	0.0047	0.9996**	TD
(7)	0.0044	0.0035	0.9997**	TD	0.0213	0.0054	0.9982**	TD
(8)	0.0269	0.0243	0.9948**	TD	0.0252	0.0226	0.9880**	TD
(9)	0.0070	0.0055	0.9992**	RD	0.0075	0.0059	0.9992**	TD
(10)	0.0067	0.0061	0.9991**	TD	0.0070	0.0065	0.9991**	RD
	Cultivar C				**Cultivar D**			
(5)	0.0167	0.0142	0.9956**	RD	0.0201	0.0169	0.9923**	RD
(6)	0.0165	0.0106	0.9976**	TD	0.0235	0.0164	0.9939**	TD
(7)	0.0174	0.0139	0.9959**	RD	0.0214	0.0167	0.9925**	TD
(8)	0.0448	0.0402	0.9640**	TD	0.0541	0.0485	0.9357**	TD
(9)	0.0218	0.0181	0.9936**	TD	0.0249	0.0209	0.9898**	TD
(10)	0.0203	0.0183	0.9926**	TD	0.0265	0.0239	0.9845**	RD

Mod.: mathematical model; **: significant at 1% probability by Fisher; TD: tendentious; RD: random.
Source: The authors.

In cultivar A, the residual randomness was observed for model (9), while for B, models (5) and (10). Model (5) also presented heterogeneous distribution of residues for cultivars C and D, along with equations (7) for C and (10) for D.

From the parameters, the models selected to describe soybean drying were Midilli for cultivar A, Page for cultivars B and D and Diffusion Approximation for C, prioritizing those with the least adjustable parameters.

The adjustment of different models among cultivars indicates that differences in physical and chemical properties influence the drying process. Coradi et al. (2016) concluded that humidity influenced soybean drying in their study.

The Page model was selected by Araújo et al. (2017) in the study of the drying kinetics of peanut fruits. Silva et al. (2014) determined the Cavalcanti and Mata and Midilli models to predict the drying kinetics of guandu beans.

Wang and Singh's model was adequate to the drying curves of soybean in the work of Coradi et al. (2016), while in de Oliveira et al. (2014) the Page model.

Table 4 shows the adjustment parameters of the models chosen for each cultivar. When observing the variable “k”, it is noted an increase of the temperature from 40 to 60°C. This fact is expected, since it is related to effective diffusivity, which increases at higher temperatures (Oliveira et al. 2015).

Table 4. Midilli model parameters for cultivar A; Page, cultivar B; Diffusion Approximation, cultivar C; Page, cultivar D; at temperatures of 40 and 60 ° C

Cultivar A – Midilli Model

Temperature (°C)	**a**	**k**	**n**	**b**
40	1.0052	0.0047	0.9072	4.4603E-13
60	1.0043	0.0102	0.7958	9.4955E-05

Cultivar B - Page Model

Temperature (°C)	**k**	**n**
40	0.0036	0.9487
60	0.0100	0.8006

Cultivar C – Diffusion Approximation Model

Temperature (°C)	**a**	**k**	**b**
40	0.1124	0.0149	0.1686
60	0.2237	0.0258	0.0971

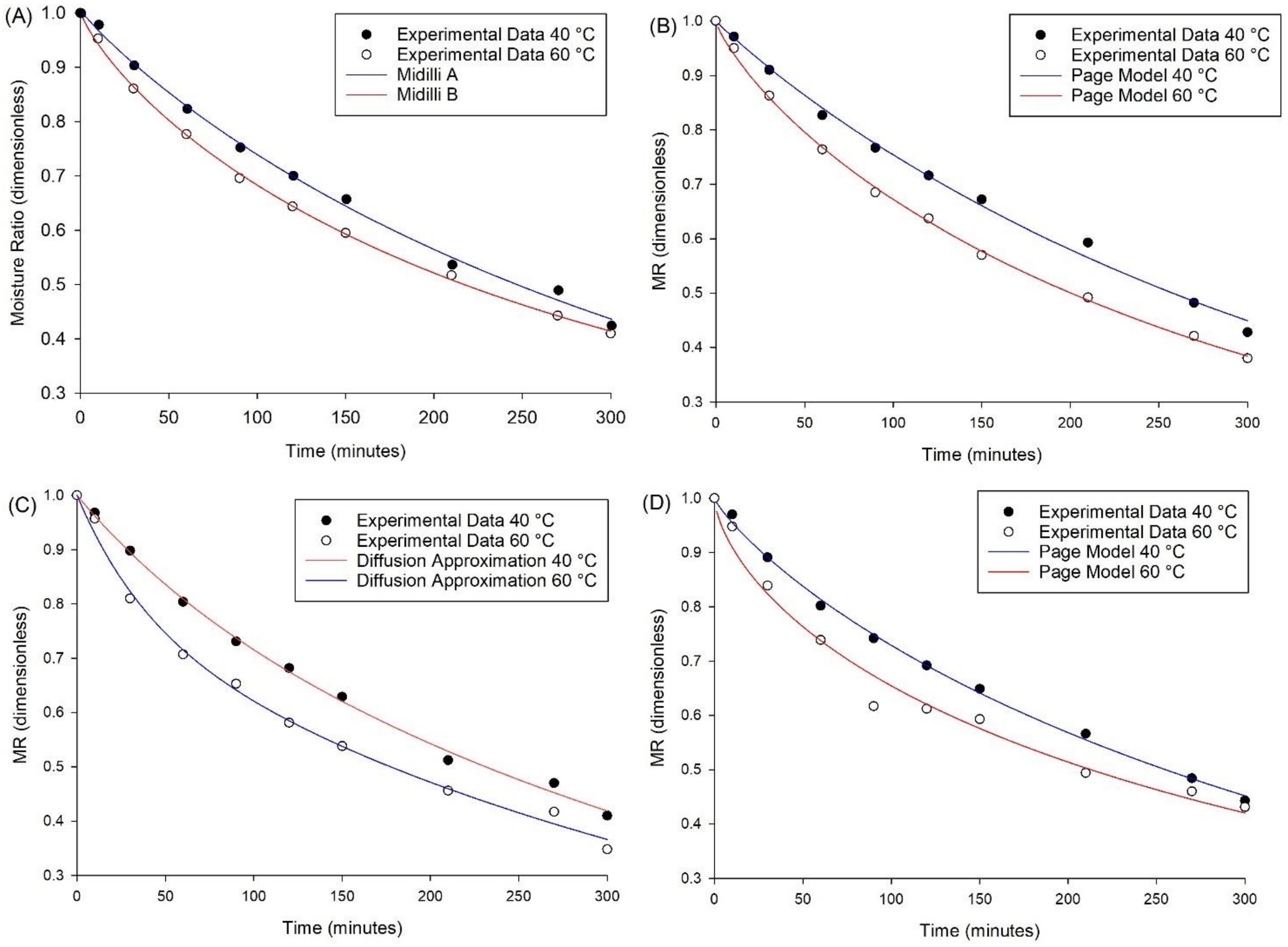
Cultivar D – Page Model

Temperature (°C)	**k**	**n**
40	0.0066	0.8388
60	0.0211	0.6511

Source: the authors.

The highest values of the bag constant "k" were those of cultivar C at both temperatures. This finding infers that it had a greater effective diffusivity, therefore, greater movement of water in the grain, drying faster, which can be noticed in the drying curves estimated by the models (Figure 4).

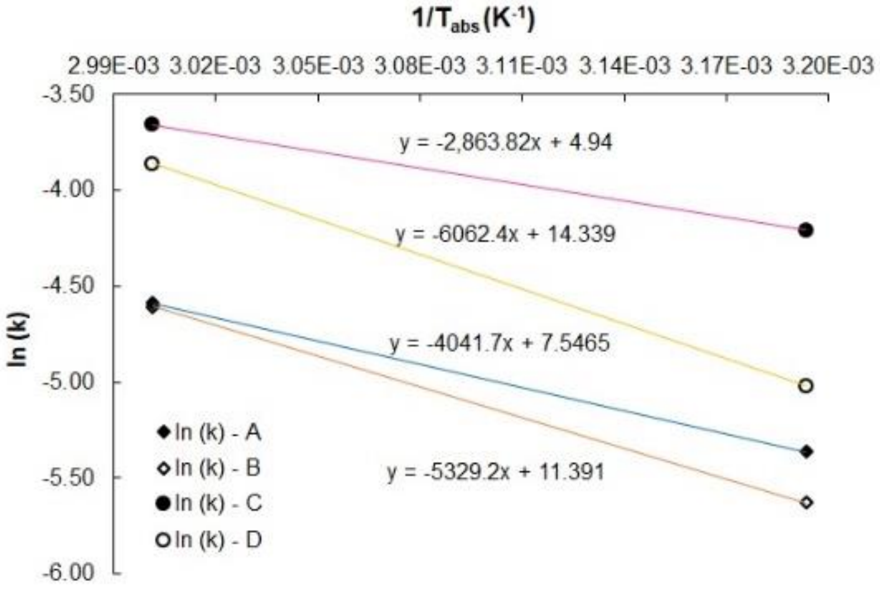
Figure 4. Drying kinetics curves adjusted by Midilli models for cultivar A (A), Page model for cultivar B (B); Diffusion Approximation, cultivar (C); Page model, cultivar (D), to the experimental moisture ratio values.



Source: the authors.

The Arrhenius diagram, constructed from the linearization of equation 13, is expressed in figure 5, relating ln (k) by the inverse of the absolute drying temperature (K^{-1}).

Figure 5. Arrhenius diagram as a function of absolute air temperature and drying constant (k) over drying of soybean cultivars A, B, C and D.



Source: the authors.

Through the equations of the straight lines of the diagram, the Drying Activation Energy for each cultivar is determined through the ratio of the angular coefficient and the E_a/R ratio, being the known universal gas constant. Therefore, for Cultivars A, B, C and D E_a values of 33.60, 44.31, 23.81 and 50.40 kJ mol^{-1}, respectively, were obtained. Due to the lower E_a demonstrating greater ease in the transformation of liquid free water into steam (Baptestini et al., 2015), it is noted that this process required a lower energy to cultivate C, although D statistically had levels of equal water and oil, which demonstrates the effect of size.

Activation energy magnitudes were within the range for agricultural products 12.7 to 110.0 kJ mol^{-1}, this way, Oliveira et al. (2014) found to cultivate soybean Valiosa an activation energy of 22.7 kJ mol^{-1}. Borges et al. (2018) determined an E_a of 36.13 kJ mol^{-1} by studying the cultivar BRS257. The energy required for the liquid-vapor water transformation for cowpea was 35.04 kJ mol^{-1}, in the work of Camicia et al. (2015).

Table 5 contains the thermodynamic properties for cultivars A, B, C and D. It is observed that the temperature increase decreased the enthalpy. This results from the fact that the pressure gradient increases between grain and air, increasing the effective diffusivity, requiring less energy in the process of breaking the intermolecular bond water product

(Oliveira et al., 2010). Positive values of □h characterize the process as endergonic (Costa et al., 2016).

Table 5. Thermodynamic properties of the seed drying process of soybean cultivars A, B, C and D.

Temperature (°C)	**Δh (J mol^{-1})**	**Δs (J mol^{-1} K^{-1})**	**ΔG (J mol^{-1})**	**Δh (J mol^{-1})**	**Δs (J mol^{-1} K^{-1})**	**ΔG (kJ mol^{-1})**
		Cultivar A			**Cultivar B**	
40	31,000.88	-229.00	102,711.08	41,705.75	-225.57	112,343.92
60	30,834.59	-229.51	107,296.21	41,539.46	-226.09	116,860.57
Temperature (°C)		**Cultivar C**			**Cultivar D**	
40	21,207.44	-232.52	94,020.87	47,801.91	-223.66	117,840.82
60	21,041.15	-233.03	98,676.46	47,635.62	-224.17	122,319.20

Source: the authors.

The highest values of Δh was observed for cultivar D. Since the moisture and lipid content of the same were statistically equal to C, the higher water-product binding energy can be explained by the higher volume. However, comparing cultivars A and B, where the only characteristic that distinguished them was volume, it was observed that B (smaller volume) presented higher enthalpy. Therefore, possibly other properties may have interfered, especially regarding the proportion of substances that make up the grain reserve tissues.

The temperature increase promotes a higher degree of agitation of the molecules, which justifies the entropy decrease from 40 to 60 °C, since this property is related to the degree of molecular arrangement order. The lowest values of Δs was calculated for cultivar C, which infers lower molecular order. The lower amount of protein may justify, since the proportion of protein constituents (amino acids) may vary depending on climatic, genetic and nutritional factors, consequently, hydrophilic or hydrophobic relationships.

Positive values of ΔG demonstrate non-spontaneity of the process, therefore endergonic. The work done by the process is represented by the Gibbs energy, according to Nkolo Meze'e, et al. (2008). The largest studies were observed for cultivars B and D, which differed among all properties analyzed. The drying of cultivar C performed a smaller work, being possible to be related to the smaller dimensions of the grain, that allows greater diffusivity, being that the 2nd Law of Fick related the movement of a solute the dimensions and sizes of the product.

The values of thermodynamic properties for the studied cultivars were close to those of the cultivar Valiosa, which obtained Δh, Δs and ΔG in the ranges of 19.12 and 20.16 kJ mol^{-1}, -263.8 and -257.3. J mol^{-1} and 103.81 and 115.68 kJ mol^{-1} respectively (Oliveira et al., 2014). Other products, such as peanuts, strawberries and acuri, presented similar values for thermodynamic properties (Araújo et al., 2017, Oliveira et al., 2015, Santos et al., 2019).

The present results are in line with the other studies regarding the drying of agricultural products. However, the differences evidenced in the present study demonstrate that the main factors hitherto considered for the drying operation, such as humidity and temperature, are not the only ones. Thus, the influence of chemical constituents is evident, as well as the size and shape, already considered by Fick's Law.

4. Conclusions and Suggestions

All cultivars can be considered spheroidal and circular, with difference between cultivars, in all evaluated properties, being cultivar C the smallest.

Due to differences in properties, different models were adjusted for cultivars: the Midilli model for cultivar A, Page for cultivars B and D and the Diffusion Approximation for cultivar C. The lowest volume cultivar C had higher values for the constant. drying rate and higher drying rate in the studied period.

The lowest Activation Energy values as well as the thermodynamic properties were found for cultivar C, the highest for cultivar D.

The main influence on drying was as a function of grain volume.

It is necessary that there are studies that take into account the factor of chemical constituents, not only in empirical knowledge, but also in mathematical models, in order to obtain a safer estimate of thermodynamic properties, since these are directly influenced the composition of the products to be dried.

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Percentage of contribution of each author in the manuscript

Thiago Aurélio Arruda Silva – 40%
Nahyara Batista Caires Galle – 25%
Carlos Caneppele – 25%
Niédja Marizze Cézar Alves – 10%