



## DRYING KINETICS, MATHEMATICAL MODELING AND VOLUMETRIC SHRINKAGE OF SUNFLOWER SEEDS (*HELIANTHUS ANNUUS L.*)

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**ABSTRACT:** Given the prominence of sunflower on the national scenario and the importance of drying steps in post-harvest, this study aimed to evaluate the drying kinetics of sunflower seeds in an oven with forced air convection in different temperatures. Thus, mathematically describe and determine the effects of drying on shrinkage of seeds. The experimental design was completely randomized, factorial (4x3), four air drying temperatures (45, 55, 65 and 75 °C) and three replications. Drying was carried out until the seeds water content reached equilibrium. The air temperature and flow were monitored with a psychrometer, and a hot wire anemometer, respectively. It has been found that the drying time was significantly ( $P<0.05$ ) reduced with increasing temperature of the air drying. The model of Wang and Sing was that better adjusted to experimental drying data. Effective diffusivity of sunflower seed ranged from  $2.83$  to  $2.93 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ , while the isosteric heat of adsorption,  $3,725.176$  to  $3,773.082 \text{ kJ kg}^{-1}$ . Reducing water content influenced the shrinkage of sunflower seeds, with emphasis on temperatures above  $55 \text{ °C}$ . The model Corrêa was that better adjusted to experimental data of sunflower seeds volumetric shrinkage.

**KEYWORDS:** Dryer, optimization, post-harvest.

## CINÉTICA DE SECAGEM, MODELAGEM MATEMÁTICA E CONTRAÇÃO VOLUMÉTRICA DE SEMENTES DE GIRASSOL (*HELIANTHUS ANNUUS L.*)

**RESUMO:** Diante do destaque da cultura do girassol no cenário nacional e da importância da etapa de secagem para a pós-colheita, este trabalho teve como objetivo avaliar a cinética de secagem de sementes de girassol, em estufa com circulação de ar convectivo e forçado em diferentes temperaturas, descrever matematicamente e determinar os efeitos da secagem na contração volumétrica das sementes. O delineamento experimental utilizado foi inteiramente casualizado, fatorial (4x3), sendo quatro temperaturas do ar de secagem (45, 55, 65 e 75 °C) e três repetições. A secagem foi realizada até o teor de água das sementes entrarem em equilíbrio higroscópico. A temperatura e o fluxo do ar foram monitorados com auxílio de um psicrômetro e um anemômetro de fio quente, respectivamente. Verificou-se, nos resultados obtidos, que o tempo de secagem foi significativamente ( $P<0.05$ ) reduzido com o aumento da temperatura do ar de secagem. O modelo de Wang e Sing foi o que melhor ajustou os dados experimentais de secagem. A difusividade efetiva das sementes de girassol variaram de  $2,83$  a  $2,93 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ , enquanto que o calor isostérico de sorção foi de  $3725,176$  a  $3773,082 \text{ kJ kg}^{-1}$ . A redução do teor de água influenciou na contração volumétrica das sementes de girassol, com ênfase para as temperaturas acima de  $55 \text{ °C}$ . O modelo de Corrêa foi o que melhor ajustou os dados experimentais de contração volumétrica das sementes de girassol.

**PALAVRAS-CHAVE:** Otimização, pós-colheita, secador.

### 1 INTRODUCTION

The sunflower (*Helianthus annuus L.*) stands as the fifth seed production and fourth in oil production, in the world (PESAGRO, 2007). Sunflower oil is one of the first oil that met the standard of quality required by European biodiesel market, and it had commercial value greatly increased due to the presence of special compounds that characterize it as a functional food.

After harvested, the seeds are subjected to pre-processing steps to guarantee quality in subsequent manufacturing processes of the seeds. Drying is an important step. With the reduction of seed water content one can storage them for a longer time, increasing the marketing and product quality.

However, drying processes need to be done carefully due to the transformations, deterioration and losses in the process, with simultaneous heat and mass transfer (CORADI et al., 2014a). To the accomplishment of a proper drying it is important to know the temperature of the drying air and seed mass, relative humidity and air flow in the dryer. Carelessness in the drying process can damage cell structures of seeds, denature proteins and

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cause cracking and change in coloring, reducing the seed physical and physiological quality (ALMEIDA et al., 2009; OLIVA ET AL., 2012; CORADI et al., 2014a).

However, there is a lack on drying process of sunflower seeds efficiency studies. The method nowadays employed is more natural, outdoor performed in which the time required for drying is usually long and not always resulting on good quality product. Thus, natural drying is giving place to artificial drying techniques, in order to increase the quality of the stored product (SILVA, 2008). In Brazil, there is little information on artificial drying of sunflower seeds, such as drying kinetics, physical characterization and isotherm equilibrium moisture content, so that the optimal drying conditions for domestic varieties are not well established (SILVA, 2008; SILVA et al., 2013; CORADI et al., 2014a).

The physical properties of agricultural products influence in the optimization of industrial, design and sizing of equipment used in harvesting operations and post-harvest processes (RESENDE et al., 2008). The knowledge of the physical and mechanical properties of agricultural products is of fundamental importance for grain conservation and for construction and operation of various equipment used in the main operations of post-harvest products (MIR et al., 2013).

One of the major changes in the physical properties that occur in agricultural products during the drying process is to reduce its external volume, i.e shrinkage. The loss of water causes damage to cell structure of the product leading to a change in shape and decrease in size of the tissue (MAYOR; SERENO, 2004; GONELI et al., 2011.).

It is crucial to do the simulation and obtain theoretical information about the behavior of each product during the removal of water, in order to develop and improve drying equipment.

Mathematical models implemented in computer programs have shown significant results in nonlinear and

complex systems in several areas, including the theory of control, recognition, and decision analysis model. These programs are able to solve issues that classic models, as a rule, are not able to do so. They are called intelligent systems, among which Neural Networks and Fuzzy Logic stand out. (CANEPPELE et al., 2010; CANEPPELE; SERAPHIM, 2010; 2013; SIQUEIRA et al., 2014). In this study, this principle mathematical models that satisfactorily represents the loss of water during drying. The objective of this work was to study the drying kinetics of sunflower seeds in an oven with forced air circulation, in different temperatures (45, 55, 65, and 75 °C), fit the experimental data to non-linear mathematical models and evaluate effects of drying on shrinkage of seeds.

## 2 MATERIAL AND METHODS

The experiment was conducted at the Federal University of Mato Grosso do Sul (UFMS), Campus of Chapadão do Sul (CPCS) in 2013. The sunflower seeds were harvested randomly, and the impurities and damaged seeds were manually separated. Then, the seeds were dried in a convection oven with forced air ventilation at temperatures of 45, 55, 65, and 75 °C. Drying was carried out until the seeds reach the hygroscopic moisture balance. For each drying air temperature, three tests were performed and for each test, 5 kg of sunflower seeds were used. The temperature and relative humidity were monitored, throughout drying with the aid of a psicrometer. The water content (% w.b.) was determined by weighing 15 g of sample. Then, the samples were placed in an oven with air heating and ventilation regulated at  $103 \text{ °C} \pm 1 \text{ °C}$  for 24 h, according to the recommendations of BRASIL, (2009). After that, the samples were removed and placed in desiccators. The water content (% w.b.) was determined by mass difference between the initial and the final sample weight. Tests were performed in three replicates.

The drying curves were fitted to the experimental data using thirteen different semi-empirical and empirical equations discriminated below:

| Equation  | Model                        |      |
|---|------------------------------|------|
| $RU = \exp(-k \cdot t)$   | Newton                       | (1)  |
| $RU = \exp(-k \cdot t^n)$   | Page                         | (2)  |
| $RU = \exp(-(k \cdot t)^n)$   | Page Modified                | (3)  |
| $RU = \exp(-a - (a^2 + 4 \cdot b \cdot t)^{1/2}) / 2 \cdot b$                             | Thompson                     | (4)  |
| $RU = a \cdot \exp(-k \cdot t)$   | Henderson and Pabis          | (5)  |
| $RU = a \exp(-kt) + c$  | Logarithmic                  | (6)  |
| $RU = a \cdot \exp(-k_0 \cdot t) + b \cdot \exp(-k_1 \cdot t)$                            | Two Terms                    | (7)  |
| $RU = a \cdot \exp(-k \cdot t) + (1 - a) \exp(-k \cdot a \cdot t)$                        | Two Exponential Terms        | (8)  |
| $RU = 1 + a t + b t^2$  | Wang and Singh               | (9)  |
| $RU = a \cdot \exp(-k \cdot t) + b \cdot \exp(-k_0 \cdot t) + c \cdot \exp(-k_1 \cdot t)$ | Henderson and Pabis Modified | (10) |
| $RU = a \cdot \exp(-k \cdot t^n) + b \cdot t$   | Midilli                      | (11) |
| $RU = a \cdot \exp(-k \cdot t) + (1 - a) \cdot \exp(-k \cdot b \cdot t)$                  | Diffusion approximation      | (12) |

wherein  $RU$  = moisture ratio (dimensionless)  $t$  = drying time (h),  $k$ ,  $k_0$ ,  $k_1$  = drying constant ( $h^{-1}$ ),  $a$ ,  $b$ ,  $c$  = model coefficients,  $n$  = number of terms of the equation,  $D$  = diffusion coefficient ( $m^2 s^{-1}$ ),  $L$  = product thickness (m). For determining the ratios of moisture during drying air under different conditions we used the following expression:

$$RU = \frac{U^* - U_e}{U_i - U_e} \quad (13)$$

wherein  $U^*$  = water content of product (d.b.),  $U_i^*$  = initial water content of the product (d.b.),  $U_e^*$  = equilibrium water content of the product (d.b.).

It is usual to consider the value of the diffusion coefficient constant or linearly dependent on the temperature of air drying. This relationship has been expressed by the Arrhenius model (MOHAPATRA; RAO, 2005).

$$D = A \exp\left(-\frac{E}{RT}\right) \quad (14)$$

wherein  $A$  = constant ( $m^2 s^{-1}$ ),  $E$  = activation energy ( $kJ kmol^{-1}$ ),  $R$  = universal gas constant ( $8,314 kJ kmol^{-1} K^{-1}$ ),  $T_{abs}$  = absolute temperature (K).

The coefficients of the Arrhenius expression were linearized by applying the logarithm:

$$\ln D = \ln A - \frac{E}{RT} \quad (15)$$

The values of water activity, temperature, and water content equilibrium were obtained from the sunflowers seeds desorption isotherms, using the model that best fit the experimental data. For the calculation of the integral isosteric heat of desorption we used the following equation:

$$Q_{st} = q_{st} + L = a \cdot \exp(-b \cdot U_e^*) + L \quad (16)$$

wherein  $Q_{st}$  = integral isosteric heat of sorption ( $kJ kg^{-1}$ ),  $L$  = latent heat of vaporization of free water ( $kJ kg^{-1}$ ),  $U_e^*$  = equilibrium water content (d.b.),  $a$ ,  $b$  = coefficient model.

The latent heat of free water vaporization was obtained using the average temperature by the following equation:

$$L = 2,502.2 - 2.39 T_m \quad (17)$$

wherein  $L$  = latent heat of free water vaporization ( $kJ kg^{-1}$ ),  $T_m$  = average temperature ( $^{\circ}C$ ).

The unitary volumetric shrinkage ( $\Psi_g$ ) during the drying of the product was determined by the ratio between the final volume for each water content and the initial volume of the seed. The volume ( $V_g$ ) of each seed was obtained during the drying process with the aid of a caliper according to the expression proposed by Mohsenin (1986):

$$V_g = \frac{\pi a b c}{6} \quad (18)$$

wherein  $a$  = major axis of the grain (mm),  $b$  = mean axis of the seed (mm);  $c$  = minor axis of the seed (mm).

| Model references    | Model                                     |
|---------------------|---|
| Bala and Woods      | $\Psi_g = a\{1 - \exp[b(U - U_0)]\}$ (19) |
| Lang and Sokhansanj | $\Psi_g = a + \beta_1(U - U_0)$ (20)      |
| Rahman              | $\Psi_g = a + \beta_2(U - U_0)$ (21)      |
| Corrêa              | $\Psi_g = 1/[a + b \exp(U)]$ (22)         |
| Line                | $\Psi_g = a + bU$ (23)                    |
| Exponential         | $\Psi_g = a \exp(bU)$ (24)                |

wherein  $\Psi_g$  = unit volume shrinkage (decimal),  $U$  = water content of the product, the decimal (d.b.),  $U_0$  = initial water content of the product, the decimal (d.b.),  $\beta_1 = a + b(UR) + c(T)$ ,  $a$ ,  $b$ ,  $c$  = parameters that depend on the product,  $UR$  = relative humidity (decimal),  $T$  = air temperature ( $^{\circ}C$ ),  $\beta_2$  = volumetric coefficient, dimensionless contraction.

The experimental design was a completely randomized design (CRD) with three tests for each relative humidities and drying temperatures. Nonlinear regressions were performed to adjust the mathematical models analysis based on Quasi-Newton method, using the computer program Statistica 7.0<sup>®</sup>. To check the fit degree of each model, the significance of the regression coefficient was determined by t-test, adopting the 5% level of probability, the magnitude of the coefficient of determination ( $R^2$ ), the mean relative error values ( $P$ ), the average estimated error (SE), and the behavior of distribution of residuals was verified. The relative average error and the average error estimated for each model were calculated according to the following expressions, respectively:

$$P = \frac{100}{n} \sum \frac{|Y - \hat{Y}|}{Y} \quad (25)$$

$$SE = \sqrt{\frac{\sum (Y - \hat{Y})^2}{GLR}} \quad (26)$$

wherein  $Y$  = experimentally observed value,  $\hat{Y}$  = value calculated by the model,  $n$  = number of experimental observations,  $GLR$  = degrees of freedom of the model (the number of observations minus the number of model parameters).

### 3 RESULTS AND DISCUSSION

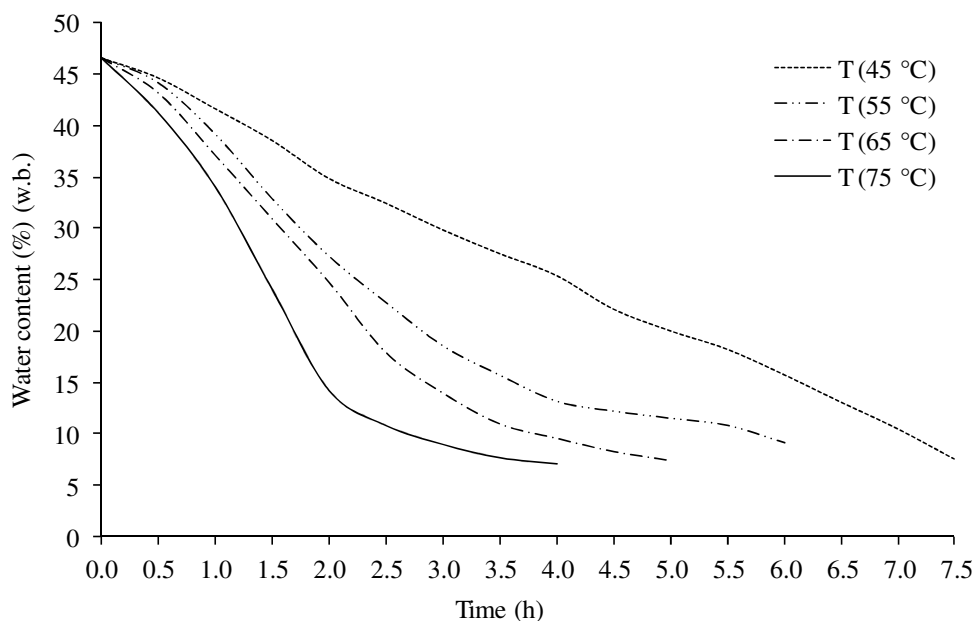
The influence of air temperature on the kinetics of drying of sunflower seeds can be observed in Figure 1. The initial water content of sunflowers seeds was about  $46.64 \pm 1\%$  (w.b.), and the final water content was 7.62, 7.76, 6.7 and 7.03% (w.b.) at 45, 55, 65, and 75  $^{\circ}C$ , respectively. The drying duration to reach the equilibrium water content for the sunflowers seeds sample were 7.5, 6.5, 5.5 and 4.0 hours at 45, 55, and 75  $^{\circ}C$ , respectively.

As expected, the drying period decreases increasing air temperature, so that there is a greater rate of water removal from the seed due to increased moisture gradient between the seed and the air, decreasing the time required to reduce water content to the desired value for storage, a factor noted by several researchers in other agricultural products: grapes (AZZOUZ et al., 2002); red pepper (AKPINAR et al., 2003); prickly pear (LAHSASNI et al., 2004); eggplant (ERTEKIN;

YALDIZ, 2004); parboiled wheat (MOHAPATRA; RAO, 2005); adzuki beans (ALMEIDA et al., 2009); and jatropha (ULLMANN et al., 2010). In each equal increased temperature interval of 10 °C, drying period decreased by 13.33% (45 to 55 °C), 15.38% (55 to 65 °C), and 27.27% (65 to 75 °C) correspondingly. The increased temperature interval of 10 °C from 65 to 75 °C has greater effect on drying period decreasing.

Moreover, the use of higher temperatures allow quicker drying, resulting in a very high humidity difference between the periphery and the center of the seed, generating over drying and problems such as deterioration in the acceleration process. The moisture ratio decreases continuously to the drying progress (Figure 1). It took 4.5, 2.7, 2.3, and 1.7 hours to remove the moisture at 45, 55, 65 and 75 °C, respectively, which is about half time of the total drying time. Therefore, half of the total drying time was required to remove the residual moisture due to slower diffusion. These observations are in agreement with previous results on drying of biological products (RESENDE et al., 2008,

ULLMANN et al., 2010; CORADI et al., 2014a, CORADI et al., 2014b). Constant rate period was not present during drying of sunflower seeds (Figure 1). Drying process took place in a falling rate period except a very short accelerating period at the beginning. At higher water content, the increase in temperature has more considerable effect on the drying rates than at lower water content, which was almost negligible at the end. Moisture loss was faster at the start of drying than at the end. This is mainly due to reduction in water content as drying advances. The rate of migration of moisture from inner surface to outer surface decreases at the final stage of drying and hence lower drying rates (RAJKUMAR et al., 2007). In practice, when the heating temperature is higher sunflower seeds quality decrease (ALMEIDA et al., 2009). Therefore, with to optimize energy efficiency and product quality, the heating temperature zone between 65 and 75 °C is a better option.



**Figure 1** - Drying curves of sunflower seeds.

The model coefficients values are reported in Table 1. The regression analysis was used to set up the relations between these parameters and temperatures. All the coefficients were dependent on drying air temperature. The coefficient 'a', 'c' varied in nearly sinusoidal shape with temperature, whereas 'k', 'n' and 'b' varied in

nearly linear shape. Among the evaluated mathematical models, it was found that the adjusted coefficients of determination, mean relative errors and average estimated errors (Table 3), determined that the Wang and Singh model showed better fit the experimental data to describe the drying process of sunflower seeds, in the temperature range studied (45 to 75 °C).

**Table 1** - Parameters obtained from models fitted to the data for drying sunflowers seeds\*.

| Mathematical models          |  | T (°C) | k         | n        | c         | k <sub>1</sub> |
|------------------------------|--|--------|-----------|----------|-----------|----------------|
| Exponential                  |  | 45     | 0.289430  |          |           |                |
|                              |  | 55     | 0.464078  |          |           |                |
|                              |  | 65     | 0.550907  |          |           |                |
|                              |  | 75     | 0.759458  |          |           |                |
| Page                         |  | 45     | 0.320876  | 0.921232 |           |                |
|                              |  | 55     | 0.483817  | 0.953479 |           |                |
|                              |  | 65     | 0.524997  | 1.064947 |           |                |
|                              |  | 75     | 0.729502  | 1.092830 |           |                |
| Page Modified                |  | 45     | 0.291157  | 0.921232 |           |                |
|                              |  | 55     | 0.466978  | 0.953479 |           |                |
|                              |  | 65     | 0.546038  | 1.064947 |           |                |
|                              |  | 75     | 0.749310  | 1.092830 |           |                |
| Henderson and Pabis          |  | 45     | 0.908492  | 0.259222 |           |                |
|                              |  | 55     | 0.918698  | 0.424069 |           |                |
|                              |  | 65     | 0.928217  | 0.511096 |           |                |
|                              |  | 75     | 0.918991  | 0.700129 |           |                |
| Logarithmic                  |  | 45     | 1.037938  | 0.189904 | -0.15334  |                |
|                              |  | 55     | 0.903337  | 0.450262 | 0.021476  |                |
|                              |  | 65     | 0.978978  | 0.437512 | -0.063986 |                |
|                              |  | 75     | 0.947295  | 0.638264 | -0.035473 |                |
| Two terms                    |  | 45     | 0.45446   | 0.259220 | 0.454246  | 0.259220       |
|                              |  | 55     | 0.459349  | 0.424060 | 0.459349  | 0.424069       |
|                              |  | 65     | 0.464108  | 0.511096 | 0.464108  | 0.511096       |
|                              |  | 75     | 0.459495  | 0.700129 | 0.459495  | 0.700129       |
| Two exponential terms        |  | 45     | 0.520959  | 0.400013 |           |                |
|                              |  | 55     | 0.498911  | 0.670505 |           |                |
|                              |  | 65     | 1.512833  | 0.659597 |           |                |
|                              |  | 75     | 1.586729  | 0.946706 |           |                |
| Wang and Sing                |  | 45     | -0.238528 | 0.016447 |           |                |
|                              |  | 55     | -0.374451 | 0.038879 |           |                |
|                              |  | 65     | -0.432253 | 0.050702 |           |                |
|                              |  | 75     | -0.581200 | 0.089508 |           |                |
| Henderson and Modified Pabis |  | 45     | 0.302837  | 0.259220 | 0.302837  | 0.259220       |
|                              |  | 55     | 0.306233  | 0.424060 | 0.306233  | 0.424060       |
|                              |  | 65     | 0.309406  | 0.511096 | 0.309406  | 0.511096       |
|                              |  | 75     | 0.306330  | 0.700129 | 0.306330  | 0.700129       |
| Midilli                      |  | 45     | 0.884174  | 0.211266 | 1.013423  | -0.01038       |
|                              |  | 55     | 0.882623  | 0.354036 | 1.385108  | 0.017457       |
|                              |  | 65     | 0.868485  | 0.374479 | 1.491149  | 0.013655       |
|                              |  | 75     | 0.867934  | 0.592848 | 1.572112  | 0.019016       |
| Diffusion approximation      |  | 45     | 0.064322  | 11.54381 | 0.023224  |                |
|                              |  | 55     | 0.998079  | 0.488154 | -1.129390 |                |
|                              |  | 65     | -2.421390 | 0.817318 | 0.883372  |                |
|                              |  | 75     | 9.352686  | 1.084651 | 1.049122  |                |

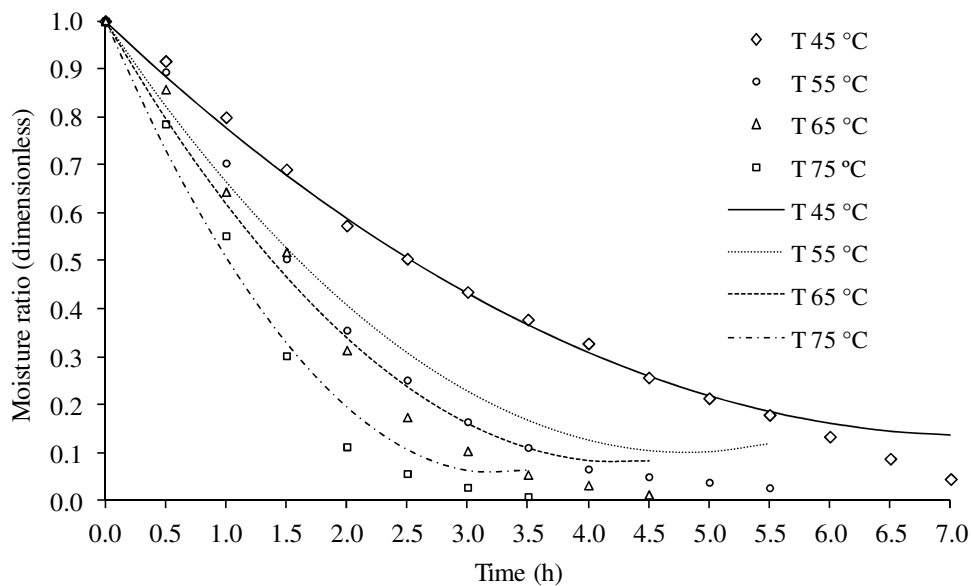
\*All estimated coefficients were significant at 5% probability by *t* test.

**Table 2** - Coefficient of determination ( $R^2$ ), mean relative error (P), estimated values of average error (SE) drying of sunflower seeds due to different temperatures.

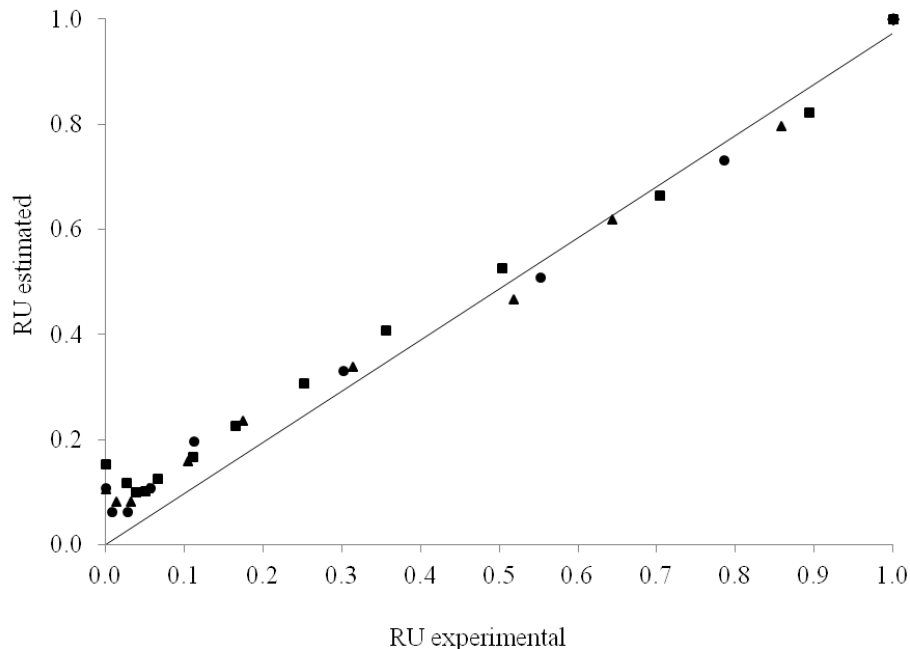
|                              | 45 °C                   | 55 °C  | 65 °C  | 75 °C  |
|------------------------------|-------------------------|--------|--------|--------|
|                              | $R^2$ (%)               |        |        |        |
| Exponential                  | 98.66                   | 98.73  | 98.66  | 98.37  |
| Page                         | 98.80                   | 98.77  | 98.73  | 98.47  |
| Page Modified                | 98.80                   | 98.77  | 98.73  | 98.47  |
| Henderson and Pabis          | 99.67                   | 99.36  | 99.15  | 98.98  |
| Logarithmic                  | 99.91                   | 99.38  | 99.28  | 99.04  |
| Two Terms                    | 99.67                   | 99.36  | 99.15  | 98.98  |
| Two exponential terms        | 98.70                   | 98.83  | 98.73  | 98.48  |
| Wang and Singh               | 97.80                   | 98.51  | 98.75  | 98.55  |
| Henderson and Pabis Modified | 99.67                   | 99.36  | 99.15  | 98.98  |
| Midilli                      | 99.61                   | 99.94  | 99.88  | 99.90  |
| Diffusion approximation      | 98.93                   | 98.98  | 98.73  | 98.46  |
|                              | SE (decimal)            |        |        |        |
| Exponential                  | 0.0491                  | 0.0704 | 0.0764 | 0.0786 |
| Page                         | 0.0629                  | 0.0804 | 0.0706 | 0.0702 |
| Page Modified                | 0.0629                  | 0.0804 | 0.0706 | 0.0702 |
| Henderson and Pabis          | 0.0761                  | 0.0936 | 0.0978 | 0.1029 |
| Logarithmic                  | 0.0691                  | 0.0955 | 0.0912 | 0.0985 |
| Two Terms                    | 0.0822                  | 0.1035 | 0.1109 | 0.1218 |
| Two exponential terms        | 0.0586                  | 0.0822 | 0.0696 | 0.0685 |
| Wang and Singh               | 0.0487                  | 0.0745 | 0.0634 | 0.0661 |
| Henderson and Pabis Modified | 0.0900                  | 0.1174 | 0.1312 | 0.1573 |
| Midilli                      | 0.0745                  | 0.0969 | 0.0925 | 0.0991 |
| Diffusion approximation      | 0.0676                  | 0.0871 | 0.0740 | 0.0747 |
|                              | P (%)                   |        |        |        |
| Exponential                  | 14.24                   | 7.67   | 5.84   | 8.51   |
| Page                         | 12.27                   | 8.20   | 5.23   | 7.55   |
| Page Modified                | 12.27                   | 8.20   | 5.23   | 7.55   |
| Henderson and Pabis          | 0.62                    | 6.14   | 3.25   | 5.08   |
| Logarithmic                  | 4.15                    | 6.33   | 2.69   | 4.75   |
| Two Terms                    | 0.62                    | 6.14   | 3.25   | 5.08   |
| Two exponential terms        | 13.72                   | 8.40   | 5.20   | 7.74   |
| Wang and Singh               | 23.56                   | 10.15  | 8.76   | 10.94  |
| Henderson and Pabis Modified | 7.74                    | 6.14   | 8.25   | 5.08   |
| Midilli                      | 4.18                    | 6.95   | 8.79   | 4.70   |
| Diffusion approximation      | 10.45                   | 8.11   | 5.88   | 7.10   |
|                              | Distribution of residue |        |        |        |
| Exponential                  | A                       | A      | A      | A      |
| Page                         | A                       | A      | A      | A      |
| Page Modified                | A                       | A      | A      | A      |
| Henderson and Pabis          | A                       | A      | A      | A      |
| Logarithmic                  | A                       | A      | A      | A      |
| Two Terms                    | A                       | A      | A      | A      |
| Two exponential terms        | A                       | A      | A      | A      |
| Wang and Singh               | A                       | A      | A      | A      |
| Henderson and Pabis Modified | A                       | A      | A      | A      |
| Midilli                      | A                       | A      | A      | A      |
| Diffusion approximation      | A                       | A      | A      | A      |

Figure 2 shows the experimental data of water content versus drying time for each drying air temperature adjusted to Wang and Singh model. In Figure 3, the correspondence between the experimental and estimated values and the satisfactory adjustment of the Wang and Singh model to describe the drying of sunflower seeds can be observed. The responses plotted in Figure 5

demonstrates that the data points follows a straight line at 45° angle signifying the suitability of the model in describing the thin layer drying of the sunflower seeds. Similar approach for selecting the model for biological products drying was reported by RESENDE et al. (2008), GONELI et al. (2011) and CORADI et al. (2014a).



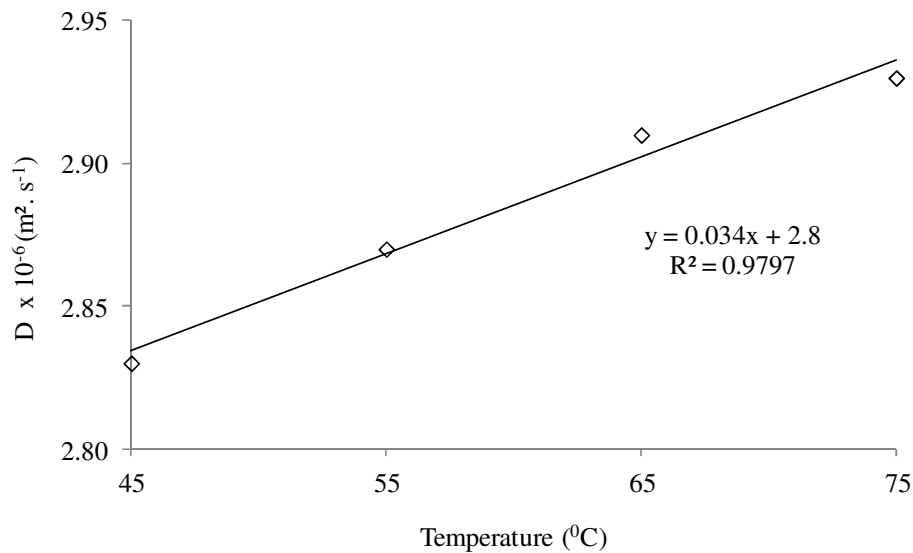
**Figure 2** - Moisture ratio of sunflower seeds adjusted to the Wang and Singh model.



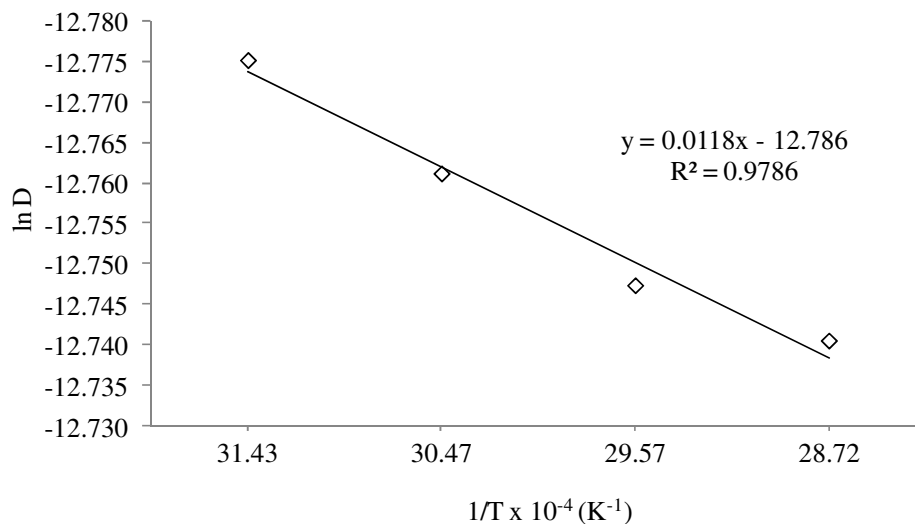
**Figure 3** - Experimental data and estimated the moisture ratio, calculated by the model of Wang and Singh.

The results indicated that internal mass transfer resistance controlled the drying period due to which, falling rate drying period dominated the drying process. The average values of effective diffusivities of sunflower seeds in the drying process at 45-75 °C varied in the range of  $2.83\text{-}2.93 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$  (Figure 4). It may also be observed, from Figure 4, that effective diffusivity increased with the increase in temperature. The results are in agreement with the findings from WANG et al.

(2007); RESENDE et al. (2008); GONELI et al. (2011); CORADI et al. (2014b). The evaluated effective diffusivities were within the range of published values ranging from  $10^{-11}$  to  $10^{-6}$  for food materials (WANG et al., 2006; RESENDE et al., 2008, CORADI et al., 2014a). Figure 5 shows the values of  $D$  presented as "ln  $D$ " described as a function of the reciprocal absolute temperature ( $1/T$ ). The straight line obtained indicates the uniformity of variation of diffusivity with temperature.



**Figure 4** - Mean values for the effective diffusion coefficient ( $m^2 s^{-1}$ ), due to different air temperatures in the drying of sunflower seeds.

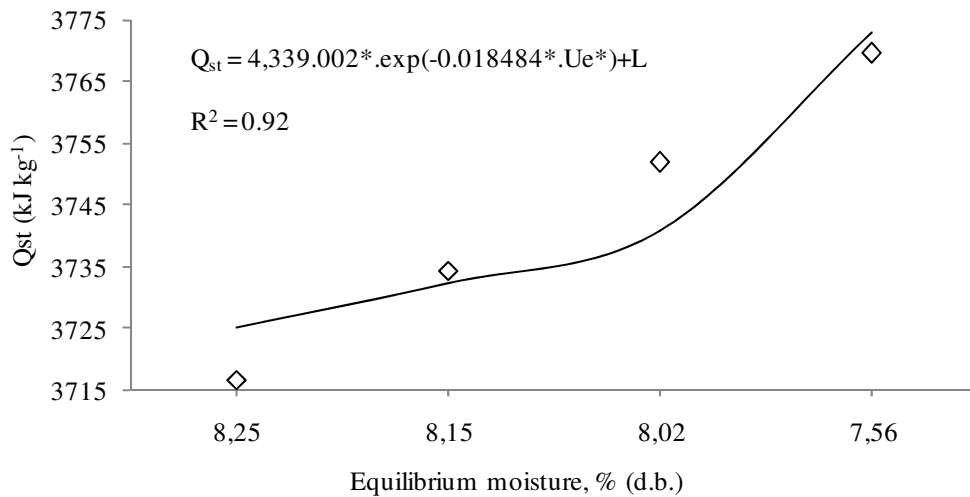


**Figure 5** - Representation of the Arrhenius relationship for the effective diffusivity and air temperature drying of sunflower seeds.

The curves of latent heat of vaporization of water from sunflower seeds at temperatures of 45, 55, 65 and 75 °C, are shown in Figure 6. The latent heat of vaporization ranged from 3,725.176 to 3,773.082 kJ kg<sup>-1</sup>, whereas with the decrease in the equilibrium water content, there was an increase in energy needed to evaporate the water from the corn kernels. According to BROOKER et al. (1992), the water content and temperature are the main factors that influence the value of the vaporization latent heat of water from the product. It was found that with

increasing temperature for the same water content, there is a reduction of the latent heat of vaporization. ALMEIDA et al. (2000) studied the latent heat of vaporization of seed cotton and lint and observed this same behavior. The same results were observed in CORADI et al. (2014a) and CORADI et al. (2014b), that studied the latent heat of vaporization in coffee grains and lemon grass plant.





**Figure 6** - Experimental values and estimated integral isosteric heat of sorption as a function of moisture content equilibrium.

The Correa et al. model (Table 3) was the most suitable for mathematical description of the phenomenon of shrinkage of sunflower seeds (Figure 7), showing a high determination coefficient and low values of the mean relative and estimated errors, and yet, all the models showed a random distribution and approximately regular residues (Tables 3 and 4). It has been observed, in

Figure 7, When reducing the water content of 0.86 to 0.09 (kg kg<sup>-1</sup> dry matter) the marked reduction in seed volume is relative to the initial volume occurred at temperatures of 75, 65, 55 and 45 °C (Figure 7).

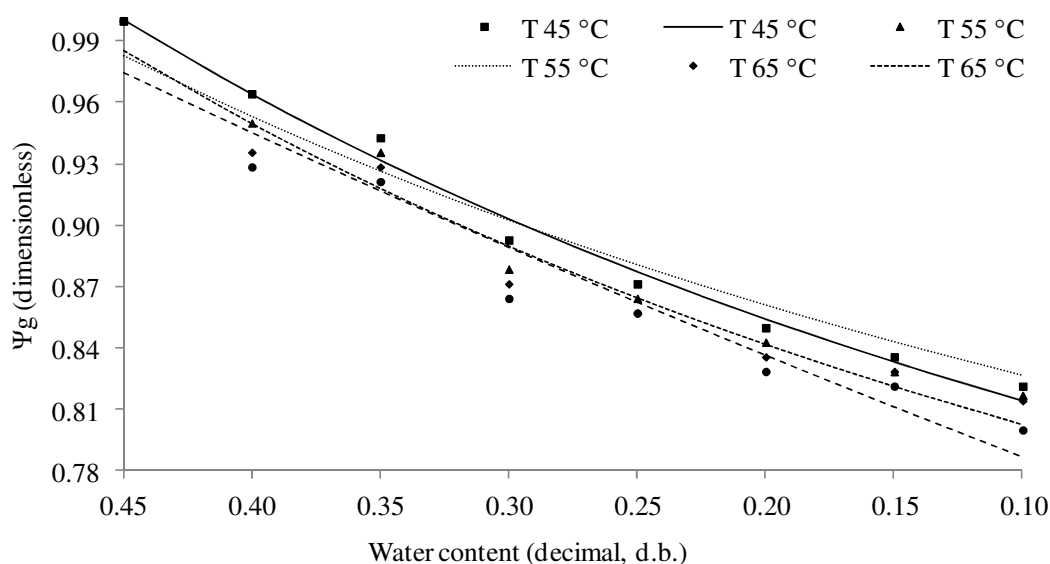
**Table 3** - Parameters estimated, coefficient of determination ( $R^2$ ) and distribution of residues of the mathematical models used to describe the shrinkage of sunflower seeds for different temperatures of the drying air.

| Mathematical models | Estimation of parameters  | $R^2$ | Distribution of residuals |
|---------------------|---------------------------|-------|---------------------------|
| Temperature 45 °C   |                           |       |                           |
| Bala and Woods      | a= 0.92912<br>b= -18.0258 | 68.23 | T                         |
| Rahman              | a=0.75374<br>b= 0.52211   | 98.35 | A                         |
| Correa              | a= 1.77125<br>b= -0.4918  | 98.86 | A                         |
| Exponential         | a= 0.79186<br>b= 0.58681  | 98.77 | A                         |
| Temperature 55 °C   |                           |       |                           |
| Bala and Woods      | a= 0.90889<br>b= -25.7737 | 28.94 | T                         |
| Rahman              | a=0.78178<br>b= 0.419414  | 87.10 | A                         |
| Correa              | a= 1.6682<br>b= -0.41392  | 90.75 | A                         |
| Exponential         | a= 0.78537<br>b= 0.478184 | 88.09 | A                         |
| Temperature 65 °C   |                           |       |                           |
| Bala and Woods      | a= 0.91238<br>b= -18.7278 | 62.48 | T                         |
| Rahman              | a=0.74456<br>b= 0.506803  | 96.00 | A                         |
| Correa              | a= 1.79890<br>b=-0.4999   | 98.03 | A                         |
| Exponential         | a= 0.75167<br>b= 0.581219 | 96.65 | A                         |
| Temperature 75 °C   |                           |       |                           |

|                |                           |       |   |
|----------------|---------------------------|-------|---|
| Bala and Woods | a= 0.90963<br>b=-17.8313  | 66.13 | T |
| Rahman         | a=0.73223<br>b= 0.528912  | 96.29 | A |
| Correa         | a= 1.84398<br>b= -0.52740 | 98.13 | A |
| Exponential    | a= 0.74023<br>b= 0.610357 | 96.90 | A |

**Table 4** - Values of mean relative error (P), estimated values of average error (SE) of sunflowers seeds drying in different temperatures.

|                | 45 °C        | 55 °C    | 65 °C     | 75 °C    |
|----------------|--------------|----------|-----------|----------|
|                | SE (decimal) |          |           |          |
| Bala and Woods | 0.051336     | 0.060971 | 0.0545230 | 0.054501 |
| Rahman         | 0.012667     | 0.031287 | 0.0195408 | 0.019595 |
| Correa         | 0.007480     | 0.026750 | 0.0137760 | 0.013976 |
| Exponential    | 0.010959     | 0.030143 | 0.0179071 | 0.017941 |
|                | P(%)         |          |           |          |
| Bala and Woods | 5.84627      | 1.926450 | 5.1696970 | 5.595600 |
| Rahman         | 0.75000      | 0.130000 | 0.1010000 | 0.760000 |
| Correa         | 0.32463      | 0.653270 | 0.4535350 | 0.414200 |
| Exponential    | 2.20796      | 4.005950 | 3.3492420 | 3.357070 |



**Figure 7** - Volumetric shrinkage of sunflower seeds adjusted to the Corrêa model due to drying with different air temperatures.

The drying temperature of 45 °C reduced to a lesser extent the seeds volume, possibly caused the low rate of water removal, causing stiffening of the integument, which hindered the seeds contraction. . Whereas, temperatures of 65 to 75 °C were the ones that the most influenced seeds volume, once the water was removed quickly and seeds contracted orthogonal axes in accordance with the reduction of water content. Corroborating SIQUEIRA et al. (2011) who found that the decrease in the geometric mean diameter of the seeds is proportional to the reduction of the water content and also depends on drying condition, that is, the air drying temperature.

#### 4 CONCLUSION

The drying time significantly reduced with increasing air drying temperature. The model of Wang and Sing was the one that better adjusted to experimental drying data. Effective diffusivity of sunflower seed ranged from 2.83 to 2.93x10<sup>-6</sup> m<sup>2</sup> s<sup>-1</sup>, while the isosteric heat of adsorption varied from 3,725.176 to 3,773.082 kJ kg<sup>-1</sup>. Reducing the water content influenced the shrinkage of sunflower seeds, with emphasis on temperatures above 55 °C. The model Correa et al. was that better adjusted to experimental data of sunflower seeds volumetric shrinkage.

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