Original Article
Food Science and Technology

ISSN 0101-2061 (Print)
ISSN 1678-457X (Online)

DOI: https://doi.org/10.5327/fst.00412

Mathematical modeling of sunflower seed (*Helianthus annuus* L.)

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Abstract

Sunflower seeds are an important source of edible oil and animal protein, with potential uses in the biofuel industry. It is produced in a wide range of geographical areas due to its ability to adapt to different growing conditions. The aim of this study was to select the mathematical models that best fit the drying kinetics of sunflower seeds, cultivar Altis 99, at different temperatures. The seeds were dried in an oven with forced air circulation at temperatures of 40, 50, 60, 70, and 80 °C. The reduction in mass during drying was monitored by weighing at pre-established intervals. Ten mathematical models were fitted to the experimental moisture content ratio data based on nonlinear regression analysis using the Gauss-Newton method and complemented by the chi-square test (χ^2) and the Akaike information and Schwarz's Bayesian information criteria. The drying time of sunflower seeds decreased as the temperature of the drying air increased, representing higher rates of water removal. The Midilli model is recommended for describing the drying kinetics of sunflower seeds due to the quality of the fit and the simplicity of its application.

Keywords: Altis 99; drying rate; Midilli model; AIC and BIC.

Practical Application: Knowledge of sunflower seeds' drying for physiological quality maintenance.

1 INTRODUCTION

Sunflower (*Helianthus annuus* L.) is an oilseed crop that stands out for its multiple uses as it is cultivated in different soil and climate conditions due to its good adaptability, making it feasible to grow in various regions of Brazil (Vieira et al., 2017).

The increase in demand for energy sources, especially fossil fuels, has generated discussions about the necessary diversification of the global energy matrix, with a focus on clean or plant-based energy sources, due to their renewable nature, as part of the concern associated with climate change (Silva et al., 2018; Sivakumar et al., 2000). Sunflower seeds are widely used as one of the main sources of human food oil, within the class of vegetable oils, with oil content ranging from 30 to 50% and with considerable protein content, very useful in the production of bran for animal feed, directly impacting the production of meat, eggs, milk, and their by-products (Castro & Leite, 2018; Khanali et al., 2022).

According to the Food and Agriculture Organization of the United Nations (FAO), Ukraine, Russia, and Argentina are among the world's largest sunflower producers with production volumes of 14.23, 13.52, and 3.52 million tons, respectively, for a total of 53.06 million tons in terms of average global production over the last 5 years (Faostat, 2024). Its production in Brazil is still limited, but there is a considerable demand for human consumption, the food industry, and bioethanol production (Castro & Leite, 2018).

According to Kaya et al. (2015), sunflower oil processing has been increasing, with small factories being replaced by large, modernized ones in areas of greater production and consumption. Sunflower oil processing aims to maintain the oil's properties through the correct adoption of postharvest processes. In general, processing begins when the oil is collected at the processing plant and goes through the stages of classification, pre-cleaning, and drying, before being extracted (Feix & Zanin, 2018).

The processing of sunflower oil for consumption in Brazil involves a sequence of stages, starting with the collection of the product from the fields, followed by classification, cleaning, and drying of the seeds (Feix & Zanin, 2018). Drying can be natural, which takes place on the plant itself. Although it does not require high implementation costs and an expert workforce, its use is dependent on climatic conditions at harvest time, making it difficult to use for large volumes. Artificial drying, in contrast to the risks associated with natural drying, such as the occurrence of pests and diseases and adverse climatic events, when carried out properly, is a viable alternative for preserving the product, thus preserving its quality, health, and nutritional composition (Feix & Zanin, 2018).

Drying usually takes place using air heated by a difference in partial vapor pressure and occurs through the simultaneous transfer of heat and mass between the product and the drying

Received: Oct. 18, 2024.
Accepted: Nov. 19, 2024.
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Conflict of interest: nothing to declare.
Funding: PROAP CAPES, Instituto Federal Goiano, and CNPq (Process: 310222/2021-4), Brazil.

air, a process that depends on conditions such as temperature, relative humidity, physicochemical properties, and the initial moisture content of the product. It basically aims to remove excess water from the seeds until they reach a safe moisture content for storage (Bala, 2017; Resende et al., 2008).

In order to improve or even design new seed drying systems and equipment, it is extremely important to have information on the behavior of each product during drying, which is provided by mathematical modeling (Resende et al., 2010). The modeling of drying kinetics, carried out through the continuous drying of seeds in a thin layer, adjusting the behavior to mathematical models helps to describe the removal of water during the process (Santos et al., 2013).

Several mathematical models have been used in the literature to describe the drying process of grains and seeds, but their applicability is restricted to the conditions under which the experimental data is generated. Obtaining this data is extremely important for describing the behavior of the drying models of agricultural products such as sunflower seeds, making it possible to perform the drying process of this product in both thin and thick layers, successfully reproducing the estimate of the time spent during the process (Camicia et al., 2015; Resende et al., 2009).

The information provided by the drying models is essential for developing processes, sizing oil extractors, and estimating energy costs in production, which is reflected in the final value of the product and the quality of the oil produced (Reis et al., 2011). In this context, the aim of this study was to assess the mathematical models that best fit the drying kinetics of sunflower seeds.

2 MATERIAL AND METHODS

The sunflower seeds (cultivar Altis 99) were harvested manually on a rural farm in the village of Montividiu, GO, with an initial moisture content of 0.17 ± 0.002 kg kg^{-1} db. The experiment was conducted at the Laboratório de Pós-Colheita de Produtos Vegetais (LPCPV) of the Instituto Federal de Educação, Ciência e Tecnologia Goiano - Campus Rio Verde.

Initially, the achenes (seeds) were collected from each capitulum of sunflower and then cleaned using a fan and four trays, which were placed horizontally one behind the other based on the principle that the lighter impurities present in the mass of seeds were carried to the trays furthest from the air emitted by the fan, optimizing the cleaning process. A Boerner homogenizer was then used to obtain similar samples. Approximately 10 g of the sample was separated to determine the moisture content using the gravimetric method, in a forced circulation oven at 105 ± 3 °C for 24 h, with three repetitions (Brasil, 2009). The seeds were dried on four non-perforated trays made of stainless steel, each containing approximately 127 g of product, evenly distributed in an oven with forced air circulation set to operate at temperatures of 40, 50, 60, 70, and 80°C. The temperatures were selected to obtain a range that included seeds and grains. The means of relative humilities of the air during drying were 22.32, 9.52, 6.86, 4.09, and 2.69% for temperatures of 40, 50, 60, 70, and 80°C, respectively. The reduction in mass during drying was monitored using a semi-analytical balance with a resolution of 0.01 g by weighing the trays with the samples at pre-established intervals until the seeds reached hygroscopic equilibrium with the drying air conditions, i.e., when the variation in mass was constant to the second decimal place for three consecutive weighings.

After the drying process, the drying curves were obtained from the experimental data collected, relating the moisture content ratio over the drying time according to the Equation 1:

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

Where:

RX: the moisture content ratio (dimensionless);

X: the current moisture content (decimal, db);

X_e: the equilibrium moisture content (decimal, db);

X_i: the initial moisture content (decimal, db).

Ten mathematical models were fitted to the experimental data on the moisture content ratio during the drying of sunflower seeds (Table 1).

The mathematical models were adjusted using nonlinear regression analysis using the Gauss-Newton method. The significance of the model parameters was assessed using the t-test with a significance level of $p < 0.05$. The adjustment level of each model was assessed according to the magnitudes of the coefficient of determination (R^2), relative mean error (P), estimated mean error (SE), and χ^2 test at a significance level of $p < 0.01$. The estimated and relative mean error, as well as the chi-squared test for each of the models, were calculated according to the following equations, respectively (Equations 12, 13 and 14):

Table 1. Thin-layer models employed in mathematical modeling of drying kinetics of sunflower seeds.

Equation	Model designation	
$RX = a \exp(-k\, t) + (1-a) \exp(-k\, b\, t)$	Approximation of diffusion	(2)
$RX = a \exp(-k_0\, t) + b \exp(-k_1\, t)$	Two terms	(3)
$RX = a \exp(-k\, t) + (1-a) \exp(-k\, a\, t)$	Two-term exponential	(4)
$RX = a \exp(-k\, t)$	Henderson & Pabis	(5)
$RX = a \exp(-k\, t)$	Logarithmic	(6)
$RX = a \exp(-k\, t^n) + b\, t$	Midilli	(7)
$RX = \exp(-k\, t)$	Newton	(8)
$RX = \exp(-k\, t^n)$	Page	(9)
$RX = \exp\{[-a - (a^2 + 4\, b\, t)^{0.5}] / (2\, b)\}$	Thompson	(10)
$RX = 1 + a\, t + b\, t^2$	Wang & Singh	(11)

where t: drying time; k, k_0, and k_1: drying constants; a, b, c, d, g, and n: model coefficients.

$$SE=\sqrt{\frac{\sum_{i=1}^{n}\left(Y-\widehat{Y}\right)^{2}}{DF}} \quad (12)$$

$$P=\frac{100}{n}\sum_{i=1}^{n}\left(\frac{\left|Y-\widehat{Y}\right|}{Y}\right) \quad (13)$$

$$\chi^{2}=\sum_{i=1}^{n}\frac{\left(Y-\widehat{Y}\right)^{2}}{DF} \quad (14)$$

Where:

Y: the value observed experimentally;

Ŷ: the value estimated by the model;

n: the number of experimental observations;

DF: the degree of freedom of the model (difference between the number of observations and the number of model parameters).

The Akaike Information Criterion (AIC) and Schwarz's Bayesian Information Criterion (BIC) were used as auxiliary analyses to choose the best mathematical model to predict the phenomenon according to the following equations, respectively (Equations 15 and 16):

$$AIC=-2\log L+2p \quad (15)$$

$$BIC=-2\log L+pLn(n) \quad (16)$$

Where:

p and n: the number of model parameters and observations;

L: the maximum likelihood considering the estimates of the parameters.

3 RESULTS AND DISCUSSION

The sunflower seeds were dried until reaching their equilibrium moisture content. It can be seen that as the temperature of the drying air increased, the drying time decreased (Figure 1). The drying rate is proportional to the increase in drying air temperature, especially at the beginning of the drying process. At the end of the process, the values are closer, and in general, there is a reduction as the drying time increases as a consequence of the lower availability of water, as well as being more strongly linked. This expected behavior was also observed by several studies, such as *Carapa spp.* (Mendonça et al., 2019), *Crambe abyssinica* (Costa et al., 2017), *Guizotia abyssinica* Cass (Silva et al., 2017), and *Arachis hypogaea* L. (Araujo et al., 2017).

The sunflower seeds reached equilibrium moisture content of 0.035, 0.025, 0.019, 0.016, and 0.014 kg kg^{-1} db in 16.16, 11.16, 9.16, 4.91, and 4.41 h for the temperatures of 40, 50, 60, 70, and 80°C, respectively. This increase in drying air temperature resulted in a higher drying rate from the product due to the higher partial water vapor pressure of the sunflower seeds at higher temperatures (Smaniotto et al., 2017).

Another aspect that can be attributed to the shorter drying time at higher temperatures is that, as the temperature rises, the level of vibration of the water molecules increases, thus contributing to faster water diffusion (Goneli et al., 2009), since at higher temperatures, the water molecules are less resistant; in other words, the water is less bound to the molecules that make up the dry mass of the material.

Table 2 shows the values obtained for χ^2, relative mean error (%, P), estimated mean error (SE), coefficient of determination (%, R^2), AIC, and Schwarz's BIC for the mathematical models throughout the drying process.

The coefficients of determination (R^2) range from 0 to 100 (%) and show the strength of the relationship between the observed and estimated data (Mendonça et al., 2019), i.e., as closer to 100 as possible, the more informative the model is, the better it will fit the experimental data. It was observed that for the coefficient of determination (R^2), the Wang and Singh model at all the drying temperatures tested, and the Newton, approximation of diffusion, and Thompson models for 40°C showed values of less than 99% and, according to Chayjan and Shadidi (2014), the other models indicate a satisfactory representation of the drying process, which is above 99%. However, Madamba et al. (1996) emphasized that the coefficient of determination (R^2) alone cannot satisfactorily determine the best model, making a joint analysis including other statistical parameters feasible.

In the behavior of the magnitude of the estimated mean error (SE), there is a predominance of low values for 50, 60, 70, and 80°C in the Midilli model and 40°C for the two-term model. Therefore, these models validate the relationship that the lower the value found for SE, the better the fit of the model to the experimental data (Moscon et al., 2017; Siqueira et al., 2013).

The chi-square analysis (χ^2) shows the same trend for the Midilli model at drying temperatures of 50, 60, 70, and 80°C

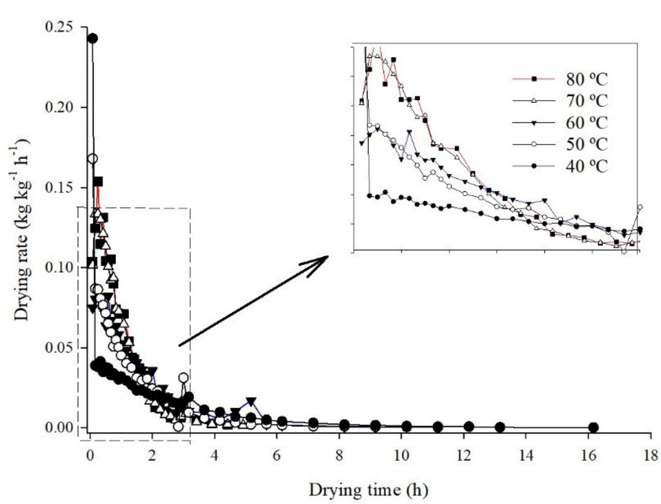

Figure 1. Drying rate of sunflower seeds at different drying air temperatures.

Table 2. Mean values of χ^2, coefficient of determination (%, R^2), estimated mean error (SE), relative mean error (%, P), Akaike information criterion (AIC), and Schwarz's Bayesian information criterion (BIC) of sunflower seeds (*Helianthus annuus* L.) subjected to temperatures of 40, 50, 60, 70, and 80°C.

Model	T (°C)	χ^2 (×10⁻⁴)	*p* (%)	SE	R^2 (%)	AIC	BIC
Approximation of diffusion	40	0.8	10.97	4.7	98.97	-261.4	-254.7
	50	5.5	23.99	32.3	99.39	-213.6	-203.9
	60	2.2	6.18	12.5	99.79	***	***
	70	3.5	15.41	17.6	99.67	***	***
	80	3.6	12.16	17.9	99.66	***	***
Two terms	40	0.8	10.97	4.6	99.91	-259.4	-251.0
	50	0.7	2.68	3.8	99.92	-244.9	-236.8
	60	1.5	5.11	8.4	99.86	-202.8	-195.0
	70	1.7	6.72	8.3	99.85	-164.6	-157.7
	80	1.5	5.05	7.5	99.86	-160.9	-154.2
Two-term exponential	40	7.1	13.86	43.7	99.15	-172.6	-167.5
	50	1.3	14.23	7.9	99.84	-221.0	-216.1
	60	2.9	13.49	16.6	99.71	-181.9	-177.3
	70	2.7	15.88	13.8	99.74	-152.5	-148.4
	80	3.2	14.38	16.2	99.68	-142.2	-138.2
Henderson and Pabis	40	4.5	12.97	27.7	99.47	-190.9	-185.8
	50	2.6	19.72	15.2	99.71	-196.9	-192.0
	60	2.7	14.60	15.7	99.73	-183.9	-179.2
	70	2.2	14.87	11.2	99.79	-154.6	-158.7
	80	2.4	12.48	12.4	99.76	-149.5	-145.5
Logarithmic	40	3.5	3.84	21.1	99.60	-200.4	-193.7
	50	0.9	8.46	5.2	99.90	-235.4	-229.0
	60	1.5	4.39	8.4	99.86	-204.2	-198.0
	70	1.7	6.60	8.8	99.84	-164.2	-158.7
	80	1.7	5.73	8.6	99.84	-158.5	-153.2
Midilli	40	2.4	3.94	14.6	99.73	-213.6	-205.2
	50	0.5	7.15	2.6	99.95	-259.1	-251.1
	60	1.3	6.53	7.1	99.88	-208.8	-201.1
	70	0.6	8.24	2.9	99.95	-195.0	-188.1
	80	0.5	4.99	2.2	99.96	-195.2	-188.6
Newton	40	22.4	23.74	140.1	97.25	-127.5	-124.1
	50	5.2	24.00	31.4	99.40	-171.5	-168.3
	60	2.9	14.65	17.0	99.70	-182.6	-179.5
	70	3.3	14.23	17.3	99.67	-147.5	-144.8
	80	3.3	11.96	17.2	99.66	-141.9	-139.2
Page	40	4.1	6.45	24.9	99.52	-195.2	-190.1
	50	9.3	14.54	5.5	99.90	-234.5	-229.7
	60	2.9	15.05	16.7	99.71	-181.7	-177.0
	70	2.3	17.58	11.9	99.77	-156.8	-152.7
	80	2.8	14.09	14.2	99.72	-145.8	-141.5
Thompson	40	8.5	11.05	52.6	98.98	-165.2	-160.2
	50	1.1	9.95	6.5	99.88	-228.5	-223.7
	60	2.9	13.85	16.9	99.71	-181.4	-176.7
	70	3.4	14.23	17.6	99.67	***	***
	80	3.4	11.95	17.6	99.66	***	***
Wang and Singh	40	233.7	129.17	1440.1	72.02	-32.8	-27.8
	50	252.8	190.22	1495.4	88.09	-27.1	-22.3
	60	112.5	90.64	646.4	88.87	-53.8	-49.1
	70	81.6	91.47	423.8	91.97	-53.2	-49.1
	80	49.6	51.40	252.8	95.05	-65.2	-61.2

*** Model not adjusted by the AIC and BIC.

(Table 2) and the approximation of diffusion and two-term models for the temperature of 40°C, with the lowest values under these conditions, which, according to Oliveira et al. (2018), is a better fit for the model since it is an analysis that evaluates the difference in the model's estimate, and therefore, the lowest values of this parameter are recommended.

Based on these aspects, it can be concluded that the Midilli and two-term models presented the best fits to the experimental data for R^2, SE, and χ^2. The relative mean error (P) indicates the deviation of the observed values from the curve estimated by the model (Kashaninejad et al., 2007). According to Mohapatra and Rao (2005), values greater than 10% relative mean error are considered inadequate for properly describing the phenomenon. Therefore, the lower the P value, the smaller the deviations between the experimental values and those estimated by the model (Siqueira et al., 2013). In this study, few models showed relative mean error values of less than 10% and only the logarithmic and Midilli models showed $p < 10\%$ for all drying air temperatures.

The AIC and Schwarz's BIC were used as auxiliary criteria for choosing the best mathematical model for predicting the drying curve of sunflower seeds (Table 2). The higher the absolute values of AIC and BIC, the better the fit of the model to the experimental data (Gomes et al., 2018). Therefore, according to the values obtained for AIC and BIC, the Midilli model satisfactorily represents the drying kinetics of sunflower seeds at temperatures of 50, 60, 70, and 80 °C and the approximation of diffusion model for 40°C, in line with the trend observed in the parameters described above.

According to Moscon et al. (2017), the selection and recommendation of the best model are also based on the simplicity of the application and the number of favorable parameters. Although both the Midilli and Approximation of diffusion models analyzed were more efficient in describing the drying process of sunflower seeds, the Midilli model was selected based not only on its favorable statistical coefficients for most of the drying temperatures studied but also on the greater simplicity of the equation.

There are several studies in the literature in which the Midilli model presented a satisfactory representation of the phenomenon under study, which has been recommended, for example, for the drying kinetics of soybeans (Silva et al., 2020) and jatropha (Siqueira et al., 2012). On the other hand, Smaniotto et al. (2017) recommended the Wang and Singh model for describing the drying of sunflower grains. It should be noted that the selection of empirical models to represent drying processes can be influenced by the species, cultivar, and even external factors such as air conditions.

Table 3 shows the values of the Midilli model coefficients fitted to the experimental drying data at different temperatures. The drying constant "k," which represents the external drying conditions, can be used as an approximation to characterize the effect of temperature and is related to the effective diffusivity in the drying process in the decreasing period and to the net diffusion that controls the process (Madamba et al., 1996), i.e., the constant "k" normally tends to increase since high temperatures lead to higher drying rates, reaching the equilibrium moisture content faster (Côrrea et al., 2010).

Nascimento et al. (2018) studied the drying of commercial sunflower seeds, and the values for the drying constant "k" increased with increasing drying air temperature in all the models evaluated. On the other hand, Mendonça et al. (2019) estimated the drying curves of two species of andiroba seeds, and Moscon et al. (2017), studying the drying curves of quinoa, observed the same behavior found in the present work, where the value of the constant "k" of the Midilli model decreased or varied with increasing temperature.

The oscillation of the "k" constant found in this study can be explained by differences in the environment at the time of drying, such as temperature and relative humidity, since drying did not take place during the same period for all temperatures (Moscon et al., 2017). According to Goneli et al. (2014), the differences in the values of the constants available in the literature are explained not only by the complexity of the products but also by the different evaluation methods, drying methodology and process, type of material, moisture content, chemical composition, and physical properties of the products.

The coefficients of the Midilli model ("a," "n," and "b") increased as the drying air temperature increased, except for the "a"

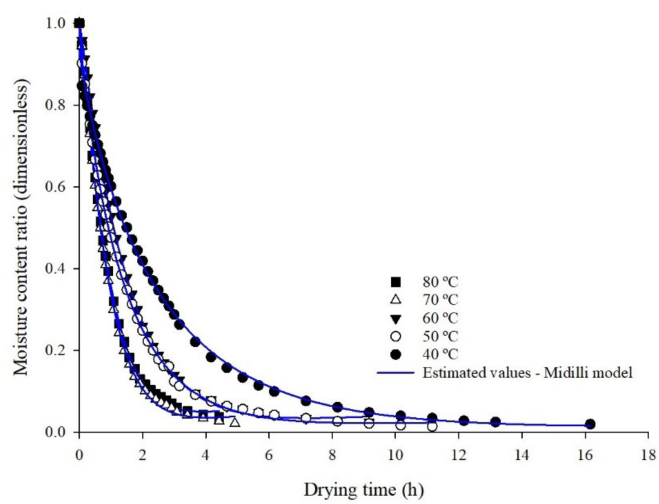

Figure 2. Moisture content ratio values by the Midilli model for drying sunflower seeds at temperatures of 40, 50, 60, 70, and 80°C.

Table 3. Coefficients for the Midilli model adjusted for sunflower seeds' drying at temperatures of 40, 50, 60, 70, and 80°C.

Coefficients	Temperature (°C)				
	40	50	60	70	80
a	0.9359**	0.9886**	1.0068**	1.0112**	1.0091**
k	0.4549**	0.7407**	0.6531**	1.1198**	1.0685**
n	0.8688**	0.9089**	1.0467**	1.1020**	1.1083**
b	0.0006ns	0.0020**	0.0045**	0.0075**	0.0108**

**Significant at $p < 0.01$ by the t-test; nsnot significant by the t-test.

coefficient, which decreased at a temperature of 80 °C. The variations in these coefficients are more attributable to mathematical adjustments than to any drying phenomenon since the Midilli model is a semiempirical model (Midilli et al., 2002).

Figure 2 shows the experimental and estimated moisture content ratio (RX) data for the selected model, representing a good fit between the experimental and estimated values.

It is possible to see a satisfactory correspondence between the experimental values and those estimated by the model for the temperatures throughout the drying process (Figure 2). It can be seen that water loss is faster at the start of the process with a higher drying rate, as shown by the steeper slope of the curves. Considering the same value of the moisture content ratio, the time needed to remove the water decreases as the temperature of the drying air increases. The drying curves also show that water loss tends to stabilize. According to Resende et al. (2010), at the end of drying, the water is found in more intrinsic regions of the sample, requiring more energy to evaporate.

4 CONCLUSION

The drying time of sunflower seeds decreased proportionally as the temperature of the drying air increased due to a higher drying rate under these conditions. The Midilli model is recommended to describe the drying kinetics curves of sunflower seeds with satisfaction as it presented the best statistical criteria for most of the temperatures under study and due to its simplicity of application.

ACKNOWLEDGMENTS

The authors thank Instituto Federal Goiano, UFGD, CAPES, FAPEG, FINEP, and CNPq for providing support, which was indispensable to the execution of this study.

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