Convective drying of black rice grains (*Oryza sativa* L.): new mathematical modeling insights and thermodynamic properties

Secagem convectiva de grãos de arroz preto (*Oryza sativa* L.): novos insights de modelagem matemática e propriedades termodinâmicas

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ABSTRACT
The aim of this study was to investigate the thin layer drying of brown rice grains at different temperatures (35-75 °C), exploring its kinetics and thermodynamic properties. Black rice grains (30% b.u.) were subjected to convective drying, and the experimental data were subjected to analysis of theoretical, semi-theoretical and empirical drying models, and thermodynamic parameters were calculated. Increasing temperature accelerated drying, shortening the time required to reach moisture balance. The modified Page model modified by Cavalcanti-Mata showed excellent fit to the experimental data, standing out for its simplicity and effectiveness in describing the relationship between water content and drying time. The analysis of thermodynamic properties revealed that the activation energy increased with temperature, evidencing its influence on moisture removal. The observed variations in thermodynamic properties reinforce the importance of considering energy factors in drying. The results offer insights to optimize the black rice grain drying process, contributing to advances in the food industry and providing a basis for future research in the processing of agricultural products.

Keywords: effective diffusivity, food industry, process engineering.

RESUMO
O objetivo deste estudo foi investigar a secagem em camada delgada de grãos de arroz integral em diferentes temperaturas (35-75°C), explorando sua cinética e propriedades termodinâmicas. Os grãos de arroz preto (30% b.u.) foram submetidos à secagem convectiva, e os dados experimentais foram submetidos à análise de modelos de secagem teóricos, semi-teóricos e empíricos, e os parâmetros termodinâmicos foram calculados. O aumento da temperatura acelerou a secagem, encurtando o tempo necessário para atingir o equilíbrio de umidade. O modelo de Page modificado por Cavalcanti-Mata apresentou excelente ajuste aos dados experimentais, destacando-se pela simplicidade e eficácia na descrição da relação entre teor de água e tempo de secagem. A análise das propriedades termodinâmicas revelou que a energia de ativação aumentou com a temperatura, evidenciando sua influência na remoção de umidade. As variações observadas nas propriedades termodinâmicas reforçam a importância de considerar fatores energéticos na secagem. Os resultados oferecem insights para otimizar o processo de secagem de grãos de arroz preto, contribuindo para avanços na indústria alimentícia e fornecendo base para futuras pesquisas no processamento de produtos agrícolas.
1 INTRODUCTION

Rice is one of the most consumed cereals globally, especially in developing countries, due to its significant nutritional value (Gouvêa et al., 2017). Since before the Green Revolution, pigmented rice varieties were already appreciated and consumed by several cultures, recognized for their food potential (Prasad et al., 2019). One of these varieties is black rice, which stands out for the presence of pigments known as anthocyanins, responsible for the red, purple and blue colors in various products derived from this grain (Norkaew et al., 2019). These pigments are concentrated in the grain’s karyopsy, giving it the name "black rice". The use of black rice in the food industry as a raw material is of great relevance, due to its high nutritional value and attractive sensory characteristics (Alencar et al., 2019).

The conservation of agricultural products is essential to ensure their durability, and drying is a unitary operation widely used in this context. It plays a crucial role in reducing the water activity of products, inhibiting chemical and microbiological reactions that cause spoilage. During the drying process, a mass transfer occurs between the grains and the surrounding air until the equilibrium water content, related to the equilibrium relative humidity, is reached (Schemmingera et al., 2019). The study of the drying of agricultural products is importance for the industry, since it allows the development and improvement of equipment, as well as the optimization of projects for viable commercial application (Santos et al., 2020). Different mathematical models have been used to describe the kinetics of drying in a thin layer for agricultural products, the theoretical model, the semi-theoretical models and the empirical ones, which consider only the external resistance to the temperature and the relative humidity of the drying air (Midilli et al. al., 2002). This approach enables a deeper understanding of the process, contributing to the efficiency and quality of the methods used in the conservation of products.
Several researchers have dedicated themselves to studying the drying of black rice, using different approaches to analyze the kinetic parameters of this process. For example, the work of Lang et al. (2018) investigated the drying of black rice grains in a fixed bed dryer, with temperatures varying between 20 and 100 °C, analyzing the drying kinetics and grain diffusivity. In another research, Santos et al. (2019) explored the drying kinetics of black rice by applying different mathematical models (empirical and diffusive) to experimental data, while examining the effect of drying air temperature (40 to 80 °C).

Furthermore, Rashid et al. (2023) carried out a comprehensive study on the effects of drying temperature (50, 60 and 70 °C) and ultrasonic treatment durations (10, 20 and 50 min) on drying attributes, mathematical modeling and thermodynamics, of germinated black rice. In turn, Santos et al. (2023) explored the processing of black rice grains to obtain flour, focusing on applying the diffusion model to experimental data on the drying kinetics of the grain subjected to different pre-treatments.

Despite current studies in the literature, the substantial innovation of this study resides in the introduction of new concepts proposed by Cavalcanti-Mata et al. (2020) for the field of drying agricultural products, especially in the context of black rice. These new concepts, based on the Fick model, provide a new perspective to the traditional equations proposed by Page, Henderson & Pabis and Cavalcanti-Mata, expanding the frontiers of understanding the kinetics of thin layer drying. By incorporating these advances, our study aims to improve the prediction of black rice behavior during the drying process, enabling a more accurate analysis of the implications for the properties and characteristics of the final product. The introduction of these new concepts represents a significant step in the search for more efficient and innovative strategies in the processing and use of black rice in the food industry.

In this sense, the present study aims to investigate the kinetics of drying in a thin layer of black rice grains at different drying temperatures (35, 45, 55, 65 and 75 °C), also aiming to determine the effective diffusivity, the activation energy of the product and the thermodynamic properties (enthalpy, entropy and Gibbs free energy). Furthermore, the determination of the effective diffusivity and activation
energy will offer valuable information about the mass transfer rate and thermal sensitivity of the product during drying. The results obtained may have significant implications for the food industry, allowing the development of more efficient and economical technologies for drying black rice grains and other agricultural products.

2 MATERIALS AND METHODS

The study was conducted at the Drying Laboratory of the Food Engineering Department of the Federal University of Campina Grande (UFCG), Campina Grande Campus, Paraíba (PB), Brazil. Camil brand black rice grains were purchased at the local market in the city and moistened until reaching a water content of 30% in wet basis (b.u.), determined by the oven method, at 105 ± 3 °C, for a period of 24 hours (Brasil, 1992).

2.1 DETERMINING THE MEAN RADIUS

To obtain the radius of equivalence to a cylinder of randomly selected black rice grains, we performed the calculation by measuring the three orthogonal axes. Measurements were made for 100 grains using a digital caliper (Mitutoyo®, 0.01 mm resolution). The equations used represent the black rice grain as a volume of an irregular cylinder, according to Equation 1.

\[ V_c = \pi r_1 \cdot r_2 \cdot L \]  

(1)

Where:

\( V_c \) cylinder volume (mm\(^3\)); \( r_1 \) and \( r_2 \), radii referring to the orthogonal axes (mm); \( L \), grain length (mm).

The equivalent radius, considering black rice as having the same volume as a cylinder, is expressed by Equation 2.

\[ r_{eq} = \sqrt{\frac{V_{cilindro}}{\pi L}} \]  

(2)

Where:
2.2 GRAIN DRYING AND KINETIC MONITORING

In the drying process of black rice grains, 300g samples with an initial water content of 30% wet basis (b.u.) were used. Subsequently, the samples were divided into three equal parts, packed in plastic bags and stored at 6 °C until drying. The three samples of black rice grains were distributed in steel mesh trays (20 x 10 cm) previously weighed and dried in a dryer with forced air ventilation, at five temperatures: 35, 45, 55, 65 and 75 °C. The drying process was carried out until the grains reached equilibrium water content, at which point there was no longer any considerable variation in the mass of the samples. To obtain the drying kinetics, mass loss readings were performed at regular intervals of time, with measurements every 5, 10, 30 and 60 minutes, being digitally identified by a panel coupled directly to a load cell. To determine the water content grains at each temperature at the end of the drying process, the gravimetric method was used, at 105 ± 3 °C, for a period of 24 hours (Brasil, 1992).

2.2.1 Calculation of Water Content Ratio

The experimental data on water loss throughout the drying process were expressed as moisture ratio (RX), as shown in Equation 3:

\[
RX = \frac{X_{bs} - X_e}{X_{bs\text{ initial}} - X_e}
\]

Where:

RX, water content ratio (dimensionless); Xe, equilibrium water content, decimal (dry basis); Xbs, water content, decimal (dry basis); Initial xbs, initial water content, decimal (dry basis).

2.3 MATHEMATICAL MODELS

2.3.1 Fick’s Model

Diffusion theory is based on Fick’s second law, which expresses the diffusion of water in a solid through a concentration gradient (Cavalcanti-Mata et al., 2006). This conceptualization can be expressed by Equation 4.
\[
\frac{\partial X}{\partial t} = \nabla (D \nabla X)
\]  

(4)

Where:

\(X\), water content of the product, decimal, dry basis; \(D\), diffusion coefficient, \(m^2.s^{-1}\); and, \(t\), drying time, s.

Equation 4 expressed for cylindrical coordinates is given by Equation 5.

\[
\frac{\partial X}{\partial t} = \frac{1}{r} \left\{ \frac{\partial}{\partial r} \left( r D \frac{\partial X}{\partial r} \right) + \frac{\partial}{\partial \theta} \left( D \frac{\partial X}{\partial \theta} \right) + \frac{\partial}{\partial z} \left( D \frac{\partial X}{\partial z} \right) \right\}
\]  

(5)

Where:

\(r\), radial coordinate, \(\theta\), polar coordinate and “z” is the axial coordinate.

The analytical solution given by Crank (1975) for Fick's second Law, considering the theoretical geometric shape of an infinite cylinder, where the process occurs in a unidirectional system, disregarding the volumetric contraction of the grains and considering the equilibrium boundary conditions as the known temperature and relative humidity on the surface of the grain is given by Equation 6.

\[
RX = \frac{X_s - X_e}{X_0 - X_e} = \sum_{n=1}^{\infty} \frac{4}{\lambda_n^2} \exp \left[ -\frac{\lambda_n^2}{r_e^2} D_{ef} \cdot t \right]
\]  

(6)

Where:

\(RX\), the water content ratio, dimensionless; \(\lambda_n\), root of the zero order Bessel function; \(D_{ef}\), effective diffusion coefficient, \(m^2/s\); and \(r_e\), equivalent radius, m; \(t\), time, s.

For the development of the analytical equation of Fick's Law, the first six roots obtained from the first type and zero order Bessel Function, Equation 7, were used.
\[ y = x^r \sum_{n=0}^{\infty} a_n x^n = \sum_{n=0}^{\infty} a_n x^{n+R}, \text{ com } a_0 \neq 0 \] (7)

2.3.2 Model by Henderson & Pabis Modified by Cavalcanti-Mata

When considering the first term of the series, Fick's equation for cylindrical coordinates can be expressed by Equation 8.

\[
RX = \frac{X_t - X_e}{X_0 - X_e} = \frac{4}{\lambda_n^2} \exp \left[ -\frac{\lambda_n^2}{r_e^2} D_e f t \right]
\] (8)

Cavalcanti-Mata et al. (2020) considered that the Henderson & Pabis Model can be a simplified equation of the Fick equation using the first term of the series where the independent value \(4/\lambda_n^2\) can be replaced by a coefficient “A” to be determined, that non-linear regression equation. Thus, the Henderson & Pabis Model modified by Cavalcanti-Mata et al. (2020) can be expressed by Equation 9.

\[
RX = \frac{X_t - X_e}{X_0 - X_e} = A \exp \left[ -\frac{\lambda_n^2}{r_e^2} D_e f t \right]
\] (9)

Where:

\(RX\), water content ratio, dimensionless; \(X_t\), water content of the product (b.s.); \(X_0\), initial water content of the product (b.s.); \(X_e\), product equilibrium water content (b.s.); \(\lambda_n\), root of the zero order Bessel function; \(D_e f\), effective diffusion coefficient, \(m^2/s\); \(r_e\), equivalent radius, \(m\); \(t\), time, \(s\).

2.3.3 Model by Page Modified by Cavalcanti-Mata

A similar reasoning can be made to Page's equation where in Equation 9, considering the boundary conditions that for \(x = 0\); \(RX = 1\), therefore, for this condition to be satisfied \(A = 1\) and Equation 8 becomes Equation 10, where a temporal correction proposed by Page is made, involving a factor \(N\), then we have the Page Model modified by Cavalcanti Mata and can be expressed by Equation 11.

\[
RX = \frac{X_t - X_e}{X_0 - X_e} = \exp \left[ -\frac{\lambda_n^2}{r_e^2} D_e f t \right]
\] (10)
\[ RX = \frac{X_t - X_e}{X_0 - X_e} = \exp \left[ -\frac{\lambda_1^2}{r_e^2} D_{ef} t^n \right] \]  
\hspace{1cm} (11)

Where:

\( RX \), water content ratio, dimensionless; \( X_0 \), water content of the product (b.s.); \( X_0 \), initial water content of the product (b.s.); \( X_e \), product equilibrium water content (b.s.); \( \lambda_n \), root of the zero order Bessel function; \( D_{ef} \), effective diffusion coefficient, m²/s; \( r_e \), equivalent radius, m; \( t \), time, s.

### 2.3.4 Cavalcanti-Mata’s Model

In the model proposed by Cavalcanti-Mata (2006), the author is based on the Fick Model using 2 terms of the series. In this case, Equation 6 would look like Equation 12.

\[ RX = \frac{X_t - X_e}{X_0 - X_e} = 4 \frac{\lambda_1^2}{\lambda_1^2 - \lambda_2^2} \exp \left[ -\frac{\lambda_1^2}{\lambda_1^2} D_{ef} t^n \right] + 4 \frac{\lambda_2^2}{\lambda_2^2} \exp \left[ -\frac{\lambda_2^2}{\lambda_2^2} D_{ef} t^n \right] \]  
\hspace{1cm} (12)

Other considerations were made in the Model proposed by Cavalcanti-Mata et al. (2020), using 2 terms from the Fick series. In this model, the independent values \( 4/\lambda_1^2 \) and \( 4/\lambda_2^2 \), are replaced respectively by coefficients \( A_1 \) and \( B_1 \) to be determined by nonlinear regression. In this model, corrections of temporal order are also included, in addition to a \( C_1 \) coefficient of adjustment to the initial condition, where for \( t = 0 \) \( RX = 1 \), therefore \( A_1 + B_1 + C_1 = 1 \). Cavalcanti Mata’s Model can be described by Equation 13.

\[ RX = A_1 \exp \left( -\frac{\lambda_1^2}{r_e^2} D_{ef} t^{n_1} \right) + B_1 \exp \left( -\frac{\lambda_2^2}{r_e^2} D_{ef} t^{n_2} \right) + C_1 \]  
\hspace{1cm} (13)

Where:

\( RX \), water content ratio, dimensionless; \( A_1, B_1 \), coefficients determined by dimensionless linear regression; \( C_1 \), initial condition adjustment coefficient; \( D_{ef} \), effective diffusion coefficient, m²/s; \( \lambda_n \), root of the zero order Bessel function; \( r_e \), equivalent radius, m; \( t \), time, s.
2.3.5 Midilli’s Model

An empirical model that has been used to express experimental drying data is the model by Midilli et al. (2002), although this model does not allow to determine the thermodynamic properties. This model is expressed by Equation 14.

\[ RX = a \cdot \exp(-k \cdot t^n) + b \cdot t \]  

(14)

Where:

RX, moisture ratio (dimensionless); t, drying time (min); a, n, b are the empirical constants of the drying models; k, empirical coefficients (dimensionless).

2.4 ACTIVATION ENERGY (EA)

The activation energy was determined using an Arrhenius-type equation (Equation 15) where the effective diffusivity is interdependent with temperature, and this equation can be linearized and expressed by Equation 16 (Horn et al., 2010).

\[ D_{ef} = D_o \cdot \exp\left(-\frac{E_a}{R \cdot T_a}\right) \]  

(15)

\[ \ln(D_{ef}) = \ln(D_o) - \left(\frac{E_a}{R \cdot T_a}\right) \]  

(16)

Where:

\[ D_{ef}, \text{ effective diffusivity, m}^2\text{s}^{-1}; D_o, \text{ constant called the pre-exponential factor, m}^2\text{s}^{-1}; E_a, \text{ activation energy, kJmol}^{-1}; R, \text{ universal gas constant, 8,314 J mol}^{-1}\text{K}^{-1}; T_a, \text{ absolute temperature, K}. \]

2.5 THERMODYNAMIC PROPERTIES

By determining the activation energy, it was possible to calculate the various thermodynamic properties of the black rice grain, such as: enthalpy, entropy and Gibbs free energy. According to Jideani and Mpotokwana (2009), these three parameters can be determined from, respectively, Equations 17, 18 and 19:
\[ \Delta H = E_a - R T \]  
\[ \Delta S = R \left[ \ln D_o - \ln \left( \frac{k_b}{k_p} \right) - \ln T \right] \]  
\[ \Delta G = \Delta H - T \Delta S \]

Where:

\( \Delta H \), enthalpy, J mol\(^{-1}\); \( \Delta S \), entropy, J mol\(^{-1}\) K\(^{-1}\); \( \Delta G \), Gibbs free energy, J mol\(^{-1}\); \( k_b \), Boltzmann constant, 1,38 \times 10^{-23} \) J K\(^{-1}\); \( h_p \), Planck's constant, 6,626 \times 10^{-34} \) J s\(^{-1}\).

2.6 STATISTICAL ANALYSIS

Through nonlinear regression analysis using the Statistica 8.0 software (StatSoft Inc., Tulsa, OK, USA), the determination coefficient (\( R^2 \)), the adjusted determination coefficient (\( R_a^2 \)), mean relative error (\( P \)), the standard deviation of the estimate (\( SE \)) and the mean squared deviation (\( DQM \)), using equations (20), (21), (22) and (23), respectively. These parameters were used as selection criteria to obtain the model that best represents the experimental data.

\[ R_a^2 = 1 - \frac{(n-1)(1-R^2)}{(n-1)-p} \]  
\[ P = \frac{100}{n} \sum_{i=1}^{n} \frac{(Y-Y_i)}{Y} \]  
\[ SE = \sqrt{\frac{\sum_{i=1}^{n}(Y-Y_i)}{GLR}} \]  
\[ DQM = \sqrt{\frac{\sum(RX_{exp}-RX_{pre})^2}{N}} \]

Where:
$R^2$, adjusted coefficient of determination; $p$, number of equation coefficients; $n$, number of observations throughout the experiment; $P$, mean relative error; $Y$, value observed experimentally; $\hat{Y}$, value calculated by the model; SE, estimated standard error; GLR, model degree of freedom; DQM, root mean square deviation; RX$_{exp}$, ratio of water content obtained experimentally; RX$_{pre}$, water content ratio predicted by the mathematical model; N, number of observations throughout the experiment.

3 RESULTS

3.1 DRYING KINETICS OF BLACK RICE GRAINS IN THIN LAYER

In Figure 3 are the experimental data of the water content ratio as a function of the drying time for black rice grains in a thin layer for drying air temperatures of 35 to 75 ºC. The curves presented represent the reduction in the water content of the product over the drying time, that is, the loss of mass of the material during the process for a specific drying condition (Park et al., 2014). In drying processes, increasing the temperature of the drying air results in faster removal of water, exponentially decreasing the time required for drying. As the process progresses, the drying rate decreases, demonstrating greater resistance in removing water from the product until equilibrium is reached between the product and the drying air. According to Sousa et al. (2016), in this period, the internal resistance to water transport becomes greater than the external resistance, allowing water transport to occur by capillary flow, liquid diffusion or vapor diffusion.

Figure 3. Experimental data on drying black rice at temperatures of 35 to 75 ºC

Source: The authors (2023).
In Figure 3, we can see that the average times needed to complete the drying process of black rice were 1710, 1530, 1110, 1050 and 810 minutes, respectively, for temperatures of 35, 45, 55, 65 and 75°C. As expected, the relationship between the temperature used in the drying process and the time required to reach the equilibrium water content is inversely proportional. According to Santos et al. (2019), this behavior occurs because the removal of water from the product is more efficient at higher temperatures, which reduces the total drying time.

The equilibrium water content values obtained were also inversely proportional to the increase in temperature, the highest values were obtained for dry grains under temperatures of 35 and 45 °C, 11.91 and 9.92%, respectively. However, dried grains under temperatures of 55, 65 and 75 °C showed the lowest values of equilibrium water content, 7.91, 6.39 and 4.98%, in due order. Results similar to those found by Santos et al. (2020), when drying red rice, under temperatures of 40 to 80 °C, where it obtained equilibrium water content varying between 10.99% (40 °C) and 4.15% (80 °C).

3.2 EVALUATION OF THE MATHEMATICAL MODELS USED TO DESCRIBE THE GRAIN DRYING PROCESS
3.2.1 Fick’s Model

In Table 1 are the effective diffusivity values determined by the Fick equation ranging from the 1st to the 6th term of the series, and in Figure 4 are the drying curves determined by the Fick model with 6 series terms for temperatures from 35 to 75 °C.
Table 1. Parameters of the drying kinetics of brown rice grains, using the Fick model up to the 6th term of the series, at temperatures of 35, 45, 55, 65 and 75 °C

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<th>T(°C)</th>
<th>Def ((10^{-10} \text{ m}^2 \text{s}^{-1}))</th>
<th>R²</th>
<th>R²a</th>
<th>Def ((10^{-10} \text{ m}^2 \text{s}^{-1}))</th>
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<th>R²a</th>
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</thead>
<tbody>
<tr>
<td>35</td>
<td>1.510</td>
<td>96.01</td>
<td>95.90</td>
<td>1.508</td>
<td>96.09</td>
<td>95.98</td>
</tr>
<tr>
<td>45</td>
<td>2.023</td>
<td>98.08</td>
<td>98.02</td>
<td>2.000</td>
<td>98.14</td>
<td>98.08</td>
</tr>
<tr>
<td>55</td>
<td>2.626</td>
<td>97.40</td>
<td>97.30</td>
<td>2.626</td>
<td>97.47</td>
<td>97.38</td>
</tr>
<tr>
<td>65</td>
<td>3.560</td>
<td>97.80</td>
<td>97.71</td>
<td>3.560</td>
<td>97.86</td>
<td>97.78</td>
</tr>
<tr>
<td>75</td>
<td>5.033</td>
<td>97.57</td>
<td>97.46</td>
<td>5.316</td>
<td>97.64</td>
<td>97.53</td>
</tr>
</tbody>
</table>

Note: Def, effective diffusivity; R², coefficient of determination; R²a, adjusted coefficient of determination. Source: The authors (2023).

Figure 4. Black rice grain drying curves determined by Fick’s mathematical model with 6 terms of the series at temperatures of 35, 45, 55, 65 and 75 °C

Source: The authors (2023).

As shown in Table 1, it appears that increasing the number of terms in the series resulted in a significant increase in R²a, going from 85% with 1 term to
98% with 6 terms. This result indicates that increasing the series terms made the equation more representative, providing a more realistic description of the drying process. Furthermore, when analyzing Table 1, we can observe that, although the coefficients of determination have increased with the increase in the number of terms in the series, the diffusivity \( D_{ef} \) showed little change and oscillation in the order of magnitude of the values. This observation is relevant, as it suggests that the \( D_{ef} \) was not significantly affected by the inclusion of more terms in the series, indicating the robustness of the proposed modeling.

It is observed that the higher the drying air temperature, the greater the \( D_{ef} \) value and, consequently, the higher the speed of water removal from the product. This behavior is consistent with studies by Santos et al. (2019), as when drying black rice grains, obtained values ranging from 2.24 to 5.21×10^{-9} m^2 min^{-1} at temperatures from 40 to 80°C and Sadaka (2022) examining the drying kinetics parameters of paddy rice with a grain layer thickness of 2.5 cm, found results ranging from 1.34×10^{-9} to 5.93×10^{-9} m^2 s^{-1} for the diffusivity in the temperatures from 40 to 100°C. Therefore, the values are in accordance with the literature and recommended by Madamba et al. (1996), where these mass diffusivity values for drying agricultural products range from 10^{-9} m^2 s^{-1} to 10^{-11} m^2 s^{-1}.

3.2.2 Model by Henderson & Pabis and Page Modified by Cavalcanti-Mata and Cavalcanti-Mata’s Model

Table 2 shows, respectively, the parameters of the Henderson & Pabis and Page models modified by Cavalcanti-Mata and the Cavalcanti-Mata model, as well as the values of the statistical parameters, which are \( R^2 \), \( R^2_a \), P, SE and DQM. In Figure 5 are the black rice grain drying curves determined by the mathematical models of Henderson & Pabis (Figure 5A) and Page (Figure 5B) modified by Cavalcanti-Mata and model by Cavalcanti-Mata (Figure 5C) for the temperatures of 35, 45, 55, 65 and 75°C.
Table 2. Estimated parameters of the model by Henderson & Pabis and Page modified by Cavalcanti-Mata and model by Cavalcanti-Mata obtained through non-linear regression for drying black rice at temperatures from 35 to 75°C

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>a</th>
<th>D_{ef} (10^{-10} m^2 s^{-1})</th>
<th>R² (%)</th>
<th>R²a (%)</th>
<th>P (%)</th>
<th>SE</th>
<th>DQM</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>1.012</td>
<td>2.488</td>
<td>99.94</td>
<td>99.94</td>
<td>3.97</td>
<td>0.014</td>
<td>0.013</td>
</tr>
<tr>
<td>45</td>
<td>0.961</td>
<td>3.273</td>
<td>99.78</td>
<td>99.77</td>
<td>6.53</td>
<td>0.012</td>
<td>0.045</td>
</tr>
<tr>
<td>55</td>
<td>0.968</td>
<td>4.453</td>
<td>99.55</td>
<td>99.51</td>
<td>6.48</td>
<td>0.009</td>
<td>0.057</td>
</tr>
<tr>
<td>65</td>
<td>0.956</td>
<td>6.016</td>
<td>99.38</td>
<td>99.33</td>
<td>2.40</td>
<td>0.017</td>
<td>0.011</td>
</tr>
<tr>
<td>75</td>
<td>0.963</td>
<td>8.493</td>
<td>99.52</td>
<td>99.47</td>
<td>1.00</td>
<td>0.031</td>
<td>0.009</td>
</tr>
</tbody>
</table>

Note: a, b and n, model constants; D_{ef}, effective diffusivity; R², determination coefficients; R²a, adjusted coefficient of determination; P, mean relative error; SE, estimated mean error; DQM, root mean square deviation.

Source: The authors (2023).
Figure 5. Black rice grain drying curves determined by mathematical models by Henderson & Pabis (A) and Page (B) modified by Cavalcanti-Mata, and by mathematical model by Cavalcanti-Mata (C) at temperatures of 35 to 75 °C

The mathematical models adjusted to the experimental data, as shown in Table 2, exhibit $R^2_a$ greater than 99.33% for all models. These results indicate that both the Henderson & Pabis and Page modified mathematical models, as well as the Cavalcanti-Mata Model, demonstrated a satisfactory fit to describe the drying process of black rice at temperatures of 35 to 75 °C. However, it is important to point out, as observed by Corrêa et al. (2010), that the coefficient of determination ($R^2$) in non-linear models may not be a decisive indicator by itself in the analysis of drying processes. Thus, a comprehensive approach involves the joint evaluation of other statistical parameters, including $P$ and SE, as suggested by Madamba et al. (1996). Furthermore, as highlighted by Martins et al. (2014), DQM analysis can be a valuable additional criterion in these evaluation situations. As observed by Mohapatra & Rao (2005), it is suggested that the magnitude of this relative error ($P$) is less than 10%, indicating that the equation in question more accurately
describes the drying process compared to others. The analysis of Table 2 reveals that all models showed low values for SE, P and DQM.

In the models studied, parameters in addition to mass diffusivity such as, for example, "a" in the modified Henderson & Pabis model, parameter "n" in the modified Page model and parameters A₁, B₁, C₁, n₁ and n₂ in the Cavalcanti-Mata model does not seem to be affected by temperature, therefore, these values are more linked to mathematical adjustments than to the drying phenomenon itself, a fact also observed by Santos et al. (2019) in their research on drying black rice. This observation also echoes a previous study by Mendonça et al. (2015), in which the "n" parameter in Page's equation is discussed as having a moderating effect on drying time, correcting possible errors resulting from neglecting the internal resistance to water transport. Therefore, this trend of behavior suggests that such parameters may be more related to mathematical nuances than to the nuances of the drying process itself.

Regarding effective diffusivity, according to Araújo et al. (2017) this parameter represents the external drying conditions decreasing with increasing drying time, with this decrease being faster the higher the temperature and lower relative humidity. It can be seen in Table 2 that in all models studied, Dₑ increased with increasing drying temperature, ranging from 2.488 a 8.493 10⁻¹⁰ m² s⁻¹ for the modified Henderson & Pabis model, 2.047 a 13.702 10⁻¹⁰ m² s⁻¹ for the modified Page model and 2.260 a 13.411 10⁻¹⁰ m² s⁻¹ for the Cavalcanti-Mata model, with a temperature variation from 35 to 75 °C. This fact was also observed by Sadaka (2022) studying the drying kinetics of paddy rice with a grain layer thickness of 2.5 cm, at temperatures from 40 to 80 °C; by Quequeto et al. (2017) studying bean grains cultivar IPR Tangará; Silva, et al. (2019) studying the drying kinetics of soybean grains; and Botelho et al. (2015) studying the drying and determination of the effective diffusion coefficient of sorghum grains.

Therefore, this research reveals that the empirical models fitted the experimental data more effectively than Fick's six-term theoretical model. Among the empirical models, the highlight goes to Page's modified model, due to its smaller number of terms and the impressive values of R², SE, P and DQM. This model was adopted as the superior option to represent the black rice drying curves.
in a temperature range between 35°C and 75°C. In line with Santos et al. (2019), who explored the drying kinetics of black rice and applied different mathematical models (empirical and diffusive) to the experimental data, our findings highlight that, among the empirical models, the Page model demonstrated the lowest DQM and R². Additionally, it was observed that, for the diffusion model, there was an increase in the values of effective mass diffusivity and convective heat transfer coefficient as the temperature of the drying air was increased.

3.2.3 Midilli’s Model

Table 3 brings together the parameters related to the Midilli model, adjusted to the drying kinetics of black rice grains at temperatures ranging from 35 to 75 °C. It also presents the statistical values of R², R²a, P, SE and DQM. Figure 6 shows the grain drying curves determined by this same model for temperatures from 35 to 75 °C.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>a</th>
<th>k</th>
<th>n</th>
<th>b</th>
<th>R² (%)</th>
<th>R²a (%)</th>
<th>P (%)</th>
<th>SE</th>
<th>DQM</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>1.01</td>
<td>0.004</td>
<td>1.026</td>
<td>0.5×10⁻⁵</td>
<td>99.96</td>
<td>99.95</td>
<td>4.37</td>
<td>0.013</td>
<td>0.001</td>
</tr>
<tr>
<td>45</td>
<td>1.001</td>
<td>0.011</td>
<td>0.871</td>
<td>0.6×10⁻⁵</td>
<td>99.97</td>
<td>99.96</td>
<td>2.65</td>
<td>0.015</td>
<td>0.002</td>
</tr>
<tr>
<td>55</td>
<td>0.990</td>
<td>0.011</td>
<td>0.933</td>
<td>2.4×10⁻⁵</td>
<td>99.75</td>
<td>99.73</td>
<td>2.91</td>
<td>0.014</td>
<td>0.006</td>
</tr>
<tr>
<td>65</td>
<td>0.987</td>
<td>0.017</td>
<td>0.897</td>
<td>2.1×10⁻⁵</td>
<td>99.58</td>
<td>99.55</td>
<td>4.05</td>
<td>0.025</td>
<td>0.002</td>
</tr>
<tr>
<td>75</td>
<td>0.981</td>
<td>0.019</td>
<td>0.940</td>
<td>2.4×10⁻⁵</td>
<td>99.63</td>
<td>99.59</td>
<td>1.48</td>
<td>0.036</td>
<td>0.002</td>
</tr>
</tbody>
</table>

Note: a, k, b and n, model constants; R², determination coefficients; R²a, adjusted coefficient of determination; P, mean relative error; SE, estimated mean error; DQM, root mean square deviation.

Source: The authors (2023).
As emphasized by Botelho et al. (2018), the use of the SE is especially valuable, as it measures the error made by the model in the same physical unit of the estimated variable. In the present study, it was found that all models derived from Fick’s 2nd Law achieve a high degree of fit, with DQM values equal to or less than 0.0573. However, it is noticeable that these high adjustments may be linked to a greater number of coefficients, as is the case of the Cavalcanti Mata model, which has six constants. These results suggest that this was the most representative model for drying black rice grains. According to Mendonça et al. (2015), the superiority of these non-linear mathematical equations can be attributed to the greater number of adjustment parameters. However, the adjusted coefficient of determination corrects these values, transforming them into a comparative measure between the equations.

The Midilli model proved to be the one that best represented the experimental drying data. Other researchers also reached the same conclusion, such as Corrêa et al. (2017), who studied the thermodynamic properties of the drying process and water absorption of white rice grains at temperatures from 35 to 75 °C. Santos et al. (2019), in their investigation into the drying process of black rice grains, obtained $R^2$ values greater than 98% and DQM values lower than 0.0497, indicating a satisfactory representation of the studied phenomenon. In a subsequent study, focused on determining the thermodynamic properties of the drying process and water absorption of rice grains, Corrêa et al. (2017) described Midilli’s mathematical model as the best fit for the drying curve. However, a disadvantage of the Midilli model is its empirical nature, which does not allow the determination of the effective mass diffusivity. Instead, it replaces this with a "$k$" value, representing a drying constant.

In conclusion, it can be stated that the mathematical models of modified Henderson & Pabis, modified Page, Cavalcanti-Mata and Midilli presented satisfactory statistical coefficients in the description of the drying curves of black rice grains in all the studied temperatures. However, the modified Page model, due to the lower number of terms, excellent $R^2$ and DQM values, efficient representation of the drying curves for different temperatures and ease of application, emerged as the preferred choice.
3.2.4 Activation Energy and Thermodynamic Properties of the Process

The relationship between the effective diffusivity coefficient of black rice grains and the drying air temperature was properly characterized using the Arrhenius expression. Thus, the Neperian logarithm values of the effective diffusivity coefficients \( \ln(\text{Def}) \) were represented as a function of the inverse of the absolute temperature, making it possible to obtain the angular coefficients of each straight line, which reflect the E/R ratio for each temperature range. By multiplying the slope of the line by 8.314, we get the activation energy for each temperature range. From a thermodynamic point of view, in drying processes, a lower activation energy implies a higher speed of water removal from the grains (Resende et al., 2010; Matin et al., 2017). Table 4 presents the activation energy values and thermodynamic properties (enthalpy, entropy and Gibbs free energy) of the black rice grain drying process for the models studied at different temperatures.

<table>
<thead>
<tr>
<th>Models</th>
<th>( E_a ) (kJ mol(^{-1})</th>
<th>T (°C)</th>
<th>( \Delta H ) (kJ mol(^{-1})</th>
<th>( \Delta S ) (J mol(^{-1}) K(^{-1})</th>
<th>( \Delta G ) (kJ mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fick</strong></td>
<td>30.20</td>
<td>35</td>
<td>27.64</td>
<td>-144.76</td>
<td>72.22</td>
</tr>
<tr>
<td></td>
<td></td>
<td>45</td>
<td>27.55</td>
<td>-145.02</td>
<td>73.66</td>
</tr>
<tr>
<td></td>
<td></td>
<td>55</td>
<td>27.47</td>
<td>-145.28</td>
<td>75.12</td>
</tr>
<tr>
<td></td>
<td></td>
<td>65</td>
<td>27.40</td>
<td>-145.53</td>
<td>76.57</td>
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<td></td>
<td></td>
<td>75</td>
<td>27.30</td>
<td>-145.77</td>
<td>78.03</td>
</tr>
<tr>
<td><strong>Henderson &amp; Pabis (modified)</strong></td>
<td>28.84</td>
<td>35</td>
<td>26.28</td>
<td>-144.65</td>
<td>70.83</td>
</tr>
<tr>
<td></td>
<td></td>
<td>45</td>
<td>26.19</td>
<td>-144.92</td>
<td>72.28</td>
</tr>
<tr>
<td></td>
<td></td>
<td>55</td>
<td>26.11</td>
<td>-145.17</td>
<td>73.73</td>
</tr>
<tr>
<td></td>
<td></td>
<td>65</td>
<td>26.03</td>
<td>-145.42</td>
<td>75.18</td>
</tr>
<tr>
<td></td>
<td></td>
<td>75</td>
<td>25.94</td>
<td>-145.67</td>
<td>76.64</td>
</tr>
<tr>
<td><strong>Page (Modified)</strong></td>
<td>28.42</td>
<td>35</td>
<td>25.85</td>
<td>-141.18</td>
<td>69.34</td>
</tr>
<tr>
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<td>25.77</td>
<td>-141.44</td>
<td>70.75</td>
</tr>
<tr>
<td></td>
<td></td>
<td>55</td>
<td>25.69</td>
<td>-141.70</td>
<td>72.16</td>
</tr>
<tr>
<td></td>
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<td>65</td>
<td>25.61</td>
<td>-141.95</td>
<td>73.58</td>
</tr>
<tr>
<td></td>
<td></td>
<td>75</td>
<td>25.52</td>
<td>-142.19</td>
<td>75.01</td>
</tr>
<tr>
<td><strong>Cavalcanti-Mata</strong></td>
<td>32.20</td>
<td>35</td>
<td>29.63</td>
<td>-130.42</td>
<td>69.80</td>
</tr>
<tr>
<td></td>
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<td>29.55</td>
<td>-130.68</td>
<td>71.11</td>
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<td>29.47</td>
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<td>29.38</td>
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<td></td>
<td></td>
<td>75</td>
<td>29.30</td>
<td>-131.43</td>
<td>75.04</td>
</tr>
</tbody>
</table>

Note: activation energy (\( E_a \)), enthalpy (\( \Delta H \)), entropy (\( \Delta S \)) and Gibbs free energy (\( \Delta G \)).
Source: The authors (2023).
According to the results presented in Table 4, the activation energy values for the net diffusion of black rice grains were 30.20 kJmol⁻¹ for the Fick model, 28.84 kJmol⁻¹ for the Henderson & Modified Pabis, 28.42 kJmol⁻¹ for the modified Page model and 32.20 kJmol⁻¹ for the Cavalcanti-Mata model. These values indicate the amount of energy required for the drying process to occur and represent the barrier to mass transfer during grain drying (Corrêa et al., 2017). In this context, the results obtained in this study are in accordance with the range of values mentioned by Zogzas et al. (1996), which establishes that the activation energy for agricultural products varies from 12.7 to 110 kJ mol⁻¹. The observation that the values fall within this range is of significant importance, since it strengthens the robustness of the models employed and supports previous investigations on the activation energy in drying processes of agricultural products.

Correa et al. (2017) carried out a study on the thermodynamic properties of the drying process and water absorption of rice grains at temperatures ranging from 35 to 75°C, obtaining an activation energy value of 51.03 kJ mol⁻¹. Sadaka (2022) reported that the activation energy for drying paddy rice ranged from 25.40 to 36.02 kJ mol⁻¹ for different grain layer thicknesses studied. Although no clear trend was identified between grain layer thickness and activation energy, the values obtained remained in agreement with the literature. Onwude et al. (2016) mentioned activation energy values between 14.42 and 43.26 kJ mol⁻¹ for several agricultural products, concluding that temperature and air thickness were the most influential factors in drying. As pointed out by Corrêa et al. (2017), lower activation energy indicates an easier occurrence of a specific process, suggesting that a smaller amount of energy is required for the physical transformation to occur. Although natural variations between samples may influence the values of thermodynamic parameters, the results obtained indicate that the methodologies used were adequate to describe the drying process of black rice grains.

Analyzing the thermodynamic properties in Table 4, the enthalpy represents the difference between the active and reacting states; therefore, it must be positive (Al-Zybaidy & Khalil, 2007). In this parameter the values ranged from 27.64 to 27.30 KJ mol⁻¹ for the Fick model, 26.28 to 25.94 KJ mol⁻¹ for the
modified Henderson & Pabis model, 25.85 to 25.52 KJ mol\(^{-1}\) for the modified Page model and 29.63 at 29.30 KJ mol\(^{-1}\) for the Cavalcanti-Mata model. Thus, it was observed that the enthalpy decreased with increasing drying air temperature for all models, with the highest values being observed for the Cavalcanti-Mata model. According to Sousa et al. (2016), this behavior is related to the increase in the partial pressure of water vapor in the grains with increasing temperature, resulting in a higher rate of diffusion of water from the interior to the surface of the grain, which leads to loss of product moisture by desorption.

Another parameter of great importance for analysis is Entropy, which reflects a thermodynamic measure of the disorder in a system, being a state function that grows during natural processes in an isolated system (Corrêa et al., 2017). In this study, values ranged from -144.76 to -145.77 J mol\(^{-1}\) K\(^{-1}\) for the Fick model, -144.65 to -145.67 J mol\(^{-1}\) K\(^{-1}\) for the modified Henderson & Pabis model, -141.18 to -142.19 J mol\(^{-1}\) K\(^{-1}\) for the modified Page model and -130.42 to -131.43 J mol\(^{-1}\) K\(^{-1}\) for the Cavalcanti-Mata model. Therefore, it is notable that this thermodynamic property presented a behavior similar to that of enthalpy, with values decreasing as the temperature increases, with the highest values recorded for the Cavalcanti-Mata model. This phenomenon can be explained by the activated complex theory, in which a substance in an activated state can acquire a negative entropy if translational or rotational degrees of freedom are lost during the formation of the activated complex (Dannenberg & Kessler, 1988).

According to Araújo et al. (2017), the positive value of Gibbs free energy is characteristic of an endergonic reaction, in which it requires an addition of energy from the medium in which the product is involved for the reaction to occur. Their values in this study ranged from 72.22 to 78.03 KJ mol\(^{-1}\) for the Fick model, 70.83 to 76.64 KJ mol\(^{-1}\) for the modified Henderson & Pabis model, 69.34 to 75.01 KJ mol\(^{-1}\) for the modified Page model and 69.80 to 75.04 KJ mol\(^{-1}\) for the Cavalcanti-Mata model. Consequently, these values increased with increasing temperature, demonstrating positivity throughout the temperature range studied. This indicates that the drying conditions adopted in this study did not favor the spontaneity of the process, and the Fick model presented the highest values in this context.
Thus, as predicted, this study revealed consistent results regarding the behavior of the thermodynamic properties of the mathematical models used, as the drying temperature was increased. This pattern of behavior was also observed in previous studies, such as that by Sousa et al. (2016), who investigated the thermodynamic properties of the drying kinetics of unhusked red rice grains at different temperatures. Furthermore, authors such as Rashid et al. (2023) found a similar behavior when evaluating the drying of black rice grains at temperatures of 50, 60 and 70 °C.

4 CONCLUSIONS

The study of black rice drying brought with it valuable insights to improve this fundamental process. A notable point was the direct impact of increasing temperature, which resulted in a decrease in the time required for drying, producing steeper and more informative drying kinetics curves. The detailed analysis of the mathematical models led to the conclusion that the modified Page model modified by Cavalcanti-Mata emerges as the preferred choice to represent the drying dynamics of black rice grains at different temperatures. Its ability to fit experimental data, combined with its simple formulation, offers a highly effective approach to describing the correlation between water content and drying time. Furthermore, the exploration of thermodynamic properties, including activation energy, enthalpy, entropy and Gibbs free energy, added a deeper layer to our understanding of the mechanisms underlying the drying process. Notably, the direct relationship between activation energy and temperature emphasizes the crucial role that temperature plays in the rate of moisture removal from brown rice grains. The variations in thermodynamic properties emphasize the importance of taking into account the energetic aspects intrinsic to the drying process, together with the impact of thermal conditions. The results achieved lay a solid foundation for the development of optimized drying strategies, contributing to significant advances in the food industry.
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