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Mathematical modeling of the drying kinetics of endive leaves

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ABSTRACT

Endive is a vegetable traditionally eaten as a raw or cooked salad. It is a source of important nutritional compounds and one of the procedures for its industrialization is drying, which increases its shelf life, preserves the nutrients and reduces losses due to microorganisms. This research evaluated the drying kinetic of endive leaves at different temperatures and adjusted the experimental data according to mathematical models. The experimental design was completely randomized in triplicate, with each sample unit being a perforated aluminum tray containing about 100 g fresh leaves. The endive leaves were dried in an oven at 50, 60, 70 and 80°C. The mathematical models were adjusted according to the experimental data; non-linear regression analysis was performed by Gauss-Newton and Quasi-Newton methods. In all conditions, the mathematical models that best fitted the drying kinetics of the endive leaves were Midilli, Logarithmic and Valcam. The Logarithmic model, under these drying conditions, can be accurately described as suitable for predicting and simulating the drying kinetic of endive leaves, as it showed the best results in the statistical parameters evaluated.

Keywords: *Cichorium intybus*, moisture loss, food processing, logarithmic model.

RESUMO

Modelagem matemática da cinética de secagem de folhas de chicória

Chicória é um vegetal tradicionalmente consumido como salada crua ou cozida. É uma fonte de importantes compostos nutricionais e um dos procedimentos para sua industrialização é a secagem, que aumenta a vida útil, preserva seus nutrientes e reduz as perdas por microrganismos. Esta pesquisa avaliou a cinética de secagem de folhas de chicória em diferentes temperaturas e ajustou os dados experimentais de acordo com modelos matemáticos. O delineamento experimental foi inteiramente casualizado, em triplicata, onde cada unidade amostral era uma bandeja de alumínio perfurada, contendo cerca de 100 g de folhas frescas. As folhas de chicória foram secas em estufa, a 50, 60, 70 e 80°C. Os modelos matemáticos foram ajustados de acordo com os dados experimentais e, a partir deles, a análise de regressão não-linear foi realizada pelos métodos de Gauss-Newton e Quasi-Newton. Em todas as condições, os modelos matemáticos que melhor se ajustaram à cinética de secagem das folhas de chicória foram o Midilli, o Logarítmico e o Valcam. O modelo logarítmico, nessas condições de secagem, pode ser descrito com precisão como adequado para prever e simular a cinética de secagem das folhas de chicória, pois apresentou melhores resultados nos parâmetros estatísticos avaliados.

Palavras-chave: *Cichorium intybus*, perda de umidade, processamento de alimentos, modelo logarítmico.

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Endive is a leafy vegetable, rarely explored industrially. It contains important nutrients, mainly inulin, and is an important source of phytochemicals. Its leaves are traditionally eaten as raw and cooked salad in Mediterranean cuisine (Bayazid *et al*., 2020). Therefore, it becomes interesting to reduce its moisture content by drying method, which promotes an increase in shelf life, preserves its nutrients and prevents microbial growth. This processing can also enable the industrial use of the endive, especially in products that use its soluble form (Schneider *et al*., 2016; Santos *et al*., 2017).

The term equilibrium is sought in all areas of knowledge; however, there is a relative portion of variables that hinder the knowledge and standardization of this equilibrium condition for different types of products. To assess drying conditions, hygroscopic equilibrium is essential. Therefore, mathematical modeling has been used to identify and optimize industrial operations (Gasparin *et al*., 2017).

Mathematical modeling can be used as an aid tool to identify the equilibrium moisture content and the mathematical model that best describes the drying kinetics. The mathematical models contribute to the sizing of drying procedures, optimizing time, standardizing mechanized activities and reducing financial costs (Brooker *et al*., 1992; Berbert *et al*., 1995).

Therefore, the aim of this research was to (i) investigate the drying kinetics of endive leaves, (ii) obtain drying curves by fits of mathematical models, (iii) determine the best fit using statistical analysis.

MATERIAL AND METHODS

The endive leaves were purchased at a store from Rio Verde, Goias, Brazil and then, selected according to similar visual aspects and absence of physical injuries. The leaves were sanitized in chlorinated water for 15 min and dried on paper towels. Approximately 100 g of fresh leaves were uniformly distributed in a thin layer on the perforated rectangular aluminum trays (30x15x2 cm), and dried in an oven, using forced air circulation at 50, 60, 70 and 80°C, to determine the drying kinetics.

The temperature and relative humidity of the ambient air were monitored using a data logger, and the relative humidity inside the oven was obtained through the basic principles of psychometrics with the GRAPSI computer program.

To determine the drying curves and fit the models, the leaves were dried to a constant mass. The moisture content was determined in an oven at 105 ± 3°C, in three replicates, until constant mass was reached (Zenebon *et al*., 2008).

At the end of each drying process, the final equilibrium moisture content was determined, being 9.1; 7.4; 5.61 and 4.28% (d.b.), respectively, for the drying temperatures of 50, 60, 70 and 80°C.

The product's moisture content ratios were determined by Equation 1.

$$RX=\frac{X^*-X_e^*}{X_i^*-X_e^*} \qquad (1)$$

where RX is the moisture ratio (non-dimensional); is the moisture content (% d.b.); is rhe initial moisture content (% d.b.); and, X_e^* is the equilibrium moisture content (% d.b.).

The experimental data obtained from the drying of the endive leaves were used to adjust the mathematical models, with twelve empirical and non-empirical equations (Equations 2 to 13) commonly used to describe the drying processes of vegetable products (Box 1).

The mathematical models were adjusted according to the experimental data, and, from these, non-linear regression analysis was carried out by the Gauss-Newton and Quasi-Newton methods.

The models were selected based on the magnitude of the coefficient of determination (R^2), the chi-squared test (χ^2), the mean relative error (P) and the estimated standard deviation (SE) (Equations. 14, 15 and 16), at the 5% significance level and the 95% confidence interval ($p<0.05$), according to adaptations presented by Martins *et al*. (2018).

$$P=\frac{100}{n}\sum\frac{|Y-\hat{Y}|}{Y} \qquad (14)$$

$$SE=\sqrt{\frac{\sum(Y-\hat{Y}^2)}{DF}} \qquad (15)$$

$$\chi^2=\Sigma\frac{(Y-\hat{Y})^2}{DF} \qquad (16)$$

Where Y is the experimental value; $\hat{Y}$ is the estimated value; n is the number of data sets; and, DF is the degree freedom.

In addition to the above parameters, Akaike's information criterion (AIC) and Schwarz's Bayesian information criterion (BIC) were used (Equations 17 and 18). The AIC is used to compare non-nested models or to compare three or more models. Lower AIC values reflect a better fit (Akaike, 1974).

$$AIC = -2\ln(L) + 2k \qquad (17)$$

Where k is the number of estimated parameters; and, L is the value of the likelihood.

BIC also considers the degree of parameterization of the model, and therefore, the smaller the BIC value, the better the model adjustment (Schwarz, 1978).

Box 1. Mathematical models (Equations. 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12 and 13) applied to drying kinetics data. Rio Verde, IF Goiano, 2020.

Equation	Model	Equation number
$RX = 1 + at + bt^2$	Wang & Sing	(2)
$RX = a.\exp(-kt)+ (1-a)\exp(-k_1t)$	Verma	(3)
$RX = \exp(\frac{(-a-(\sqrt{a^2-4.b.t})}{2.b})$	Thompson	(4)
$RX = \exp(-k.t^n)$	Page	(5)
$RX = \exp(-k.t)$	Newton	(6)
$RX = a.\exp(-k.t^n) + b.t$	Midilli	(7)
$RX = a.\exp(-k.t) + c$	Logarithmic	(8)
$RX = a.\exp(-k.t)$	Henderson & Pabis	(9)
$RX = a.\exp(-k.t) + (1-a)\exp(-k.a.t)$	Two-term exponential	(10)
$RX = a.\exp(-k_0.t) + b.\exp(-k_1.t)$	Two-term	(11)
$RX = a + (b.t) + (c.t.1,5) + (d.t.2)$	Valcam	(12)
$RX = \exp[-(k.t)^n]$	Page modified	(13)

t = Time (h); k, k_0, k_1 = Equation constants (h^{-1}); a, b, c, n = Equation parameters; RX = Moisture ratio

$$BIC = -2\ln(L) + 2\ln(N)k \qquad (18)$$

where: k is the number of estimated parameters; L is the value of the likelihood; and, N is the number of recorded measurements.

RESULTS AND DISCUSSION

Figure 1 shows the moisture ratio of endive leaves (*Cichorium intybus*) during drying time at 50, 60, 70 and 80°C.

As shown, the drying time of leaves decreases with increases of drying air temperature. In accordance to Gomes *et al*. (2017), this is due to the pressure difference of the air vapor saturated with the water inside the vegetable product, allowing the water to move from inside the leaves to the drying air in a shorter period. This fact directly influences the quality of the leaves, and a long drying can cause color deterioration, losses in nutritional composition and lead to the growth of molds (Babu *et al*., 2018). In addition, it is necessary to evaluate the bioactive compounds of the formed product at different drying temperatures, as since most of these compounds are known to be susceptible to degradation at elevated temperatures.

There was a faster loss of moisture content at the beginning of the drying process at all temperatures, due to the greater ease of water removal on the product surface. According to Babalis *et al*. (2006), after the evaporation of surface water, the velocity of drying air is minimized due to the water gradually moving to the outermost layers of the product, prevailing the process of liquid diffusion that will be influenced by the temperature of drying air. At higher temperatures, the moisture ratio of the final content was lower. According to Sagrin & Chong (2013), this occurred because more heat was supplied to the samples at higher temperatures, thus inducing more evaporation of leaf moisture.

The average times to complete the drying process were 6.5; 4; 2.33 and 2 hours, at temperatures of 50, 60, 70 and 80ºC, respectively. Similar drying times were observed in drying of salvia leaves (Radünz *et al*., 2010), *Azadirachta indica* (Vidal *et al*., 2016), *Bauhinia forficata* (Silva *et al*., 2017) and thin layer drying of scent leaves (*Ocimum gratissimum*) and lemon basil leaves (*Ocimum africanum*) (Mbegbu *et al*., 2021).

The statistical parameters for each drying condition obtained using empirical and non-empirical equations are shown in Table 1.

According to the Chi-square test, all the adjusted models showed values within the 95% confidence interval. As this is an analysis that evaluates the difference in the model's estimate, some authors evaluate the values of this parameter and recommend adjustments with lower values (Günhan *et al*., 2005; Oliveira *et al*., 2018). The Midilli and

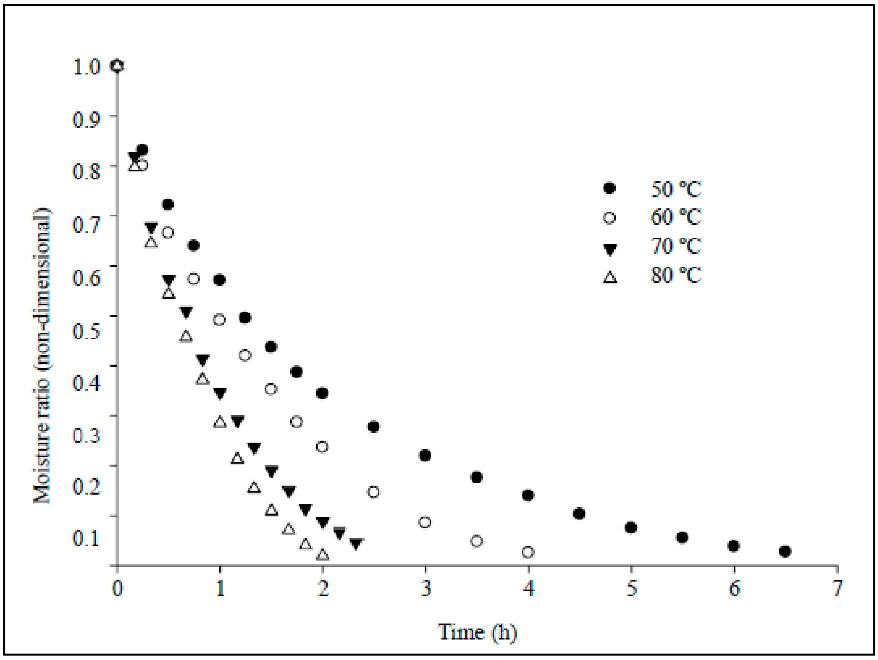

Figure 1. Moisture ratio of endive leaves during drying at 50, 60, 70 and 80°C. Rio Verde, IF Goiano, 2020.

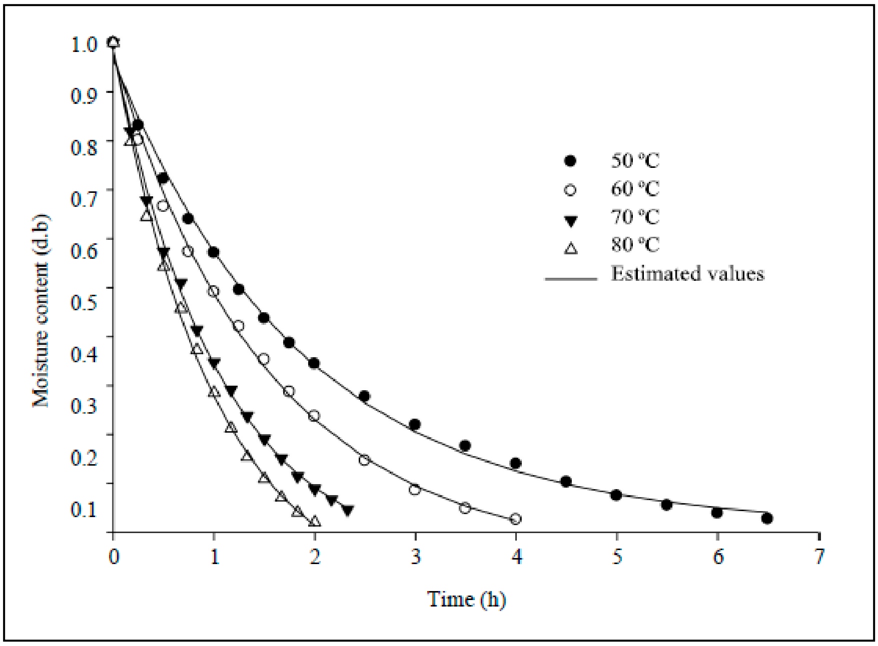

Figure 2. Estimated values from logarithmic model of drying kinetics of endive leaves. Rio Verde, IF Goiano, 2020.

Table 1. Statistical parameter values obtained in the drying of the endive leaves. Rio Verde, IF Goiano, 2020.

Temperature (ºC)	**Model**	**SE (%)**	χ^2	**P (%)**	**R² (%)**
50	Page modified	0.00042	0.00010	9.65239	99.88680
	Page	0.00042	0.00010	9.65242	99.88680
	Midilli	0.00007	0.00002	2.12671	99.98098
	Newton	0.00168	0.00041	6.42475	99.52973
	Thompson	0.00088	0.00022	11.71069	99.76177
	Henderson and Pabis	0.00089	0.00022	5.68852	99.75868
	Two-term	0.00019	0.00005	6.44606	99.95226
	Verna	0.00179	0.00046	6.42469	99.52973
	Logarithmic	0.00084	0.00021	8.20583	99.77097
	Wang and Singh	0.01726	0.00432	43.68686	99.31953
	Two-term Exponential	0.00086	0.00022	12.49230	99.76681
	Valcam	0.00019	0.00005	4.37606	99.94725
60	Page modified	0.00157	0.00047	17.50407	99.52739
	Page	0.00157	0.00047	17.50362	99.52739
	Midilli	0.00041	0.00014	8.16207	99.88822
	Newton	0.00150	0.00043	17.56482	99.52738
	Thompson	0.00157	0.00047	17.57557	99.52722
	Henderson and Pabis	0.00149	0.00045	18.45762	99.55138
	Two-term	0.00164	0.00055	18.45779	99.55138
	Verna	0.00146	0.00046	19.37658	99.52738
	Logarithmic	0.00080	0.00025	4.53503	99.77023
	Wang and Singh	0.00568	0.00171	22.80828	98.28564
	Two-term Exponential	0.00139	0.00042	19.36830	99.52738
	Valcam	0.00043	0.00014	5.46965	99.88239
70	Page modified	0.00116	0.00032	10.04876	99.65315
	Page	0.00116	0.00032	10.04881	99.65315
	Midilli	0.00025	0.00008	2.98136	99.93051
	Newton	0.00123	0.00033	11.89703	99.61603
	Thompson	0.00128	0.00036	11.90049	99.61586
	Henderson and Pabis	0.00128	0.00036	11.88703	99.61604
	Two-term	0.00098	0.00030	8.28228	99.61604
	Verna	0.00976	0.00282	32.98195	99.61603
	Logarithmic	0.00050	0.00014	2.63217	99.82722
	Wang and Singh	0.00341	0.00095	12.54784	98.61603
	Two-term Exponential	0.00128	0.00036	11.89713	99.61603
	Valcam	0.00025	0.00008	2.28777	99.92985
80	Page modified	0.00245	0.00074	26.87871	99.29912
	Page	0.00245	0.00074	26.87878	99.29912
	Midilli	0.00048	0.00016	9.07189	99.87539
	Newton	0.00356	0.00103	39.87322	98.93866
	Thompson	0.00371	0.00112	39.87827	98.93837
	Henderson and Pabis	0.00359	0.00108	38.54671	98.97394
	Two-term	0.00397	0.00132	38.54814	98.97394
	Verna	0.02403	0.00760	93.70589	93.45119
	Logarithmic	0.00061	0.00019	5.41558	99.83280
	Wang and Singh	0.00239	0.00072	15.53913	99.31747
	Two-term Exponential	0.00371	0.00112	39.87430	98.93866
	Valcam	0.00042	0.00014	5.76498	99.89207

R^2 = Coefficient of determination, χ^2 = Chi-square, P = Mean relative error, SE = Estimated standard deviation

Valcam generally showed lower values for this parameter under all drying conditions.

All the adjustments of the models presented coefficients of determination above 98% (Table 1). Madamba *et al.* (1996) indicated magnitude values of coefficient of determination (R^2) greater than 95% for fitting mathematical models to experimental data. However, these criteria cannot be used as decisive.

The recommended fit of mathematical drying models indicates that the average relative error (P) should be less than 10%, and this criterion is often used in the mathematical modeling of drying processes (Mohapatra & Rao, 2005; Vidal *et al*., 2016; Martins *et al*., 2018; Oliveira *et al*., 2018). Thus, for drying of endive leaves at 50ºC, the Thompson, Wang & Singh, and Two-terms exponential models aren't recommended, while at temperatures of 60 and 80ºC only the models of Midilli, Logarithmic and Valcam are recommended to estimate the drying kinetic of this product. At temperature of 70ºC, only Midilli, Logarithmic, Two-term and Valcam models are recommended for drying kinetics adjustments.

After analyzing all the mathematical parameters, the Midilli, Logarithmic and Valcam models showed the best fit for drying endive leaves under all conditions. The AIC and BIC parameters were used to define the best model among them (Table 2).

The AIC and BIC parameters are currently used to indicate the best model among those with a good fit to the experimental data (Quequeto *et al*., 2019; Souza *et al*., 2019). Gomes *et al.* (2018) used these parameters to adjust mathematical models for the drying of crushed jambu dough, defining that the Logarithmic model was more suitable for most drying conditions.

As stated by Akaike (1974) and Schwarz (1978), lower values for these criteria indicate a better fit, therefore, the logarithmic model is the one that best represents the drying kinetics of endive leaves under all the conditions studied, and is therefore the model selected to estimate the drying curves of the product under the different conditions (Figure 2).

Table 2. Akaike information criterion (AIC) and Bayesian Schwarz information criterion (BIC) of the models with best adjustments of endive leaves drying kinetics at different temperatures. Rio Verde, IF Goiano, 2020.

T	Midilli		Logarithmic		Valcam	
(ºC)	AIC	BIC	AIC	BIC	AIC	BIC
50	138.20530	133.75340	95.35620	91.79471	119.80960	115.35770
60	73.56327	70.73852	66.18397	63.92417	72.88560	70.06085
70	94.35863	90.81838	85.53293	82.70073	94.20406	90.66380
80	71.47202	68.64727	69.64292	67.38312	73.33870	70.51396

Table 3. Estimated values of logarithmic model coefficients to predict the drying curve of endive leaves. Rio Verde, IF Goiano, 2020.

Coefficient	50ºC	60ºC	70ºC	80ºC
a	0.95499	1.03069	1.05149	1.2733
k	0.52995	0.63899	0.93750	0.98224
c	0.00944	-0.05740	-0.06973	-0.14409

Figure 2 shows a good fit between the data estimated by the model and the experimental data. The Logarithmic model was also recommended to estimate the drying of coriander both under the action of direct and diffuse radiation, as well as drying in an oven (Sousa *et al*., 2018). The Logarithmic model was the best fit for the drying curves of the palm fruit (Santos *et al*., 2016), foamed mango pulp (Silva Filho *et al*., 2016), crushed jambu mass (Gomes *et al*., 2018), and slices of acuri (Santos *et al*., 2019).

Table 3 presents the values of the coefficients of the Logarithmic model used in the adjustment of the equations.

It can be seen that the coefficients (a) and (k) increase with increasing temperature, while the coefficient (c) shows the opposite behavior. According to Corrêa *et al*. (2010) this behavior of the k coefficient, which is a drying constant, is expected, as higher temperatures lead to a higher drying rate. The trend of coefficients (a) and (c) has not been described in the literature, as these coefficients are empirical and have no theoretical relationship to the fit of the equation to experimental data.

The conditions influence the drying behavior, because with the increase in temperature, there was a decrease in the drying time necessary to reduce the moisture content of the endive leaves.

The mathematical models of Midilli, Logarithmic and Valcam were the ones that best fitted the drying curves for all conditions. From the parameters AIC and BIC, it was determined that the best among them was the Logarithmic model, which was used to estimate the drying kinetics of the endive leaves.

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