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Research Article
Thermodynamic Properties and Kinetics of Drying Process of Chia Seeds (*Salvia hispanica* L.)

[1]G.H.H. Oliveira, [2]M.R. Costa, [3]F.M. Botelho, [3]J.L. Viana and [3]T.R.B. Garcia

[1]Instituto Federal do Sudeste de Minas Gerais, Campus Manhuaçu, BR 116, km 589,8, Distrito Realeza, 36905-000 Manhuaçu, Brazil
[2]Instituto Federal de Brasília, Campus Gama, Brasília-DF, Brazil
[3]Universidade Federal de Mato Grosso, Campus Sinop, Sinop-MT, Brazil

Abstract

Background and objective: Chia (*Salvia hispanica* L.) is used for human and animal consumption as nutritional supplements. For its correct handling and processing, drying is required. Thus, this work aimed to evaluate and model drying process of chia seeds and determine thermodynamic properties in three different temperatures (40, 50 and 60°C). Chia seeds were acquired with initial moisture content of 9.0% (d.b.) and submitted to drying until average moisture content of 2.3% (d.b.). **Methodology:** Experimental data were fitted to six mathematical models usually used to represent drying of agricultural products. Diffusion Approach and Verma models were the ones that best fitted. **Results:** Thermodynamic properties presented a high correlation with drying temperature, in which higher temperature resulted in lower values of entropy and enthalpy values, whilst this increment increased values of Gibbs free energy. Activation energy of drying process was 10.67 kJ mol^{-1}. **Conclusion:** Diffusion approach and Verma models are suitable to represent drying curves of chia seeds.

Key words: Moisture content, activation energy, enthalpy, entropy, storage

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Corresponding Author: G.H.H. Oliveira, Instituto Federal do Sudeste de Minas Gerais, Campus Manhuaçu, BR 116, km 589,8, Distrito Realeza, 36905-000 Manhuaçu, Brazil Tel: +55 32 98442-3922

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Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

Production and consumption of chia is increasing considerably during the past years due to its properties that provides benefits to human health. Currently, chia seeds are used as nutritional supplements in order to produce cereal bars, morning cereals and cookies, mainly in USA, Latin America and Australia (Munoz *et al*., 2012). It is also used at medicine and ink formulation (Ixtaina *et al*., 2008), in addition to mixtures at animal rations. Previous study reported the digestibility of rations for rabbits formulated with three percentages of chia (0, 10 and 15%), concluding that ration with 10% of chia presented better digestibility (Meineri and Peiretti, 2007). An important factor for diseases prevention, antioxidant activity, was evaluated in chia seeds (Alfredo *et al*., 2009), in which it presented value above several cereals and similar to wine, coffee, tea and orange juice.

Chia was approved as a new food by the European Parliament and European Council at 2009, thus being an important source of important nutrients (European Commission, 2009). Consumption of chia seeds is recommended due to its oil content, protein, fiber and antioxidant activity. Chia seeds possess high levels of oil 25-38% and protein (19-23%) (Ayerza, 1995), when compared to with widely used products, such as wheat, corn, rice, oat and barley (Coates and Ayerza, 1996). Thus, it is required the study of post-harvest procedures of this product in order to aid its correct processing at industry.

Among post-harvest procedures of agricultural products, drying is widely known and used in order to assure quality and stability during storage and shelf life. Variation of moisture content through drying is important in order to understand the interactions between water molecules and the products components, which is key factor for correct drying and storage. High moisture content may lead to fungi and insect growth, compromising germination and vigor of seeds, deteriorating quality and increasing post-harvest loss. On the other hand, extreme moisture content reduction may promote economic loss due to weight loss of the product, but it decreases the biological activity of the product and chemical and physical alterations throughout storage. Thus, it is necessary the drying kinetics of chia seeds, providing parameters for the industry in order to perform correct drying, assuring sanitary quality and feasibly economic exploitation of chia seeds.

Simulation of the behavior of each product during moisture content reduction is an important parameter to develop and improve drying equipment. To do so, mathematical models that satisfactory represents moisture loss during drying are used (Berbert *et al*., 1995). Furthermore, knowledge of the water molecules movement within the product is of great importance to the correct study of water and chemical components interactions at agricultural products. Thus, calculation of effective diffusion coefficient and thermodynamic properties of drying process is also an important source of information to design drying equipment, calculate energy required related to drying, evaluate foodstuff microstructure and to study physical phenomenon that occurs at food surface (De Oliveira *et al*., 2011).

Enthalpy modification provides a measurement of energy variation related to the interaction between moisture and the products component during drying. Entropy is associated to the spatial arrangement between moisture and the products components. Therefore, entropy characterizes the order or disorder degree related to the system moisture-product (McMinn *et al*., 2005). Gibbs free energy is an indicative of the product affinity by moisture. Alterations of Gibbs free energy during drying is linked to energy required to transfer water molecules at vapor state to a solid surface or vice-versa.

Considering the importance to study the drying process and the absence of data of chia seeds drying, this study aimed to acquire drying curves of chia seeds (*Salvia hispanica* L.) using mathematical models. In addition, it was obtained the effective diffusion coefficient and thermodynamic properties for the drying process.

MATERIALS AND METHODS

Raw material: Chia seeds with initial moisture content of 9.0% (d.b.) were used. This process was accomplished with the analysis of seeds rules (Brasil, 2009), in triplicate. Subsequently, chia seeds were submitted to drying at an oven with forced air circulation at temperatures of 40, 50 and 60°C, until constant moisture content (<0.01 g) in three consecutive readings.

Mathematical modeling: In order to determine Moisture Ratio (MR) of chia seeds during drying, Eq. 1 was used.

$$MR = \frac{X^* - X^*_{eq}}{X^*_i - X^*_{eq}} \quad (1)$$

where, MR: Moisture ratio, dimensionless, X^*: Moisture content of chia seeds at time "t", decimal dry basis, X_{eq^*}: Equilibrium moisture content, decimal dry basis, X_{i^*}: Initial moisture content and decimal dry basis.

Table 1: Mathematical models used to predict drying process

Model	Equation	Equation No.
Page (Overhults *et al.*, 1973)	$MR = \exp(kt^c)$	(2)
Logarithmic (Chandra and Singh, 1995)	$MR = a\exp(-kt)+b$	(3)
Modified Midilli (Ghazanfari *et al.*, 2006)	$MR = \exp(-kt^c)+bt$	(4)
Diffusion Approach (Kassem, 1998)	$MR = a\exp(-kt)+(1-a)\exp(-kbt)$	(5)
Two terms (Henderson, 1974)	$MR = a\exp(-kt)+b\exp(-ct)$	(6)
Verma (Verma *et al.*, 1985)	$MR = a\exp(-kt)+(1-a)\exp(-bt)$	(7)

a, b, c: Model coefficients, dimensionless; k: Drying constant, (h^{-1}) and t: Drying time, h

Mathematical models used to predict drying kinetics of chia seeds are presented at Table 1.

For fitting judgment of mathematical models, non-linear regression analysis through Gauss Newton method was made. The best model was chosen based on standard deviation of estimate (SEE), Mean Relative Error (MRE), determination coefficient (R^2) and residue analysis. Values below 10% of MRE indicates a good fit for practical applications (Mohapatra and Rao, 2005). The model capacity to describe with fidelity a certain physical process is inversely proportional to SEE (Draper and Smith, 1998). Calculation of SEE and MRE are presented at Eq. 8 and 9, respectively:

$$SEE = \sqrt{\frac{\sum_{i=1}^{n}\left(Y-\hat{Y}\right)^2}{DF}} \tag{8}$$

$$MRE = \frac{100}{n}\sum_{i=1}^{n}\left(\frac{\left|Y-\hat{Y}\right|}{Y}\right) \tag{9}$$

where, MRE: Mean relative error (%), n: No. of observed data, SEE: Standard error of estimate (% d.b), Y: Observed value, (% d.b.), $\hat{Y}$: Estimated value through the model (% d.b.) and DF: Degrees of freedom of the model.

Activation energy: Activation energy is defined as the minimum energy necessary to initiate a chemical reaction. In the drying process, the lower the activation energy is, the higher the water diffusivity in the product will be. This means that lower values of activation energy allow for a higher moisture transfer rate and, consequently, lower drying time and cost.

Arrhenius Eq. 10 was employed to obtain the values of activation energy in this stuyd. This equation states the relationship between activation energy and the velocity at which the reaction occurs.

$$k = A_0 \exp\left(\frac{-E_a}{RT}\right) \tag{10}$$

where, A_0: Pre-exponential factor (h^{-1}), E_a: Activation energy (J mol^{-1}); R: Universal gas constant (8.314 J mol^{-1} K^{-1}) and T: Temperature (K).

Thermodynamic properties: Thermodynamic properties were acquired by means of drying rate values obtained by the best model to represent the experimental data of chia seeds drying. Thus, Eq. 11, 12 and 13, respectively, calculates enthalpy, entropy and Gibbs free energy (Correa *et al.*, 2012).

$$\Delta H\ E_a\text{-}Rt \tag{11}$$

$$\Delta S = R\left(\text{In } A_0 - \text{In}\frac{k_B}{h_P} - \text{In } T\right) \tag{12}$$

$$\Delta G = \Delta H\text{-}T\Delta S \tag{13}$$

where, ΔH: Differential enthalpy (J mol^{-1}), ΔS: Differential entropy (J mol^{-1}), ΔG: Gibbs free energy (J mol^{-1}), k_B = Boltzmann constant (1.38×10^{-23} J K^{-1}), h_P: Planck's constant (6.626×10^{-34} J sec).

RESULTS AND DISCUSSION

Models suitability: The statistical parameters obtained in order to verify the fit of each model to the observed data during the chia seeds drying at temperatures of 40, 50 and 60°C are presented in Table 2.

In Table 2, we notice that, for the three drying air temperatures, all of the models presented determination coefficients (R^2) greater than 98%, satisfactory values of Standard Error of Estimate (SEE) and Mean Relative Error (MRE) lower than 10%, which represents a good fit for practical purposes (Mohapatra and Rao, 2005). However, Page, Logarithmic and Modified Midilli models (Eq. 2, 3 and 4, respectively), presented biased distributions of the residual plots at certain temperatures, being inappropriate to represent drying curves. The remaining models are suitable to

Table 2: Mean Relative Error (MRE), Standard Error of Estimate (SEE), determination coefficients (R^2) and Residual Distribution (RD) behavior {random (R) or biased (B)}, of the models and drying air temperatures

		Equation No.					
Temperature (°C)	Statistical parameters	2	3	4	5	6	7
40	MRE	0.42	0.57	0.28	0.29	0.30	0.29
	SEE	0.01	0.01	0.01	0.01	0.01	0.01
	R^2	99.68	99.52	99.84	99.82	99.83	99.82
	RD	R	R	R	R	R	R
50	MRE	1.82	0.94	0.61	0.50	0.51	0.50
	SEE	0.03	0.02	0.01	0.01	0.01	0.01
	R^2	99.05	99.69	99.90	99.89	99.90	99.89
	RD	B	B	R	R	R	R
60	MRE	3.57	2.24	1.32	0.97	0.97	0.97
	SEE	0.05	0.03	0.02	0.02	0.02	0.02
	R^2	98.87	99.56	99.87	99.87	99.88	99.87
	RD	B	B	B	R	R	R

Table 3: Diffusion approach model fit coefficients for temperatures of 40, 50 and 60°C

	Temperatures (°C)		
Coefficients	40	50	60
a	0.1145	0.3396	0.4967
k	0.6601	0.6611	0.8465
b	0.0310	0.0453	0.0584

Table 4: Variation of diffusion approach model coefficients with temperature (T), with their respective determination coefficients (R^2)

Equation	R^2 (%)
a = 0.0191T-0.6385	98.95
B = 0.0014T-0.0234	99.93
K = 0.0093T+0.2565	75.40

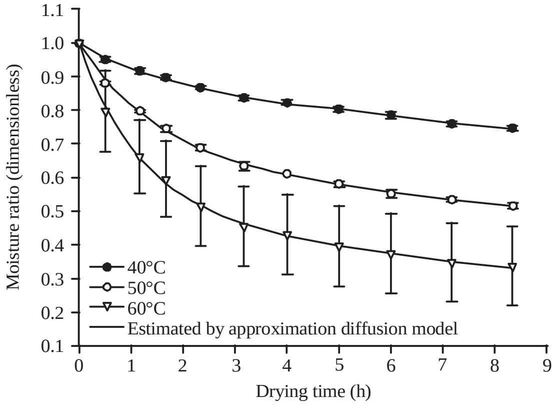

Fig. 1: Drying curves of chia seeds at different temperatures.

predict drying curves of chia seeds. Nonetheless, two terms model (Eq. 6) have slightly higher values of MRE than Diffusion Approach and Verma models. Finally, these two models presented the exact same values of MRE, SEE and R^2, being equally suitable to represent drying data of chia seeds.

In order to complete remaining objectives of the present study, diffusion approach model was chosen to represent drying curves of chia seeds, as can be seen at Fig. 1. Previous study also recommended the diffusion approach model as the one most suitable to describe potato pulp waste drying (De Carvalho *et al*., 2014).

Table 3 presents the diffusion approach fit coefficients which are designed for the three air drying temperatures for chia seeds.

Approach diffusion model coefficients varied with temperature, being that all three coefficients (a, k and b) increased with temperature increment. Regarding the drying constant (k), it can be used as an approximation for characterizing the temperature effect, relating to the effective diffusivity of the drying process's falling period and the liquid diffusion that governs this process (Babalis and Belessiotis, 2004). From Table 3, increase of k values are expected, since higher temperature provides more energy for water molecules movement and/or phase alteration (liquid to vapor), decreasing the required time for the product to achieve equilibrium moisture content. This trend can also be observed at Fig. 1.

The equations that describe the diffusion approach model coefficients, correlating to temperature are shown in Table 4.

Diffusion approach model can be presented with the described coefficients as a function of temperature in the chia seeds drying modeling with the temperature range of 40-60°C, according to Eq. 14, in which T is the drying temperature (°C) and t is the drying time (h).

$$\begin{aligned}\text{MR} = (0.0191\text{T}-0.6385)\ \exp[-0.0093\text{T}-0.2565]\\ \text{t}+(1.6385-0.0191\text{T})\ \exp(-1.302\times10^{-5}\text{T}^2-1.4148\times10^{-4}\\ \text{T}+6.0021^{-}10^{-3})\text{t}\end{aligned} \tag{14}$$

Activation energy: Activation energy regarding water diffusion of chia seeds during the drying process was 10,676.01 J mol^{-1}. Previous study reported that activation

Table 5: Values of thermodynamic parameters at different temperatures for the drying process of chia seeds

Temperature (°C)	ΔH (J mol^{-1})	ΔS (J mol^{-1} K^{-1})	ΔG (J mol^{-1})
40	8,072.40	-215.05	75,418.03
50	7,989.26	-215.31	77,569.87
60	7,906.12	-215.57	79,724.27

ΔH: Differential enthalpy, ΔS: Differential entropy, ΔG: Gibbs free energy

energy generally ranges from 12.7-110 kJ mol^{-1} for food (Zogzas *et al*., 1996). Value encountered at the present work was slightly lower, indicating the need for further researches for new foodstuff, as in the case of chia seeds. An activation energy lower than the range (10.08 kJ mol^{-1}) for edible beans, in a temperature range of 25-55°C, was reported (Correa *et al*., 2007). Lower values of activation energy indicate less amount of energy required to the process to happen; in this case, drying. Thus, chia seeds are easily dried than other agricultural products, as can be seen at Fig. 1 (<9 h).

Enthalpy, entropy and Gibbs free energy: Enthalpy and entropy values of activation decreased, while the Gibbs free energy increased with increased drying temperatures (Table 5).

Water diffusion process for the product during drying responds to sensible heat and requires energy (ΔH>0) in order to promote changes. Lower values of enthalpy indicate a less amount of energy required to remove moisture linked to the product during drying. As expected, this trend occurred at higher drying temperatures, indicating that fewer energy is required, so drying can occur.

Entropy is associated to degree of disorder, being a function of the products state in which its values increases during the natural process at an isolated system. Negative values of this thermodynamic property are attributed to the existence of chemical adsorption and/or structural alterations of the adsorbent (Moreira *et al*., 2008). Entropy values decrease with temperature increment can be explained by the fact that when the product is being dehydrated, moisture content decreases and the movement of water molecules become more restricted, meaning that there are less available sites (Correa *et al*., 2011).

Gibbs free energy is related to required study in order to sorption sites to become available (Meze'e *et al*., 2008). Its values were positive, indicating that drying is a non-spontaneous process. This trend is characteristic of endergonic reaction, in which needs an energy addition from the environment where the product is located in order to reaction occurs. This behavior is expected, since drying process is not spontaneous: Samples are encountered in an environment with higher relative humidity prior to drying process, being lately submitted to a lower relative humidity environment (provided by higher drying temperatures), until equilibrium is reached (Meze'e *et al*., 2008).

CONCLUSION

Based on the results obtained and the conditions in which the experiment was conducted, the following conclusions are presented:

- Diffusion Approach model was used to construct drying curves of chia seeds
- Activation energy of drying process was 10.68 kJ mol^{-1}
- Thermodynamic properties presented a high correlation with drying temperature, in which higher temperature resulted in lower values of entropy and enthalpy values, whilst this increment increased values of Gibbs free energy

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