Modeling kinetics of convective drying of *Curcuma longa* L.

Modelagem e cinética de secagem da *Curcuma longa* L. sob convecção

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ABSTRACT: This study aimed to determine drying curves of land saffron (*Curcuma longa* L.) rhizomes at different temperatures and ventilation conditions to adjust non-linear regression models, and to calculate effective diffusion coefficients and activation energies. Saffron rhizomes were randomly collected *in natura* with a hoe from the soil in Rio Verde, Goiás, Brazil. They were subsequently sized, sanitized, and sliced into 2.63 ± 0.1 mm thick sections. Rhizomes were dried in an oven with forced air ventilation at 45, 55, 65 and 75 °C for 18, 14, 10 and 9 hours, respectively. As the temperature increased, drying time was reduced. Consequently, moisture content also decreased, facilitating the drying process by decreasing the energy required to remove water molecules. Among the analyzed models, the Midilli model was best adjusted to the data under different drying air conditions. Effective diffusion coefficients (D) were 9.17 × 10⁻¹¹, 13.33 × 10⁻¹¹, 20.09 × 10⁻¹¹, and 35.89 × 10⁻¹¹ m² s⁻¹ at 45, 55, 65 and 75 °C, respectively, increasing with higher temperatures. Activation energy for liquid diffusion during drying was 21.186 kJ mol⁻¹.

Key words: land saffron, drying curves, effective diffusion coefficient, Midilli model

RESUMO: Objetivou-se, com este estudo, determinar as curvas de secagem dos rizomas de açafraão da terra em diferentes temperaturas, ajustar modelos de regressão não linear ao processo, em diversas condições de ar, bem como determinar o coeficiente de difusão efetiva e obter a energia de ativação. Os rizomas de açafraão da terra foram coletados com o auxílio de uma enxada e manualmente, de forma aleatória, no município de Rio Verde, GO. Em seguida, foram selecionados, medidos, higienizados e submetidos ao fatiamento com 2,63 ± 0,1 mm de espessura. Os rizomas foram submetidos a secagem em estufa com ventilação de ar forçada nas temperaturas de 45, 55, 65 e 75 °C. O tempo de secagem foi de 18; 14; 10 e 9 horas, respectivamente, para as temperaturas de 45, 55, 65 e 75 °C. À medida que a temperatura aumentou, o tempo de secagem diminuiu e, consequentemente, o teor de água final de equilíbrio também diminui, uma vez que o aumento da temperatura facilita o processo de secagem, por diminuir a energia necessária para remover moléculas de água ligadas ao produto. Entre os modelos ajustados, o de Midilli foi o que melhor se ajustou aos dados nas diferentes condições do ar de secagem. O coeficiente de difusão efetiva aumentou com a elevação da temperatura, com valores de 9,17 × 10⁻¹¹, 13,33 × 10⁻¹¹, 20,09 × 10⁻¹¹ e 35,89 × 10⁻¹¹ m² s⁻¹ para as temperaturas de 45, 55, 65 e 75 °C, respectivamente, e a energia de ativação para a difusão líquida na secagem foi de 21,186 KJ mol⁻¹.

Palavras-chave: açafraão da terra, curvas de secagem, coeficiente de difusão efetiva, modelo de Midilli

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**Introduction**

Saffron rhizomes are often dried and ground into powder for coloring purposes because of their bright yellow color. Oils can also be extracted and used to make natural dyes, antioxidants, and antimicrobials since the main compound, curcumin, gives a peculiar smell and flavor (Gounder & Lingamallu, 2012).

Mathematical modeling of a dynamic system is defined as a set of equations that can predict the accuracy of the process. Mathematical models can be quite different depending on the system; therefore, some models may be more appropriate than others under different circumstances (Ogata, 2003). Mathematical modeling of drying kinetics have been reported for many different products, such as banana slices (Leite et al., 2015), cambre seeds (Faria et al., 2012), black saffron (Lakshmi et al., 2018), strawberries (Oliveira et al., 2015), and babassu mesocarp (Rosa et al., 2017). However, studies are still needed to identify the best model to define drying kinetics of saffron.

The objective of this study was to characterize the kinetics of drying saffron rhizomes to obtain flour by mathematical modeling, and to determine effective diffusion coefficients ($D$), activation energies, and thermodynamic properties at 45, 55, 65 and 75 °C.

**Material and Methods**

Rhizomes of *Curcuma longa* L., were collected in natura on a rural property located in Rio Verde, Goiás (latitude 17° 37' 38.26" S, longitude 50° 45' 18.94" W, altitude of 704 m). The rhizomes were collected at random by plucking and with the help of a hoe.

Fresh rhizomes were selected and subsequently sanitized with sodium hypochlorite at 100 ppm for 10 min. Rhizomes were then peeled and cut uniformly to 59.46 mm long, 15.62 mm wide, and 2.63 mm thick slices. Fresh rhizomes were packed in plastic bags and frozen in a horizontal freezer at -18 °C until needed for experiments.

Saffron rhizomes were dried to determine the initial moisture content on a dry basis (d.b.) in an oven at 105 ± 2 °C. The reduction in the moisture content during drying was determined by gravimetric analysis, measuring the moisture content of the product until the mass of saffron rhizomes remained consistent.

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Rhizomes were placed in three stainless steel trays with approximately 150 g of turmeric, and evenly spread with stainless steel spatulas. The rhizomes were then dried in an oven with forced air ventilation at 45, 55, 65 and 75°C, with an average air relative humidity of 23.3, 14.2, 8.9, and 5.8%, respectively. The reduction in mass during drying was monitored regularly with a 0.01 g resolution scale.

The temperature of the drying air and the ambient temperature were monitored with a thermometer inside and outside the dryer. The air relative humidity inside the greenhouse was calculated by psychrometric analysis using GRAPSI software.

The following equation was used to determine saffron moisture content ratio during drying:

$$RX = \frac{X - X_e}{X_i - X_e}$$  \hspace{1cm} (1)

where:

- $RX$ - moisture content ratio of the product, dimensionless;
- $X$ - moisture content of the product, d.b.;
- $X_i$ - initial moisture content of the product, d.b.; and,
- $X_e$ - equilibrium moisture content of the product, d.b.

Non-linear regression models used to represent the drying of plant products were adjusted to the experimental data on drying saffron (Table 1).

**Table 1. Mathematical models used to predict drying of plant products**

| Model | Designation of the model | Eq. |
|-------|--------------------------|-----|
| $RX = 1 + a + b t^2$ | Wang and Sing | (2) |
| $RX = a \exp(-k t) + (1 - a) \exp(-k_2 t)$ | Verma | (3) |
| $RX = \exp(-a - (a^2 + 4 b t)^{0.5}/2 b)$ | 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 and Pabis | (9) |
| $RX = a \exp(-k t) + (1 - a) \exp(-k a t)$ | Exponential of Two Terms | (10) |
| $RX = a \exp(-k_1 t) + b \exp(-k_2 t)$ | Two Terms | (11) |
| $RX = a \exp(-k t) + (1 - a) \exp(-k b t)$ | Diffusion approach | (12) |

$\text{t}$ - Time of drying; $k$, $k_1$, $k_2$ - Drying constant (h$^{-1}$); $a$, $b$, $c$, $n$ - Model parameters

Adjustments made to non-linear regression models based on experimental drying data were performed using the Gauss-Newton method (Statistica 7.0, StatSoft, Tulsa, USA). Components were analyzed in triplicate. Optimal adjustments were made based the magnitude of the determination coefficient generated by statistical software ($R^2$) (Barros Neto et al., 2010), the relative error of the mean (P, %), standard deviation of the estimate (SE), and reduced chi-square ($\chi^2$), according to Eqs. 13, 14, and 15. The values from these equations are dependent on experimental and predicted values (Doyraz, 2005). A P (relative mean error) value for a successful model needs to be below 10% (Mohapatra & Rao, 2005).

$$P = \frac{100}{N} \sum \frac{Y - \hat{Y}}{Y}$$  \hspace{1cm} (13)

$$SE = \sqrt{\frac{\sum (Y - \hat{Y})^2}{GLR}}$$  \hspace{1cm} (14)

$$\chi^2 = \frac{\sum (Y - \hat{Y})^2}{GLR}$$  \hspace{1cm} (15)

where:

- $P$ - standard deviation of the estimate;
- $\chi^2$ - reduced chi-square;
- $Y$ - experimental value;
- $\hat{Y}$ - estimated value by the model;
- $N$ - number of experimental points; and
- GLR - degrees of freedom of the model (number of experimental observations minus the number of model coefficients).
The liquid diffusion model for flat geometric plates was adjusted using experimental saffron rhizome drying data. This model contains eight variables, such as surface area and volume, according to the following expression:

\[
RX = \frac{X^* - X^*_e}{X^* - X^*_{infty}} = \frac{8}{\pi^2} \sum_{n=1}^{\infty} \left( \frac{1}{(2n+1)^2} \right) \exp \left[ -\left( \frac{(2n+1)^2 \pi^2 D \left( \frac{S}{V} \right)}{4} \right) t \right]
\]

where:
- \( n \) - number of terms;
- \( S \) - surface area of the product, m²; and,
- \( V \) - volume of the product, m³.

The surface area \( S \) of saffron rhizomes was calculated according to the expressions:

\[
S = \pi D_g
\]

where:
- \( D_g \) - average geometric diameter, mm;
- \( A \) - length, mm;
- \( B \) - width, mm; and
- \( C \) - thickness, mm.

The volume of saffron rhizomes was calculated according to the expression proposed by Mohsenin (1986):

\[
V = \frac{\pi ABC}{6}
\]

The relationship between the effective diffusion coefficient \( D \) and the drying air temperature was described by the Arrhenius equation:

\[
D = D_o \exp \left( -\frac{E_a}{RT_{ab}} \right)
\]

where:
- \( D_o \) - pre-exponential factor;
- \( E_a \) - energy of activation, KJ mol⁻¹;
- \( R \) - universal gas constant, 8.134 KJ kmol⁻¹ K⁻¹; and
- \( T_{ab} \) - absolute temperature, K.

Arrhenius equation coefficients were linearized using the following logarithmic equation:

\[
\ln D = \ln D_o - \frac{E_a}{R} \left( \frac{1}{T_{ab}} \right)
\]

Results and Discussion

Figure 1 shows drying curves of saffron rhizomes at 45, 55, 65 and 75 °C. The values shown in the graph are moisture content ratio (RX) as a function of drying time. Higher temperatures contributed to heat energy transfer to the samples, consequently decreasing the time needed for the sample to reach a consistent mass. Thus, the increase in temperature decreased the total time of the drying process, since higher air temperatures quickened the rate of water evaporation.

The time required for the saffron rhizomes to dry based on moisture content (d.b.) was 18, 14, 10 and 9 hours at 45, 55, 65 and 75 °C, respectively.

Figure 1 shows water loss during the process of drying saffron rhizomes. As expected, the temperature influenced drying kinetics. The predicted model was similar to experimental data, but presented a lower final moisture content and shorter drying times.

The dehydration time was lowest at 75 °C compared to other temperatures. The increase in the temperature of the drying air meant that water was removed quicker from the product due to a larger water gradient between the product and the air, decreasing the time necessary to reduce the moisture content (Smaniotto et al., 2017).

The same drying trend was observed by Loha et al. (2012) and Leite et al. (2015) for sliced ginger and plantain, respectively. Additionally, Botelho et al. (2011) noted that carrot slices dried uniformly at the evaluated temperatures, differing only in drying times.

Table 2 shows standard error of the estimated mean (SE) from the chi-square test (\( \chi^2 \)) of the various models analyzed showing the kinetics of drying saffron (\( Curcuma longa \) L.) at 45, 55, 65 and 75 °C.

According to Oliveira et al. (2012), the lower the \( \chi^2 \) value, the more the model fits the experimental data. The Midilli model had the lowest \( \chi^2 \) and SE values compared to the other models (Table 2).

Table 3 shows relative mean error (\( P \), %) and the coefficients of determination (\( R^2 \), %) for eleven methods of modeling the
kinetics of drying turmeric (Curcuma longa L.) at 45, 55, 65 and 75 °C.

Coefficients of determination (R², %) ranged from 96.20 to 99.96% and were highest for the Midilli and Page models.

Relative mean error (P , %) values indicate deviations between the estimated model and observed value (Kashani-Nejad et al., 2007). Relative mean error (P , %) values were greater than 10% for most models, except for Midilli and Page models which were lower than 10%, a recommended criteria for choosing a model (Mohapatra & Rao, 2005). The Midilli model had the lowest values at the four temperatures studied, making it the optimal model, according to Silva et al. (2015), for adjusting conditions for drying agricultural products.

Coefficients of the Midilli model were adjusted based on experimental data obtained from drying saffron rhizomes at different air temperatures. The parameter “k” increased with higher temperatures, and was associated with a quicker drying rate (Table 4). The parameter “n” reflects the product’s internal resistance to drying, and there was no trend in how these values changed with different temperatures. Variations in parameters “a” and “b” were more likely due to adjustments than to an unknown drying phenomenon since the Midilli model is semi-empirical (Midilli et al., 2002).

The effective diffusion coefficient (D) of drying saffron rhizomes relative to the temperature of the air were calculated using the Arrhenius equation (Figure 2). Coefficient values (D) obtained for drying saffron rhizomes were consistent with those reported for drying agricultural products, which are typically in the 10⁻¹¹ to 10⁻⁹ m² s⁻¹ range (Madamba, 2003; Silva et al., 2015). For food products, such

Table 2. Chi-square test (χ²) values and standard error of estimated mean (SE) calculated for eleven methods of modeling kinetics of saffron (Curcuma longa L.) drying

| Model              | 45 °C  | 55 °C  | 65 °C  | 75 °C  |
|--------------------|--------|--------|--------|--------|
|                    | SE     | x²     | SE     | x²     | SE     | x²     | SE     | x²     |
| Wang and Sing      | 0.0687 | 0.0047 | 0.0860 | 0.0074 | 0.0988 | 0.0097 | 0.1005 | 0.0101 |
| Verma              | 0.1026 | 0.0105 | 0.0936 | 0.0087 | 0.2700 | 0.0729 | 0.1197 | 0.0143 |
| Thompson           | 0.1007 | 0.0110 | 0.1126 | 0.0127 | 0.1260 | 0.0159 | 0.1232 | 0.0152 |
| Page               | 0.0263 | 0.0007 | 0.0244 | 0.0066 | 0.0226 | 0.0005 | 0.0394 | 0.0015 |
| Newton             | 0.0598 | 0.0098 | 0.1103 | 0.1229 | 0.0151 | 0.0151 | 0.1200 | 0.0144 |
| Midilli            | 0.0098 | 9.70E-05| 0.0129 | 0.0001 | 0.0149 | 0.0002 | 0.0199 | 0.0039 |
| Logistic           | 0.0572 | 0.0032 | 0.0746 | 0.0055 | 0.0838 | 0.0070 | 0.0863 | 0.0078 |
| Henderson and Pabis| 0.0746 | 0.0055 | 0.0823 | 0.0068 | 0.0912 | 0.0083 | 0.0863 | 0.0074 |
| Exponential of Two Terms | 0.1007 | 0.0101 | 0.1126 | 0.0127 | 0.1260 | 0.0159 | 0.1232 | 0.0152 |
| Two Terms          | 0.0775 | 0.0060 | 0.0746 | 0.0055 | 0.0964 | 0.0093 | 0.0916 | 0.0083 |
| Diffusion approach | 0.0281 | 0.0007 | 0.0936 | 0.0087 | 0.1075 | 0.0115 | 0.1197 | 0.0143 |

Table 3. Relative average error (P , %) and coefficients of determination (R², %), for eleven methods of modeling the kinetics of drying turmeric (Curcuma longa L.) at 45, 55, 65 and 75 °C

| Models              | 45 °C  | 55 °C  | 65 °C  | 75 °C  |
|--------------------|--------|--------|--------|--------|
|                    | P      | R²     | P      | R²     | P      | R²     | P      | R²     |
| Wang and Singh      | 18.61  | 0.9824 | 26.54  | 0.9752 | 34.18  | 0.9671 | 48.82  | 0.9668 |
| Verma              | 28.08  | 0.9612 | 32.68  | 0.9718 | 50.20  | 0.9458 | 46.41  | 0.9497 |
| Thompson           | 28.02  | 0.962   | 38.13  | 0.9717 | 50.25  | 0.9458 | 46.41  | 0.9497 |
| Page               | 9.54   | 99.74  | 7.52   | 99.53  | 8.24   | 99.54  | 8.24   | 99.54  |
| Newton             | 28.01  | 96.2   | 38.14  | 95.71  | 50.25  | 94.58  | 46.41  | 94.97  |
| Midilli            | 1.81   | 99.96  | 4.46   | 99.94  | 5.34   | 99.93  | 9.60   | 99.02  |
| Logistic           | 15.85  | 98.83  | 26.05  | 98.22  | 33.17  | 97.76  | 40.42  | 97.59  |
| Henderson and Pabis| 19.17  | 97.93  | 23.90  | 97.73  | 31.03  | 97.20  | 35.87  | 97.56  |
| Exponential of Two Terms | 28.01  | 96.20  | 38.14  | 95.71  | 50.25  | 94.58  | 46.41  | 94.97  |
| Two Terms          | 19.18  | 97.93  | 25.25  | 98.30  | 31.02  | 97.20  | 35.87  | 97.56  |
| Diffusion approach | 7.48   | 99.71  | 32.68  | 97.18  | 42.06  | 96.30  | 55.50  | 95.53  |

Table 4. Midilli model parameters adjusted for different temperatures

| Temperature (°C) | 45  | 55  | 65  | 75  |
|------------------|-----|-----|-----|-----|
| Aa               | 0.979700**| 0.980121**| 0.978923**| 0.983863**|
| k                | 0.011564**| 0.024930**| 0.042519**| 0.149900**|
| n                | 2.108551**| 2.251205**| 2.505707**| 2.425654**|
| b                | 0.006612**| 0.006928**| 0.007357**| 0.008742**|

* Significant at p ≤ 0.01 by t-test; ns - Not significant by t-test

Figure 2. Effective diffusion coefficient (D) of drying saffron rhizomes as a function of temperature

Coefficient values (D) obtained for drying saffron rhizomes were consistent with those reported for drying agricultural products, which are typically in the 10⁻¹¹ to 10⁻⁹ m² s⁻¹ range (Madamba, 2003; Silva et al., 2015). For food products, such
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as tomatoes (Coskun et al., 2016), carrots (Haq et al., 2018) and ginger (Deshmukh et al., 2014), coefficient values range between 10\(^{-11}\) and 10\(^{-8}\) m\(^2\) s\(^{-1}\).

Coefficient values for drying pumpkin seeds ranged between 8.53 x 10\(^{-11}\) to 17.52 x 10\(^{-11}\) m\(^2\) s\(^{-1}\) at 40, 50, and 60 °C (Sacilik, 2007). Coefficient values for drying forage turnip ranged from 3.23 x 10\(^{-11}\) to 10.43 x 10\(^{-11}\) m\(^2\) s\(^{-1}\) between 30 and 70 °C (Sacilik, 2007). Coefficient values for drying wheat grains ranged from 8.3306 x 10\(^{-11}\) and 41.0977 x 10\(^{-11}\) m\(^2\) s\(^{-1}\) (Goneli et al., 2007).

The effective diffusion coefficient (D) is obtained by adjusting experimental curves to reflect effective diffusivity, which encompasses the effects of all phenomena that can affect water migration (Oliveira et al., 2006).

**CONCLUSIONS**

1. Drying curves of the saffron rhizomes were similar to those of most agricultural products. Optimal drying times were 18, 14, 10, and 9 hours at 45, 55, 65 and 75 °C, respectively.
2. Drying time was reduced with increased temperatures.
3. The Midilli model showed the best fit for reflecting kinetics of saffron rhizome drying.
4. The effective diffusion coefficient (D) increased with higher drying temperatures.

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