Drying kinetics of yellow mombin (Spondias mombin L.) epicarp

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ABSTRACT: Yellow mombin (Spondias mombin L.) fruits have relevant characteristics for industrialization and exhibit a pleasant aroma and sour-sweet taste, with significant amounts of vitamin A and carotenoids in their epicarp. The objective was to fit different mathematical models to the experimental data, using as criteria to select the best model - the Akaike Information Criteria (AIC) and Schwarz's Bayesian Information Criteria (BIC), as well as to evaluate the effective diffusion coefficient and to determine the activation energy for yellow mombin epicarp submitted to different drying conditions. The experiment was carried out at the Instituto Federal de Educação, Ciência e Tecnologia Goiano, Brazil. The epicarp of yellow mombin fruits with initial moisture content of 2.89 (dry basis, d.b.) were submitted to drying at temperatures of 40, 50, 60 and 70 °C until final moisture contents of 0.11, 0.10, 0.09 and 0.08 (d.b.), respectively. The Midilli model showed the best fit to the experimental data obtained. The choice of the model was confirmed by the AIC and BIC criteria. The increase of the drying temperature promoted increase in the effective diffusion coefficient, and the activation energy of the process was 21.50 kJ mol⁻¹.

Key words: mathematical modeling, AIC, BIC, Midilli model

Cinética de secagem do epicarpo dos frutos de cajá (Spondias mombin L.)

RESUMO: O fruto da cajazeira (Spondias mombin L.) apresenta características relevantes para industrialização e possuem aroma agradável e sabor acido-adocicado, possui quantidades relevantes de vitamina A e carotenoides no epicarpo do cajá. Objetivou-se, ajustar diferentes modelos matemáticos aos dados experimentais, utilizando como critérios para selecionar o melhor modelo - o Critério de Informação de Akaike (AIC) e o Critério de Informação Bayesiano de Schwarz (BIC), bem como avaliar o coeficiente de difusão efetivo e determinar a energia de ativação para o epicarpo de cajá submetido a diferentes condições de secagem. O experimento foi desenvolvido no Instituto Federal de Educação, Ciência e Tecnologia Goiano. O epicarpo dos frutos de cajá com teor de água inicial 2.89 (base seca, b.s.) foram submetidos à secagem em temperaturas de 40, 50, 60 e 70 °C até teor de água final de 0,11, 0,10, 0,09 e 0,08 (b.s.), respectivamente. O modelo de Midilli apresentou o melhor ajuste aos dados experimentais obtidos. A escolha do modelo foi confirmada pelos critérios de AIC e BIC. O aumento da temperatura de secagem promoveu aumento do coeficiente de difusão efetivo, e a energia de ativação do processo foi de 21,50 kJ mol⁻¹.

Palavras-chave: modelagem matemática, AIC, BIC, modelo de Midilli
**Introduction**

Yellow mombin, known in Portuguese as ‘cajá’, ‘tapereba’, ‘caja-mirim’ or ‘cajá verdadeiro’, has relevant characteristics for industrialization and shows pleasant aroma and sour-sweet taste, which generates interest in the region itself and also in other regions of Brazil where this fruit is not produced (Anselmo et al., 2006).

The drying process is extremely important in the technology that allows the production of high-quality food products, allowing the preservation of physical and chemical properties and reducing the moisture content to safe levels for storage, so the product can be used in periods when the fruit is not produced (Resende et al., 2018).

For the design and optimization of drying equipment, it is important to use mathematical models and select those that best fit to the water loss of each material, based on the experimental data obtained (Costa et al., 2015), hence justifying the importance of theoretical information on the drying of yellow mombin epicarp at different temperatures.

Several authors such as Alves & Rodovalho (2016) [avocado pulp], Coradi et al. (2016) [soybean grains] and Silva et al. (2015) [jenipapo leaves] have used criteria for selecting mathematical models that best fit to the drying of agricultural products, such as magnitudes of coefficient of determination, mean relative error and mean estimated error, chi-square test and residual distribution.

Based on how important the study of the drying process of plant products is, the objective was to fit different mathematical models to experimental data, using as criteria to select the best model the Akaike Information Criteria (AIC) and the Schwarz’s Bayesian Information Criteria (BIC), as well as to evaluate the effective diffusion coefficient and determine the activation energy for the yellow mombin epicarp subjected to different drying conditions.

**Material and Methods**

The experiment was conducted in the Laboratory of Postharvest of Plant Products of the Instituto Federal de Educação, Ciência e Tecnologia Goiano, Brazil, IF Goiano, Rio Verde Campus, Brazil, from January 2017 to May 2018, with yellow mombin fruits from the rural area of the municipality of Montes Claros de Goiás, GO, Brazil, with initial moisture content of 2.89 (d.b.). The epicarps were subjected to drying in forced air ventilation oven under four temperature conditions, 40, 50, 60 and 70 °C, which led to final moisture contents of 0.11, 0.10, 0.09 and 0.08 (d.b.), respectively.

For the determination of the drying curves and fitting of the models, the epicarps were dried until showing a constant mass. The moisture contents of the product were determined in an oven at 105 ± 3 °C, until constant mass.

The hygroscopic equilibrium of the epicarp was obtained using three replicates containing 5 g, kept under the previously described drying conditions and periodically weighed until the mass remained constant. The moisture content ratios of the product were determined by the expression:

\[
RX = \frac{X - X_e}{X_i - X_e}
\]  

(1)

where:
- \( RX \) - moisture content ratio, 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.

Epicarp drying was represented by the mathematical models described in Eqs. 2 to 12, commonly used for agricultural products.

- Wang and Singh
  \[
  RX = 1 + at + bt^2
  \]
  (2)

- Verma
  \[
  RX = a \exp(-kt) + (1 - a) \exp(-k_i t)
  \]
  (3)

- Thompson
  \[
  RX = \exp\left(-a - \frac{a^2 + 4bt^{0.5}}{2b}\right)
  \]
  (4)

- Page
  \[
  RX = \exp(-kt^n)
  \]
  (5)

- Newton
  \[
  RX = \exp(-kt)
  \]
  (6)

- Midilli
  \[
  RX = \exp(-kt^n) + bt
  \]
  (7)

- Logarithmic
  \[
  RX = a \exp(-kt) + c
  \]
  (8)

- Henderson and Pabis
  \[
  RX = a \exp(-kt)
  \]
  (9)

- Two-Term Exponential
  \[
  RX = a \exp(-kt) + (1 - a) \exp(-kat)
  \]
  (10)

- Two Terms
  \[
  RX = a \exp(-k_i t) + b \exp(-k_i t)
  \]
  (11)

- Approximation of Diffusion
  \[
  RX = a \exp(-kt) + (1 - a) \exp(-kbt)
  \]
  (12)
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To fit the mathematical models to the experimental drying data, a non-linear regression analysis was performed using the Gauss-Newton method. The values reported in the literature for the modeling of other agricultural products were adopted as criteria for the initial approximations of the model coefficients. The degree of fit for each drying temperature was determined by initially considering the significance of the regression coefficients by the t-test, adopting $p \leq 0.05$, the magnitude of the coefficient of determination ($R^2$), the values of the mean relative error ($P$) and mean estimated error (SE), and the chi-square test ($\chi^2$) at $p \leq 0.05$.

To determine the epicarp surface area, images of 15 different peels were taken and subjected to the computer program Image J. In addition, thickness measurements were taken in 15 epicarps, in five different regions, using a digital caliper with resolution of 0.01 mm. With the average data of peel thickness and surface area, it was possible to calculate the volume, according to the following equation:

$$V = SL$$  \hspace{1cm} (19)

where:

- $S$ - peel surface area, m$^2$; and,
- $L$ - peel thickness, m.

The relationship between the effective diffusion coefficient and the increase in drying air temperature was described by the Arrhenius equation.

$$D = D_0 \exp \left( -\frac{E_a}{RT_{ab}} \right)$$  \hspace{1cm} (20)

where:

- $D$ - effective diffusion coefficient, m$^2$ s$^{-1}$;
- $D_0$ - pre-exponential factor;
- $E_a$ - activation energy, kJ mol$^{-1}$;
- $R$ - universal gas constant, 8.134 kJ kmol$^{-1}$ K$^{-1}$; and,
- $T_{ab}$ - absolute temperature, K.

With the application of the logarithm the Arrhenius equation coefficients were linearized according to the following expression:

$$\ln D - \ln D_0 \left( -\frac{E_a}{RT_{ab}} \right)$$  \hspace{1cm} (21)

Results and Discussion

Yellow mombin epicarp was subjected to drying at different temperatures, namely 40, 50, 60 and 70 °C, until final moisture contents of 0.11, 0.10, 0.09 and 0.08 (d.b.) (Figure 1A), respectively. To reach these final moisture contents, the required times were 11.5, 9.0, 7.0 and 4.5 h, respectively, for the temperatures of 40, 50, 60 and 70 °C.

It can be noted that the time spent is inversely proportional to the drying temperature, i.e., the higher the temperature,
the shorter the time over which the product is subjected to drying, a result found by several researchers: passion fruit peel (Bezerra et al., 2015); peanut fruits (Araújo et al., 2017) and pineapple slices (Baptestini et al., 2016), because higher temperature causes the water inside the product to move faster to the outside.

Table 1 presents the coefficients of determination (R²), mean relative error (P) and mean estimated error obtained for the different models fitted to the drying curves of yellow mombin epicarp.

As shown in Table 1, all models for all drying conditions showed very low values of mean estimated error (SE), close to zero, which represents a good fit of the model. According to Draper & Smith (1998), the closer the SE is to zero, the better its ability to adequately represent a physical process, as is the case of drying.

It is also observed that, for all models, except Wang and Singh for 40 and 50 °C, there were coefficients of determination (R²) higher than 99.00%, a fact that Madamba et al. (1996) report as satisfactory representation of the drying process, and the closer the R² is to 100%, the better the representation of the model.

Also in Table 1, it can be noted that in relation to the mean relative error (P), only the Midilli and logarithmic models showed values lower than 10% for all drying conditions and, according to Mohapatra & Rao (2005), this is a situation that determines good fit of the model to the drying conditions.

Table 1 presents the values of chi-square test (χ²) obtained for the different models fitted to the drying curves of yellow mombin epicarp. All models showed very low values, and the lower this value the better the fit of the model to the conditions, as reported by Günhan et al. (2005).

Figure 1. Moisture content (A) and moisture content ratio obtained experimentally and estimated by the Midilli model (B) for the drying of yellow mombin epicarp along the drying period at different temperatures

Table 1. Statistical indices of the models for yellow mombin epicarp drying

| Models                  | SE (decimal) | P (%)  | R² (%) | χ²    | SE (decimal) | P (%)  | R² (%) | χ²    |
|-------------------------|--------------|--------|--------|-------|--------------|--------|--------|-------|
| Wang and Singh          | 0.0498       | 30.464 | 97.98  | 0.002484 | 0.0351       | 27.931 | 98.93  | 0.001233 |
| Verma                   | 0.0357       | 11.016 | 99.02  | 0.001273 | 0.0059       | 4.520  | 99.97  | 0.000035 |
| Thompson                | 0.0355       | 7.476  | 98.98  | 0.001263 | 0.0138       | 11.122 | 99.83  | 0.000190 |
| Page                    | 0.0280       | 14.835 | 99.37  | 0.000782 | 0.0071       | 3.696  | 99.96  | 0.000050 |
| Newton                  | 0.0346       | 7.481  | 99.78  | 0.001196 | 0.0134       | 11.115 | 99.83  | 0.000178 |
| Midilli                 | 0.0213       | 8.794  | 99.67  | 0.000454 | 0.0057       | 3.073  | 99.98  | 0.000032 |
| Logarithmic             | 0.0283       | 5.723  | 99.39  | 0.000799 | 0.0075       | 5.822  | 99.95  | 0.000057 |
| Henderson and Pabis     | 0.0278       | 9.034  | 99.37  | 0.000774 | 0.0126       | 9.729  | 99.86  | 0.000159 |
| Two-Term Exponential    | 0.0355       | 7.481  | 99.86  | 0.001263 | 0.0138       | 11.115 | 99.83  | 0.000180 |
| Two Terms               | 0.0295       | 9.034  | 99.37  | 0.000871 | 0.0135       | 9.728  | 99.86  | 0.000163 |
| Approximation of Diffusion | 0.0357   | 11.016 | 99.02  | 0.001273 | 0.0059       | 4.520  | 99.97  | 0.000035 |

SE - Mean estimated error; P - Mean relative error; χ² - Chi-square test
Since the Midilli and logarithmic models fitted best to the drying conditions, both were subjected to the Akaike Information Criterion (AIC) and Schwarz’s Bayesian Information Criterion (BIC) in order to choose one of them to predict the curves of yellow mombin epicarp drying, under different conditions.

Table 2 shows that the two models had very low values for AIC and BIC. According to Wolfinger (1993), the lowest values for these criteria indicate the best fit of the model to the process data. Since the Midilli model showed lower values of both AIC and BIC for all drying conditions, except for 60 °C which were the same; it was chosen to represent the drying of yellow mombin epicarp. Gomes et al. (2018), working with drying of the ‘jambu’ leaf mass, also used AIC and BIC to select the best model.

Table 3 presents the values of the parameters of the Midilli model, fitted to the experimental data of the drying kinetics of yellow mombin (Spondias mombin L.) epicarp at different temperatures.

According to Table 3, the magnitude of the drying constant k for the Midilli model increased with the increment in the drying air temperature, as also observed by Gasparin et al. (2017) when drying Mentha piperita at different temperatures. On the other hand, the parameters “a”, “n” and “b” did not show a clear tendency as the temperature increased, a result also observed by Rodovalho et al. (2015) for different mathematical models, in the drying of Capsicum chinense grains.

Figure 1B presents the yellow mombin epicarp drying curves estimated by the Midilli model. Based on the correspondence between the experimental values and those estimated by the model, it is observed that there was satisfactory fit of the model to the data obtained during the drying of yellow mombin epicarp under all conditions, confirmed by the AIC and the BIC criteria.

The Midilli model was selected by Costa et al. (2016) to describe the drying curve of ‘jabuticaba’ peel at temperatures of 40, 50, 60 and 70 °C. Freitas et al. (2018), working with foam-mat drying of yellow mombin pulp at different temperatures, also selected the Midilli model.

Drying carrots at temperatures between 50 and 80 °C, found that the Midilli and Page models fitted well to the experimental data obtained. Similarly, Silva et al. (2016) selected the Midilli model to predict the drying curve of ‘Cabacinha’ pepper fruits at temperatures between 60 and 100 °C.

The effective diffusion coefficient of yellow mombin epicarp increases linearly with the increment in the drying air temperature (Figure 2), corroborating results obtained by other researchers such as Freitas et al. (2018), for the foam-mat drying of yellow mombin pulp, and by Oliveira et al. (2013), for soybean grains.

The higher the value of diffusivity, the lower the resistance of yellow mombin epicarp to water removal. Water diffusivity is dependent on drying air temperature, i.e., the lower the temperature of the drying air, the greater the resistance of the epicarp to water removal (Muliterno et al., 2017).

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**Table 2.** Akaike Information Criterion (AIC) and Schwarz’s Bayesian Information Criterion (BIC) for the models that fitted best to the data of yellow mombin epicarp drying at different temperatures

| Model  | Temperature (°C) | AIC  | BIC  | AIC  | BIC  | AIC  | BIC  | AIC  | BIC  |
|--------|------------------|------|------|------|------|------|------|------|------|
|        | 40               | 50   | 60   | 70   | 40   | 50   | 60   | 70   | 40   | 50   |
| Midilli| -91.66           | -12.03| -117.87| -119.03| -115.04| -107.09| -103.23|
| Logarithmic| -81.12         | -77.14| -113.33| -110.00| -119.03| -115.04| -101.64| -98.55|

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**Table 3.** Parameters of the Midilli model fitted to the different conditions of yellow mombin epicarp drying at different temperatures

**Table 2.** Akaike Information Criterion (AIC) and Schwarz’s Bayesian Information Criterion (BIC) for the models that fitted best to the data of yellow mombin epicarp drying at different temperatures

| Parameters | Temperature (°C) | 40 | 50 | 60 | 70 |
|------------|------------------|----|----|----|----|
| a          |                  | 1.017383* | 0.990888** | 1.002234** | 0.993248** |
| k          |                  | 0.272054* | 0.339025** | 0.387138** | 0.585729** |
| n          |                  | 1.190162* | 1.067557** | 1.134399** | 1.086014** |
| b          |                  | 0.004595* | -0.001192** | 0.000223** | -0.006556** |

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**Figure 2.** Effective diffusion coefficient - D, as a function of drying air temperature (A) and Arrhenius representation (B) obtained for yellow mombin epicarp.
The magnitude of the effective diffusion coefficients (Figure 2A) of yellow mombin epicarp varied from 0.57 x 10^{-11} to 1.24 x 10^{-11} m^2 s^{-1} for the temperatures from 40 to 70 °C. These values corroborate those found by Oliveira et al. (2014) in their study with drying of soybean grains at temperatures between 40 and 100 °C, as these authors observed effective diffusion coefficients between 0.84 and 3.46 x 10^{-11} m^2 s^{-1}. However, the values are below those found by Silva et al. (2017a), who observed effective diffusion coefficients from 2.32 to 15.69 x 10^{-11} m^2 s^{-1} in the drying of niger seeds at temperatures between 40 and 80 °C. Bezerra et al. (2015) found higher results for the effective diffusion coefficients (0.3199 to 1.994 x 10^{-8} m^2 s^{-1}) for the drying of passion fruit peel at the temperatures of 50, 60 and 70 °C.

The Arrhenius expression (Figure 2B) was used to represent the dependence of the effective diffusion coefficient of yellow mombin epicarp on the drying temperature. The activation energy found for the drying phenomenon was 21.50 kJ mol^{-1}, a result that corroborates with those reported by Baptestini et al. (2017), who dried banana slices by infrared and found activation energy values between 16.39 and 25.20 kJ mol^{-1}. Oliveira et al. (2013), working with soybean grains found activation energy of 22.77 kJ mol^{-1}, a value close to that found in the present study.

According to Zogzas et al. (1996), the activation energy for plant products is between 12.7 and 110 kJ mol^{-1}, so the value found in the present study is within this range. The activation energy represents the degree of difficulty encountered by water molecules to overcome the energy barrier in the movement within the product (Corrêa et al., 2007). The higher the activation energy found, the greater the difficulty to remove water from the product, so it is possible to say that the movement of water from the inside to the outside is relatively easy in yellow mombin epicarp, since the activation energy found for this product was small, it was close to the lowest value found for vegetables.

**Conclusions**

1. Increase in drying temperature causes a reduction in the drying time, which was equal to 11.5 h for the temperature of 40 °C and to 4.5 h for the temperature of 70 °C.
2. The Midilli model showed the best fit to the experimental data of yellow mombin epicarp drying under the different drying conditions.
3. The Arrhenius Equation confirmed the dependence of the effective diffusion coefficient on the drying temperature.
4. The higher the temperature used for yellow mombin epicarp drying, the lower the diffusivity, i.e., the lower the resistance to water removal. The low activation energy demonstrates a certain ease of water movement to the outside of the product.

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