



# Drying kinetics and physiology of Cowpea seeds (*Vigna unguiculata* L. Walp) at different temperatures



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## ABSTRACT

The objective of this work was to describe the drying kinetics and evaluate the physiological quality of *Vigna unguiculata* L. Walp seeds after drying. Seeds were harvested with a moisture content of  $0.31 \pm 0.02$  (dry base) and subjected to drying in a forced circulation oven under different conditions of temperature and relative humidity: 40°C, 28.62%; 45°C, 26.62%; 50°C, 17.46%; 55°C, 16.57% and 60°C, 9.28%, until their moisture content reached  $0.12 \pm 0.01$  (dry base). Different mathematical models were fitted to represent the seed drying kinetics, based on the Gauss-Newton method and complemented by Akaike Information Criterion (AIC) and Schwarz's Bayesian Information Criterion (BIC). Physiological properties were determined by assessing their electrical conductivity, germination percentage, emergence, germination speed index, and emergence speed index. It was concluded that the drying rate was higher for higher drying air temperatures and reduced along the drying time; the Midilli model presented the best fit to describe the drying kinetics of cowpea seeds at the temperature of 40°C and the Two-term model for the temperatures of 45, 50, 55 and 60°C. The effective diffusion coefficient ranged from  $1.1378 \times 10^{-11}$  to  $3.3698 \times 10^{-11}$  m<sup>2</sup>/s. The activation energy was 41.9894 kJ/mol. Electrical conductivity increased with an increase in drying air temperature, while germination, emergence, germination speed index, and emergence speed index with an increase in drying air temperature.

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## INTRODUCTION

Cowpea beans (*Vigna unguiculata* L. Walp) are one of the best performing legumes, adapted to the dry regions of the tropics that bathe Africa, Asia, and America (Singh et al., 2002). It is an excellent source of protein and is also considered an important source of income in rural areas. Seeds are often harvested with moisture content unsuitable for storage. To preserve physiological quality, harvesting should occur when the moisture content allows

mechanical harvesting with minimal physical damage and should then be subjected to artificial drying (Hartmann-Filho et al., 2016; Junqueira et al., 2018). Therefore, care must be taken when conducting drying because when done inappropriately, it can result in losses immediately or throughout the storage period (Lima et al., 2016; Mabasso et al., 2019). The storage of seeds with high moisture contents is associated with high water activity, generating physicochemical changes during storage, thus affecting germination and vigorous (Resende et al., 2010).

According to Marcos-Filho (2015), drying must be carried out quickly enough to remove free water, reduce water activity and slow down the destructive metabolism

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without promoting seed disturbances. Several studies have reported losses of physiological quality in seeds immediately and during storage (Almeida et al., 2013; Hartmann-Filho et al., 2016; Junqueira et al., 2018; Quequeto et al., 2020). High temperatures promote higher drying rates; however, with the reduction of the moisture content in the product, the water tends to leave with greater difficulty because it is more strongly bound, causing damage due to the increase in the moisture gradient in the product (Lima et al., 2016).

According to Camicia et al. (2015) the development and improvement of equipment used for drying grains and seeds depends on the simulation and obtaining theoretical information about the behavior of each product during water removal, these aspects can vary depending on the species and variety. Thus, one of the forms of simulation is carried out through the continuous drying of seeds in a thin layer, adjusting the behavior to the mathematical models that best describe the removal of water during the process. Although most studies report a higher rate of damage caused by excessive temperatures resulting from the drying process during storage, some studies have revealed the occurrence of physiological damage soon after drying in various species of grains and seeds, thus reducing their potential for storage (Almeida et al., 2013; Junqueira et al., 2018).

There are few works related to understanding the drying process of seeds and physiological quality from creole varieties, which small farmers in countries like Mozambique very commonly use. In this context, the objective was to describe the drying kinetics and evaluate the physiological properties of cowpea seeds under different conditions of drying air temperature.

## MATERIALS AND METHODS

The harvest of cowpea seeds, variety, called *Chioté*, was carried out in a field belonging to the community of *Munhinga*, province of Manica, Mozambique, with a moisture content of  $0.31 \pm 0.02$  (decimal, d.b.). *Chioté* is a local variety with a four-month cycle with indeterminate and prostrate growth. The initial moisture content was determined using the standard oven method, using three replicates of 15 g each, at a temperature of  $105 \pm 1^\circ\text{C}$  for 24 h.

After harvesting and threshing, the seeds were placed in a polyethylene package inside a cold chamber at  $5^\circ\text{C}$  for 72 h to standardize the conditions of temperature and moisture content of the product. Subsequently, the seeds were submitted to the drying process in a forced circulation oven (INDELAB, model IDL-EI-120), under the conditions of temperature and relative humidity:  $40^\circ\text{C}$ , 28.62%;  $45^\circ\text{C}$ , 26.62%;  $50^\circ\text{C}$ , 17.46%;  $55^\circ\text{C}$ , 16.57%, and  $60^\circ\text{C}$ , 9.28%. For drying, the seeds were distributed among four trays, fully perforated bottom, each containing about  $400 \pm 0.5$  g

of seeds, corresponding to a layer 6 cm thick.

Drying was monitored by mass loss, weighing each tray on a semi-analytical scale, Kern brand, model PLE 4200-2N, with a resolution of 0.01 g, until reaching a mass corresponding to the final moisture content of  $0.12 \pm 0.01$  (d.b.). The weighing was carried out at regular intervals of 10 min with the mass turning at each moment, aiming to uniform the drying of the seeds.

The equilibrium moisture content of the cowpea seeds was determined experimentally by performing the drying process inside the experimental dryer under the same conditions until a constant mass was reached. To evaluate the drying effect of cowpea seeds, the drying rate was determined using Equation 1.

$$DR = \frac{X_0 - X_i}{t_i - t_0} \quad (1)$$

Where: DR - drying rate (kg/kg/h);  $X_0$  - previous moisture content (decimal, d.b.),  $X_i$  - current moisture content (decimal, d.b.);  $t_0$  - previous total drying time (h);  $t_i$  - current total drying time (h).

## Moisture content ratio

From the experimental data, the initial, final and throughout drying moisture content, the moisture content ratio values were calculated (Equation 2).

$$RX = \frac{X - X_e}{X_i - X_e} \quad (2)$$

Where: RX - moisture ratio (dimensionless);  $X$  - moisture content of the product (decimal, d.b.);  $X_e$  - equilibrium moisture content of the product (decimal, d.b.);  $X_i$  - initial moisture content (decimal, d.b.).

## Mathematical modeling

The mathematical models (Equations 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14) for drying seeds were adjusted (Table 1).

Where:  $t$  - drying time,  $k$ ,  $k_0$ ,  $k_1$  - drying constants,  $a$ ,  $b$ ,  $c$  - model coefficients.

## Effective diffusion coefficient

The effective diffusion coefficient under different conditions of drying air temperature was determined by adjusting the mathematical model of liquid diffusion

**Table 1.** Mathematical models for the representation of drying kinetics of agricultural products.

| Model designation          | Model   | Equation |
|----------------------------|---|----------|
| Page                       | $RX = \exp(-k \times t^n)$  | (3)      |
| Midilli                    | $RX = a \exp(-k \times t^n) + b \times t$   | (4)      |
| Newton                     | $RX = \exp(-k \times t)$  | (5)      |
| Thompson                   | $RX = \exp\left(\frac{-a - (a^2 + 4 \times b \times t)^{0.5}}{2 \times b}\right)$ | (6)      |
| Henderson and Pabis        | $RX = a \exp(-k \times t)$  | (7)      |
| Verma                      | $RX = -a \exp(-k \times t) + (1 - a) \exp(-k_1 \times t)$                         | (8)      |
| Logarithmic                | $RX = a \exp(-k \times t) + c$  | (9)      |
| Wang & Singh               | $RX = 1 + a \times t + b \times t^2$  | (10)     |
| Two-terms Exponential      | $RX = a \exp(-k \times t) + (1 - a) \exp(-k \times a \times t)$                   | (11)     |
| Two terms                  | $RX = a \exp(-k_0 \times t) + b \exp(-k_1 \times t)$                              | (12)     |
| Approximation of diffusion | $RX = a \exp(-k \times t) + (1 - a) \exp(-k \times b \times t)$                   | (13)     |
| Valcam                     | $RX = a + b + c \times t^{1.5} + d \times t^2$                                    | (14)     |

**Where:** t - drying time, k, k<sub>0</sub>, k<sub>1</sub> - drying constants, a, b, c - model coefficients.

(Equation 15) to the experimental data of drying cowpea seeds. This equation is the analytical solution of Fick's second law, considering the spherical geometric shape with an approximation of eight terms and the boundary condition of the known moisture content on the product surface (Brooker et al., 1992).

$$RX = \frac{X - X_e}{X_i - X_e} = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left[-\frac{n^2 \times \pi^2 \times D_{ef} \times t}{9 \left(\frac{3}{R_e}\right)^2}\right] \quad (15)$$

Where: t - drying time (h); D<sub>ef</sub> - net diffusion coefficient (m<sup>2</sup>/s); R<sub>e</sub> - equivalent radius (m); n<sub>t</sub> - number of terms.

The equivalent radius was determined by randomly selecting fifty seeds and measuring the three orthogonal axes using a digital micrometer, with a resolution of 0.01 mm according to Equations 16 and 17 (Mohsenin, 1986).

$$V_s = \frac{\pi \times a \times b \times c}{6} \quad (16)$$

$$R_e = \sqrt[3]{\frac{3V_s}{4 \times \pi}} \quad (17)$$

Where: V<sub>s</sub> - seed volume (m<sup>3</sup>); a - longest axis of the seed (m); b - middle axis of the seed (m); c - minor axis of the seed (m); R<sub>e</sub> - equivalent radius (m).

The Arrhenius equation (Equation 18) was used to

evaluate the influence of drying air temperature on the effective diffusion coefficient.

$$D_{ef} = D_0 \exp\left(\frac{E_a}{R \times T_a}\right) \quad (18)$$

Where: D<sub>0</sub> - pre-exponential factor (m<sup>2</sup>/s); E<sub>a</sub> - activation energy (kJ/mol); R - universal gas constant (8,314 kJ/kmol/K); T<sub>a</sub> - drying air temperature (K).

The relation of L<sub>n</sub> (D<sub>ef</sub>) as a function of the inverse of temperature (1/T<sub>a</sub>) provides a straight line (Equation 19) with an angular coefficient capable of estimating the value of the activation energy.

$$\ln D_{ef} = \ln D_0 - \frac{E_a}{R} \times \frac{1}{T_a} \quad (19)$$

### Germination test

To conduct the standard germination test, four (4) sub-samples of 50 (fifty) seeds for each replication were sown on paper towels moistened with distilled water at a proportion of 2.5 times the substrate mass. The test was conducted in a Biochemical Oxygen Demand (DBO) NAHITA (model 639/250), type germination chamber

under the presence of light at 25°C. The observations were made daily until the last count during 7 days, counting all normal seedlings, those that present their essential structures well developed, complete, proportional, healthy and with minimal defects. The germination speed index (GSI) was determined simultaneously with the standard germination test, recording the number of seeds germinated from the first to the last day of counting. The value of the GSI was determined using the Equation 20 (Maguire, 1962).

$$GSI = \frac{G_1}{N_1} + \frac{G_2}{N_2} + \dots + \frac{G_n}{N_n} \quad (20)$$

Where: GSI - germination speed index (dimensionless);  $G_1, G_2 \dots G_n$  - number of seedlings germinated in each count;  $N_1, N_2 \dots N_n$  - number of days after sowing.

### Emergency test

The emergence test was carried out under field conditions, 200 seeds were counted in each replication, subdivided into 4 subsamples of 50 seeds each. The seeds of each subsample were sown 1 cm deep, in a sowing row in moist soil substrate until field capacity. Periodic irrigations were carried out to maintain the substrate's moisture. The determination of emerged seedlings was made by counting the normal seedlings, those that presented with the cotyledons on the surface and the primary leaves visible in their interior, until the eighth from sowing. The emergence speed index (ESI) was performed in conjunction with the emergence test, counting the seedlings that emerged daily until stabilizing the number of emerged plants. The data were later applied to Equation 21 (Maguire, 1962).

$$ESI = \frac{E_1}{N_1} + \frac{E_2}{N_2} + \dots + \frac{E_n}{N_n} \quad (21)$$

Where: ESI - emergence speed index (dimensionless);  $E_1, E_2 \dots E_n$  - numbers of seedlings emerged in the first, second, and last count;  $N_1, N_2 \dots N_n$  - numbers of days after sowing in the first, second and last count.

### Electrical conductivity test

The electrical conductivity was determined using the mass conductivity method with four subsamples of 50 seeds in each replication. After weighing, the seeds were placed in 100 mL disposable cups, which received 75 ml of distilled water. Then, the cups were placed inside a DBO-type chamber for 24 h at a temperature of 25°C.

Likewise, four cups containing 75 mL of distilled water were also placed in the DBO-type chamber to determine the conductivity of the used water and deduct it from the reading value (Marcos-Filho, 2015; Vieira and Krzyzanowski, 1999). The reading was taken after 24 h by a conductivity meter calibrated with the standard solution. The value in  $\mu\text{S}/\text{cm}$  was converted to  $\mu\text{S}/\text{cm}/\text{g}$  by dividing devalues by the mass seeds (Vieira and Krzyzanowski, 1999).

### Statistical analysis

Data were analyzed using Sisvar 5.6®, Sigmaplot 12®, Statistica 7® and R 3.6.1® software. The adjustment of the mathematical models of drying to the experimental data was performed through the non-linear regression analysis by the Gauss-Newton method. To measure the degree of fit of each model, the magnitude of the adjusted coefficient of determination ( $R^2$ ), the mean relative error (P), and the mean estimated error (SE) were considered as described in Equations 22 and 23. For physiological properties, regression models were generated at a 5% probability level by the F-test.

$$P = \frac{100}{n} \sum_{i=1}^n \left( \frac{|Y - \hat{Y}|}{Y} \right) \quad (22)$$

$$SE = \sqrt{\frac{\sum_{i=1}^n (Y - \hat{Y})^2}{DF}} \quad (23)$$

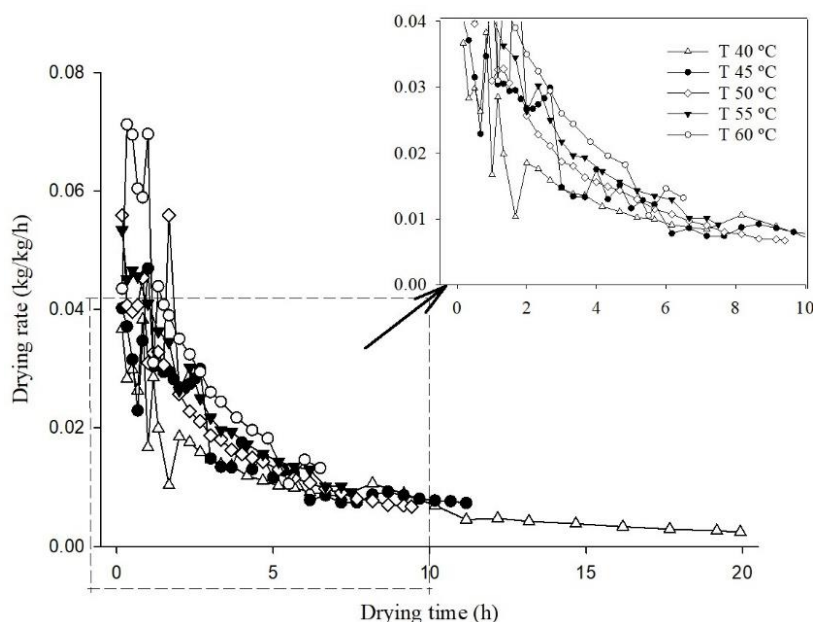
Where:  $Y$  - experimentally value;  $\hat{Y}$  - value estimated by the model;  $n$  - number of experimental observations;  $DF$  - degrees of model freedom (difference between the number of observations and the number of model parameters).

To complement the selection of the models with the best fit, the AIC and the BIC (Equations 24 and 25) were used, submitting the pre-selected models by the Gauss-Newton criterion, commonly used with good accuracy for the selection of models with the best fit (Quequeto et al., 2019; Siqueira et al., 2020).

$$AIC = -2 \log L + 2p \quad (24)$$

$$BIC = -2 \log L + p \ln(n) \quad (25)$$

Where:  $p$  and  $n$  - number of model parameters and observations;  $L$  - maximum likelihood, considering parameter estimates.



**Figure 1.** Drying rate of cowpea (*V. unguiculata* L. Walp) seeds during drying under different air-drying conditions.

## RESULTS AND DISCUSSION

Drying time was reduced with increasing drying air temperature to reduce the initial moisture content from  $0.31 \pm 0.02$  (dry base) to  $0.12 \pm 0.01$  (dry base). Drying times were 19.9, 11.17, 9.42, 7.50, and 6.50 h for the temperatures of 40, 45, 50, 55, and 60°C, respectively (Figure 1). In general, the drying time is a direct result of the drying rate; that is, as the drying air temperature increased, the drying rate was higher, and the time taken to complete the process was shorter. This behavior has also been observed in several works on the drying of agricultural products due to the internal pressure generated inside the product (Siqueira et al., 2020).

Regardless of the drying air temperature, the drying rate showed a decreasing trend over time. In the final part of the drying process, the drying rate values were lower when compared to the initial values, showing slower drying. According to Resende et al. (2010), the lower the moisture content, with the increase in drying time, the water is more strongly linked to dry matter, making the minimum energy necessary for its evaporation to be more significant. On the other hand, the lower the moisture content, the longer the time needed for water diffusion from the center to the periphery, leading to a greater imbalance between evaporation and water diffusion, thus generating high levels of energy consumption per unit of evaporated mass (Lima et al., 2016).

Table 2A shows the estimated mean error (SE), mean relative error (P), and coefficient of determination ( $R^2$ )

used to select the best fit mathematical models to describe the thin layer drying of cowpea seeds at different drying air temperatures, according to the Gauss-Newton criterion.

Relative mean error values above 10% are not recommended for selecting the models under analysis (Kashaninejad et al., 2007). The value of this statistical parameter reflects the deviation of the observed values from the curve estimated by the model. For this statistical parameter, all models were found to be adequate, except the Verma (08) model, which presented values above 10% in more than one drying air temperature, being therefore considered inadequate to describe the kinetics of drying cowpea seeds (Kashaninejad et al., 2007).

Considering the parameters  $R^2$  and SE, used as complementary in the Gauss-Newton method, it is observed that all models selected by the value of P presented a good fit for  $R^2$ . The Page (03), Midilli (04), Thompson (06), Logarithmic (09), Two-term exponential (11), Two-term (12), Diffusion approximation (13) and Valcam (14) models presented values equal to or greater than 0.99, for all temperatures considered. The models of Henderson and Pabis (07) and Wang and Singh (10), on the other hand, presented values lower than 0.99 in at least one of the air-drying temperatures, however, higher than 0.95, being according to the criteria established by Aguerre et al. (1989).

The closer to zero the estimated mean error (SE) is, the better the fit of the mathematical models to the observed data (Kashaninejad et al., 2007; Siqueira et al., 2012). In this sense, the Midilli (4) model stood out for a temperature

**Table 2.** Coefficient of determination ( $R^2$ ), mean relative error (P), mean estimated error (SE) for the twelve models used in thin layer drying (A), and AIC and BIC for the models that best fit the drying data of cowpea (*V. unguiculata* L. Walp) seeds at different temperatures (B).

| A      | Temperature |          |                |          |          |                |          |          |                |          |        |                |       |        |                |
|--------|-------------|----------|----------------|----------|----------|----------------|----------|----------|----------------|----------|--------|----------------|-------|--------|----------------|
|        | 40°C        |          |                | 45°C     |          |                | 50°C     |          |                | 55°C     |        |                | 60°C  |        |                |
|        | SE          | P        | R <sup>2</sup> | SE       | P        | R <sup>2</sup> | SE       | P        | R <sup>2</sup> | SE       | P      | R <sup>2</sup> | SE    | P      | R <sup>2</sup> |
| (03)   | 0.010       | 1.411    | 0.999          | 0.014    | 1.830    | 0.998          | 0.012    | 1.738    | 0.998          | 0.008    | 1.046  | 0.999          | 0.011 | 1.470  | 0.999          |
| (04)   | 0.005       | 0.557    | 0.999          | 0.011    | 1.155    | 0.999          | 0.005    | 0.666    | 0.999          | 0.003    | 0.344  | 0.999          | 0.006 | 0.642  | 0.999          |
| (05)   | 0.049       | 7.462    | 0.972          | 0.038    | 6.707    | 0.979          | 0.042    | 6.453    | 0.976          | 0.029    | 4.323  | 0.990          | 0.028 | 4.417  | 0.992          |
| (06)   | 0.007       | 1.040    | 0.999          | 0.016    | 1.083    | 0.999          | 0.006    | 0.775    | 0.999          | 0.002    | 0.265  | 0.999          | 0.006 | 0.627  | 0.999          |
| (07)   | 0.033       | 4.710    | 0.988          | 0.033    | 4.683    | 0.989          | 0.030    | 4.295    | 0.988          | 0.022    | 3.176  | 0.994          | 0.023 | 3.418  | 0.995          |
| (08)   | 0.102       | 15.341   | 0.881          | 0.079    | 7.126    | 0.963          | 0.075    | 10.467   | 0.929          | 0.107    | 16.509 | 0.863          | 0.183 | 30.696 | 0.585          |
| (09)   | 0.009       | 0.934    | 0.999          | 0.011    | 1.554    | 0.999          | 0.007    | 0.878    | 0.999          | 0.004    | 0.568  | 0.999          | 0.007 | 0.863  | 0.999          |
| (10)   | 0.031       | 4.353    | 0.989          | 0.018    | 3.932    | 0.992          | 0.022    | 3.286    | 0.994          | 0.014    | 2.054  | 0.998          | 0.018 | 2.660  | 0.997          |
| (11)   | 0.021       | 2.951    | 0.994          | 0.018    | 2.472    | 0.999          | 0.017    | 2.572    | 0.996          | 0.006    | 0.845  | 0.999          | 0.007 | 0.953  | 0.999          |
| (12)   | 0.008       | 0.874    | 0.999          | 0.011    | 0.805    | 0.997          | 0.004    | 0.324    | 0.999          | 0.001    | 3.170  | 0.994          | 0.005 | 0.479  | 0.999          |
| (13)   | 0.009       | 1.262    | 0.999          | 0.011    | 0.862    | 0.999          | 0.032    | 0.320    | 0.999          | 0.001    | 0.153  | 0.999          | 0.005 | 0.525  | 0.999          |
| (14)   | 0.006       | 0.626    | 0.999          | 0.012    | 0.771    | 0.999          | 0.004    | 0.396    | 0.999          | 0.002    | 0.236  | 0.999          | 0.005 | 0.515  | 0.999          |
| B      | 40°C        |          | 45°C           |          | 50°C     |                | 55°C     |          | 60°C           |          |        |                |       |        |                |
| Models | AIC         | BIC      | AIC            | BIC      | AIC      | BIC            | AIC      | BIC      | AIC            | BIC      |        |                |       |        |                |
| (04)   | -251.804    | -244.322 | -236.692       | -228.637 | -221.614 | -214.608       | -189.342 | -183.887 | -155.472       | -150.016 |        |                |       |        |                |
| (09)   | -213.549    | -207.563 | -230.533       | -224.089 | -210.389 | -204.785       | -174.484 | -170.120 | -153.101       | -148.737 |        |                |       |        |                |
| (12)   | -222.086    | -214.603 | -265.740       | -257.686 | -247.731 | -242.127       | -225.853 | -221.489 | -165.950       | -160.495 |        |                |       |        |                |
| (13)   | -222.086    | -214.603 | -260.826       | -254.383 | -245.850 | -238.844       | -224.527 | -219.071 | -160.297       | -155.933 |        |                |       |        |                |
| (14)   | -236.461    | -228.978 | -258.762       | -250.707 | -235.610 | -228.604       | -201.252 | -195.797 | -159.527       | -154.072 |        |                |       |        |                |

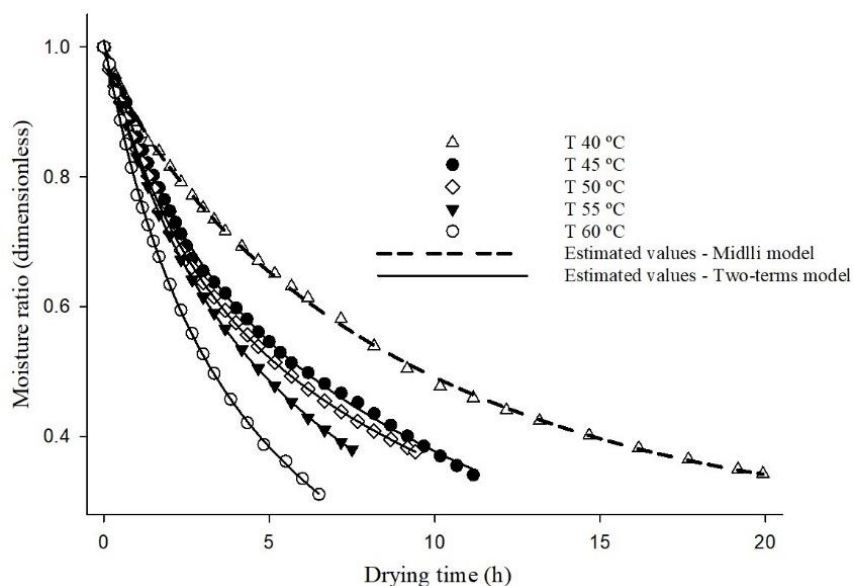
of 40°C. Those of Midilli (04), Logarithmic (09), Two-terms (12), and Diffusion approximation (13) for a temperature of 45°C, Two-terms (12) and Valcam (14) for a temperature of 50°C. Two terms (12) and Diffusion approximation (13) for a temperature of 55°C and a temperature of 60°C, the Two terms (12) models, Approximation of the diffusion (13) and Valcam (14) presented a better adjustment to the data observed according to the Gauss-Newton criterion, as they presented lower SE values.

The AIC and the BIC have been used as complementary in selecting models with a better fit, allowing reinforcing or dissipating eventual inaccuracies generated by the Gauss-Newton criterion. The AIC and BIC criteria were used in several works on drying kinetics of agricultural products favorably for grains of *Fagopyrum esculentum* Moench (Siqueira et al., 2020), leaves of *Piper aduncum* L. (Quequeto et al., 2019), and leaves of *Cecropia pachystachya* (Bastos et al., 2019). The values of the AIC and BIC of the mathematical models pre-selected by the Gauss-Newton method are shown in Table 2B. The lower the AIC and BIC values, the better the fit of the mathematical model (Wolfinger, 1993). The Midilli model (04) showed better adjustment at the temperature of 40°C and the Two-term model at the other temperatures (45, 50, 55, and 60°C). In Figure 2 are shown the mathematical modeling curves for drying cowpea seeds in a thin layer,

represented by the Midilli (04) models for a temperature of 40°C and the Two-term model (12) for the temperatures of 45, 50, 55, and 60°C.

The selected models show a good fit to describe the drying process of cowpea seeds due to the proximity of the observed and estimated values. The Midilli model has been recommended to describe the drying of several agricultural products, such as *V. angularis* (Resende et al., 2010), *Phaseolus vulgaris* L. (Melo et al., 2015), and *Sorghum bicolor* L. Moench (Ullmann et al., 2015). Other researchers have also recommended the Two-term model for products such as *Arachis hypogea* L. (Araujo et al., 2017), *Tamarindus indica* L. (Ferreira Júnior et al., 2021), *Citrus raticulada* Blanco (De Sousa et al., 2021) and *Morinda citrifolia* L. (Quequeto et al., 2019). Table 3 shows the Midilli models' parameters (04) for a temperature of 40°C and Two terms (12) for 45, 50, 55, and 60°C, adjusted for drying of the cowpea seeds.

For the Two-term model, it can be observed that the coefficients “a”, “b” and “g” did not present a clear trend as the temperature of the drying air increased. Although the parameter “k” represents the effective diffusivity of drying in the decreasing period and can be used in an approximate way to explain the behavior of the drying air temperature (Babalís and Belessiotis, 2004), it also did not present a defined behavior. Figure 3A-B shows the values



**Figure 2.** Midilli and Two-term models estimate moisture ratio values for drying cowpea (*V. unguiculata* L. Walp) seeds at different temperatures.

**Table 3.** Coefficients and parameters of Midilli and Two terms models obtained for cowpea seed (*V. unguiculata* L. Walp) at different drying air temperatures.

| Temperature (°C) | Mathematical models |         |         |         |                      |         |         |         |
|------------------|---------------------|---------|---------|---------|----------------------|---------|---------|---------|
|                  | Midilli             |         |         |         | Two-terms            |         |         |         |
|                  | k                   | n       | A       | B       | k                    | A       | b       | g       |
| 40               | 0.1233*             | 0.8297* | 0.9990* | 0.0057* | -                    | -       | -       | -       |
| 45               | -                   | -       | -       | -       | 0.4341*              | 0.3104* | 0.6990* | 0.0627* |
| 50               | -                   | -       | -       | -       | 0.4341*              | 0.3545* | 0.6462* | 0.0589* |
| 55               | -                   | -       | -       | -       | 0.1414 <sup>ns</sup> | 0.4792* | 0.4838* | 0.1326* |
| 60               | -                   | -       | -       | -       | 0.5789*              | 0.3397* | 0.6698* | 0.1213* |

\*Significant effect at 5% ( $p < 0.05$ ) level and ns non-significant effect by t-student test.

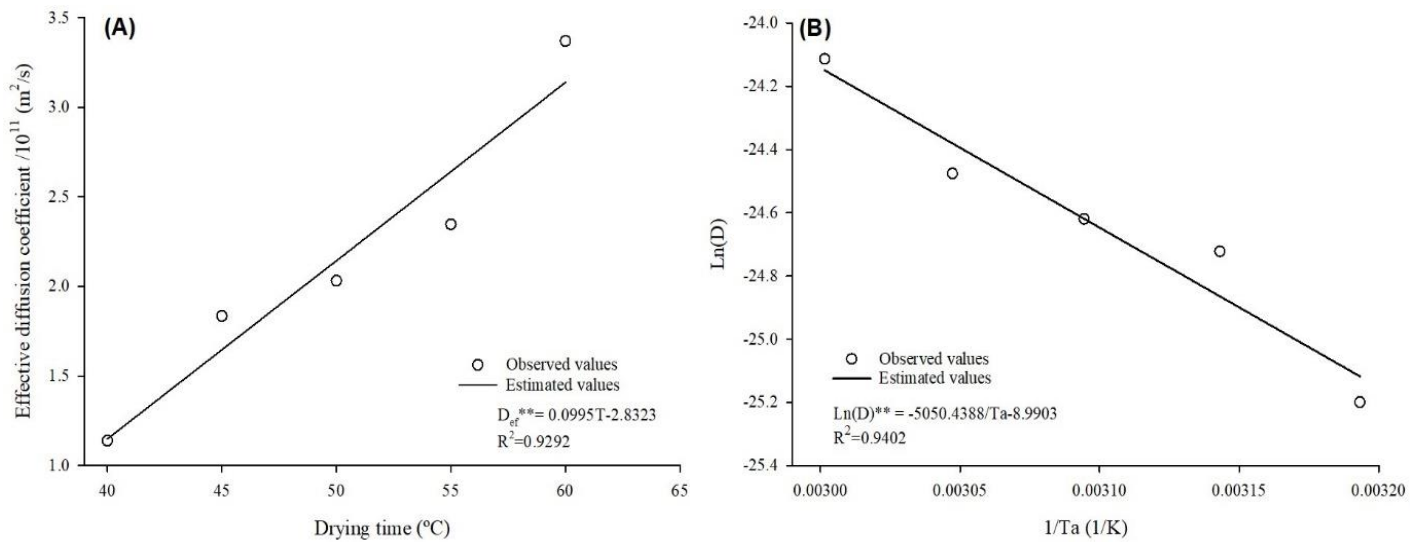
of the effective diffusion coefficients and the Arrhenius representation of the cowpea seeds for the different drying conditions. The experimental drying data were fitted to the equation based on Fick's second law, considering the spheroid geometric shape, with an equivalent radius of 3.83 mm.

The effective diffusion coefficient linearly increased with increasing drying air temperature, having varied from  $1.1378 \times 10^{-11}$  to  $3.3698 \times 10^{-11}$  m<sup>2</sup>/s for 40 and 60°C, respectively (Figure 3A). As the drying air temperature decreases, the greater is the internal resistance of water diffusion during drying; therefore, the lower the values for the effective diffusion coefficient. For higher temperatures, where the diffusion of water from the center to the periphery is greater, the effective diffusion coefficient has higher values (Silva et al., 2017). This behavior is in agreement with several studies on the drying kinetics of

various agricultural products, such as seeds of *V. unguiculata* L. Walp (Camicia et al., 2015), grains of *V. angularis* (Resende et al., 2010), and grains of *F. esculentum* Moench (Siqueira et al., 2020).

The activation energy for the drying process of cowpea seeds in a thin layer was 41.9894 kJ/mol for the temperature range of 40 to 60°C. The activation energy obtained is within the range for biological products that varies between 12.7 and 110 kJ/mol (Zogzas et al., 1996). The effective diffusion coefficient is inversely proportional to the activation energy; the smaller the activation energy, the greater the effective diffusion coefficient. Activation energy represents the minimum energy required to allow the migration movement of water molecules during the drying process (Sousa et al., 2011; Siqueira et al., 2012; Silva et al., 2017).

The activation energy of cowpea seeds obtained under



**Figure 3.** Mean values of the effective diffusion coefficient (A) e; the Arrhenius representation for the effective diffusion coefficient (B) obtained for drying cowpea (*V. unguiculata* L. Walp) seeds at temperatures of 40, 45, 50, 55, and 60°C. \*\* Significant effect at 1% ( $p < 0.01$ ) level by t-student test.

the test conditions shows certain ease in the diffusivity of water about the drying kinetics of two varieties of *V. unguiculata* L. Walp (Camicia et al., 2015), whose value was 35.04 kJ/mol in the range of 30 to 50°C, 38.94 kJ/mol and 31.16 kJ/mol for *V. angularis* in the range of 30 to 60°C (Resende et al., 2010; Almeida et al., 2013). The activation energy values in different biological materials vary, as they depend on the structure, chemical composition of the product, and how the water is bound (Zogzas et al., 1996).

The values of germination, germination speed index, emergence, and emergence speed index decreased with increasing drying air temperature (Figure 4A-D). Almeida et al. (2013) and Quequeto et al. (2020) also observed a decrease in germination with increasing drying air temperature in pigeon pea (*Cajanus cajan* L.) and niger (*Guizotia abyssinica* Cass) seeds at temperatures from 35 to 75°C and 40 to 70°C, respectively. According to Lima et al. (2016), the use of high temperatures can cause physical damage such as cracks, due to the tension generated inside the product, especially in the final step of the drying process, which can negatively affect seed germination.

Although there was a reduction in germination with increasing drying air temperature, it did not negatively influence seed quality right after drying, considering the quality standards of certified seed. It is verified that the seeds submitted to lower temperatures presented higher values of the germination and emergence speed index; that is, the seeds took less time to induce the process.

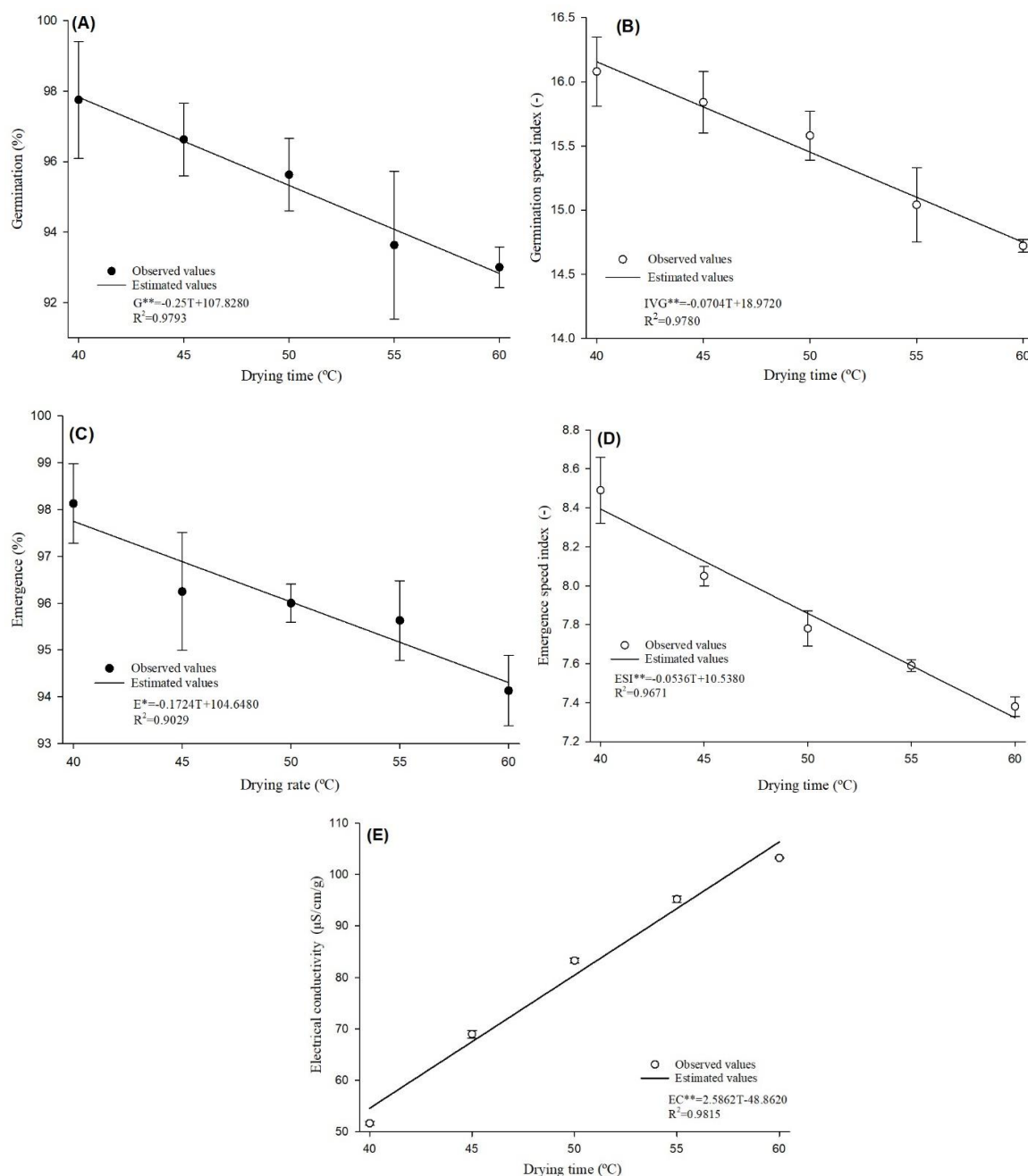
As drying at high temperatures generates a higher drying rate in the seeds, which culminates faster, the physiological potential can be compromised.

Nevertheless, the emergence speed index and emergence in the study reveal that seed vigor follows a decreasing rate as the drying air temperature is high. Junqueira et al. (2018), evaluating the performance of BRS style bean seed seedlings at temperatures of 40, 50, 60 and 70°C, found a decrease in vigor due to the increase in drying air temperature. Almeida et al. (2013) also observed a reduction in the emergence and emergence speed index due to the increase in seed drying temperature.

The electrical conductivity values increased as the drying air temperature increased (Figure 4E). This test assesses the integrity of cell membranes; the higher the value, the greater the level of damage and disorganization of the membranes responsible for the maintenance of integrity of reserves (Ullmann et al., 2015).

According to Marcos-Filho (2015), less vigorous seeds release a greater quantity of solutes when soaked because the speed of restoration of the integrity of their cell membranes during this period is reduced. Higher EC values show a greater quantity of leachates in the soaking solution, which are associated with the disruption of cell membranes resulting from the abrupt removal of water from the product during the drying process at higher temperatures, associated with a high drying rate verified at higher temperatures. The results are consistent with those obtained by Ullmann et al. (2015), who observed a direct proportionality between EC and drying air temperature of jatropha. Higher drying air temperatures cause a sharp moisture gradient between the periphery and the center of the seeds, thus causing both the disruption of cell membranes and the loss of cellular compartmentalization of the seeds, consequent reduction in vigor, or even total





**Figure 4.** Mean values of germination percentage (A); germination speed index (B); percentage of emergence (C); emergence speed index (D), and; electrical conductivity (E) of cowpea (*V. unguiculata* L. Walp) seeds as a function of drying air temperature. \*\* Significant effect at 1% ( $p < 0.01$ ) level and \* Significant effect at 5% ( $p < 0.05$ ) probability level by F test.

loss of seed viability.

### Conclusion

The drying rate was higher for higher drying air

temperatures. The Midilli model presented the best fit to represent the drying kinetics of cowpea seeds at a temperature of 40°C. At air drying temperatures of 45, 50, 55, and 60°C, the Two-term model was more suitable. The effective diffusion coefficient linearly increased with increasing drying air temperature, in the magnitude of

$1.1378 \times 10^{-11}$  to  $3.3698 \times 10^{-11}$  m<sup>2</sup>/s for temperatures from 40 to 60°C, respectively. The activation energy needed to trigger the drying process of cowpea seeds was 41.9894 kJ/mol. Germination, emergence, germination speed index, and emergence speed index showed a decreasing trend with increasing drying air temperature. The electrical conductivity increased as the drying air temperature increased.

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