


Drying kinetics and thermodynamic properties of cassava (*Manihot esculenta* Crantz) peel as a sustainable agro-industrial by-product

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Highlights

- Cassava peel is a sustainable by-product with nutritional and functional potential for the food industry.
- Cassava peel showed relevant levels of phenolic compounds and antioxidant activity.
- The logarithmic model best described the drying kinetics with high accuracy ($R^2 > 0.99$).
- Drying at 50 °C preserved bioactive compounds, while higher temperatures maintained starch.
- Thermodynamic parameters indicated drying as a non-spontaneous and energy-dependent process.

Abstract

Cassava (*Manihot esculenta* Crantz), a significant crop in the North and Northeast of Brazil, is primarily used for flour and starch production, with large quantities of peel generated as waste, and it is a valuable by-product in the food industry. This study investigated the potential of cassava peel as a sustainable by-product for the food industry, focusing on the mathematical modeling of drying kinetics and thermodynamic properties. Cassava peel has a high moisture content, which limits its conservation and favors microbial growth. Cassava peels were collected, analyzed, and processed. Physicochemical analyses were performed, including moisture (71.00%), ash (8.15%), lipids (0.29%), proteins (4.70%), and starch (42.12%). In addition, the bioactive compounds were evaluated through Total Phenolic Compounds (TPC) (12.50 mg GAE/g) and antioxidant activity (AA) by the ABTS method (150.00 $\mu\text{mol TE/g}$). Drying was conducted at temperatures of 50°C, 60°C, 70°C and 80°C, and the data were fitted to five mathematical models. The logarithmic model presented the best fit, with coefficients of determination (R^2) above 0.99 and the lowest standard error (SE) and chi-square (χ^2). Drying at 50°C better preserved total TPC (9.10 mg GAE/g) and AA (80.00 $\mu\text{mol TE/g}$), while higher temperatures reduced these compounds but maintained starch content (39.12-42.2 g/100g). Thermodynamic parameters ΔH , ΔS , and ΔG indicated that drying is a non-spontaneous process requiring external energy. This work highlights the viability of using cassava peel as a sustainable resource, contributing to reducing agro-industrial waste.

Keywords

Agrifood residues; *Manihot esculenta* Crantz; mathematical modeling; drying kinetics; waste utilization; bioactive compounds.

Introduction

The cassava crop, *Manihot esculenta* Crantz, is of great socioeconomic importance worldwide, as it is the main source of carbohydrates for millions of people, especially in developing countries. This crop plays a significant role in generating employment and income, especially for family farmers in the North and Northeast regions of Brazil.¹ The two main products of cassava are flour and starch (starch, sweet cassava starch, or gum). In the industrial processing of cassava in Brazil, it is estimated that 80% of the national production of roots is destined for the manufacture of flour, 3% for the extraction of starch, and the remainder is used to feed domestic animals.

In the processing of cassava, the peel is one of the most generated residues during the manufacture of flour or starch, consisting, in addition to the peels themselves (brown film), of inter-peel, debris from the cortex and root tips, and high moisture content.³

The disposal of urban solid waste does not always occur due to a lack of waste management but rather due to automatic behavior and a lack of responsibility linked to the desire to discard the material.⁴ The global trend to reduce industrial waste is growing, and more solutions for proper and profitable disposal are being sought.

Cassava peel is a promising residue that has great chemical and biotechnological potential and can be used in the production of bioinputs such as biochar production⁵, bioethanol production, as well as silage for animal feed.⁷ The peels have a high moisture content, and it is necessary to reduce this content to reduce biological and biochemical activities, thus increasing the shelf life and stability of possible products during storage. The drying process reduces the water content to safe levels for storage, as it involves heat and mass transfers. Depending on the drying conditions and methods adopted, this process influences the biological activities and the chemical and physical structure of the seeds⁸.

Drying is a conservation method, a very old unitary operation, and has been used to preserve perishable products. It allows reducing the water content and increasing the storage period of the product, preventing the growth of microorganisms and insects, and reducing the mass and volume to be transported³.

Kinetics and mathematical modeling are important and widely used tools in optimizing several drying processes for food products. The first is a subject commonly covered in literature for different products. The temperature and the flow and/or speed of the air used³ are among the most important variables.

According to Lopes de Menezes et al.,⁹ through drying, it is possible to analyze the behavior of solid material through curves that relate to the moisture ratio versus time and drying rate. These curves contain essential information for developing the process and for better dimensioning of the equipment, making it possible to evaluate the time required to dry a certain quantity of product.

This work aimed to study the mathematical modeling of cassava peel drying kinetics, evaluating four different temperatures to optimize the processing time and preserve the quality of phenolic compounds, antioxidant activity, and starch content. The focus was on using cassava peels from industrial waste for biotechnological applications. In addition, essential thermodynamic parameters, which are fundamental for the design of drying equipment and calculation of the necessary energy, were analyzed, contributing to a deeper understanding of the physical phenomena that occur in the process⁸.

Materials and methods

Sample Collecting

The cassava was collected in the municipality of Parauapebas-PA, located at the geodetic coordinates 49°51'19" W latitude, 06°12'58" S longitude, with an altitude of 197 m. The samples were transported to the city of Belém-PA and taken to the food laboratory of the Federal Rural University of the Amazon for sanitization (100 mg/L) for 15 min, followed by washing with chlorinated water at 10 mg/L to remove excess chlorine. The cassava was cut, the peels separated from the pulp, and vacuum-packed in polyethylene bags under freezing at -18°C until the time of analysis. This sample was coded as cassava peels or RCP. The dried cassava peels were designed as DCP.

Physicochemical Characterization

The physicochemical analyses followed, for the most part, the methods of Adolf Lutz¹⁰ for the raw residue. The samples were analyzed in triplicate, and the determinations performed were for water activity, total soluble solids (TSS°Brix), pH, total titratable acidity (TTA), moisture, ash, lipids, and proteins. According to Azzini et al.¹¹, starch was carried out. It was analyzed for the RPC and, after drying at three temperatures, to evaluate the effect of temperature on starch extraction.

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Analysis of Total Phenolic Compounds (TPC)

The hydroalcoholic extract for this analysis was carried out according to the methodology of Guindani et al.¹². This analysis was carried out for the RCP and for the DCP in all studied temperatures. TPC determination was performed according to the methodology proposed by Singleton and Rossi¹³, modified for microplates, in a spectrophotometer (Thermo Fisher Scientific Oy, Multiskan Go-SN-1530-8001397, Finland). The absorbance reading was performed at a wavelength of 765 nm. The concentration of TPC in the extracts was determined from the equation of the straight line obtained in the standard curve of gallic acid (Sigma, 99% purity) ($y=0.0059x+0.0929$, $R^2 = 0.9996$) and expressed in mg GAE/g of the sample.

Antioxidant Activity by the ABTS Method

The antioxidant capacity of the RCP hydroalcoholic extracts against the free radical ABTS^{•+} (2,2-azino-bis (3-ethylbenzothiazoline-6-sulfonic acid)) was evaluated according to the methodology proposed by Rufino et al.¹⁴ with modification. Quantification was performed using Trolox ((±)-6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid, 97%, Sigma, Brazil) to construct the analytical curve ($y = -0.0005x+0.6844$, $R^2 = 0.9911$). From the straightline equation, the calculation was performed and expressed in μM Trolox equivalent/g of sample. This analysis was performed for both RCP and DCP.

Drying Kinetics

The drying kinetics of cassava residues occurred by convection, with an average of 25.00 g of peels weighed on stainless steel trays (3 mm) with an area of 204 cm² and a height of 1 cm. The process took place in an oven with forced air circulation (Model EL 1.3 Odontobrás) at temperatures of 50 °C, 60 °C, 70 °C, and 80 °C until reaching constant mass.¹⁵ The process was carried out with an air speed of 1.4 m/s on the digital anemometer (Model AD-250 Instrutherm). These conditions were based first on preliminary tests and also on the following literature of Vilhalva et al.³ and Kosasih et al.¹⁶ As well as the choice of mathematical models used in this study. After this stage, the resulting samples were ground in a processor (W, R17625), packaged, and stored in a hermetically sealed polyethylene bag under a vacuum for future analysis.

With the results obtained, curves that relate mois-

ture (Y) and process time were constructed according to Equation 1.

$$Y = \frac{m - m_e}{m_i - m_e} \quad \text{Eq. 1}$$

Where: Y = moisture ratio (dimensionless); m, m_i , and m_e are the moisture at time t, initial, and equilibrium (g/100 g d.b.), respectively.

The thickness of the cut cassava peels was calculated using a digital caliper with a resolution of 0.01 mm¹⁷. To ensure greater representativeness, 100 repetitions of the material were performed in different parts of the waste. An arithmetic mean was calculated for these 100 measured parts.

To calculate the effective diffusion coefficient, we used the theory of water migration by diffusion as a basis, based on Fick's second law, which was considered in the study of drying kinetics. Considering that a flat plate can represent the mass of cassava peel residues, equation 1 was used, and Crank¹⁴ proposed¹⁸ it:

$$k = \frac{D_{\text{eff}} \cdot \pi^2}{L^2} \quad \text{Eq. 2}$$

Where k = drying constant, D_{eff} = effective diffusivity, and L = characteristic dimension to model the drying kinetics.

The Arrhenius equation, described in Equation 3, was used to evaluate the influence of temperature on the effective diffusion coefficient.

$$D_{\text{eff}} = D_0 \cdot \exp\left(\frac{E_a}{R \cdot T_a}\right) \quad \text{Eq. 3}$$

Where: D_{eff} = Effective diffusion coefficient; D_0 = pre-exponential factor; E_a = energy activation (kJ/mol); R = universal gas constant (8.314 kJ/mol.K); T_a = absolute temperature (K).

Equation 3 can be linearized to determine the drying process's energy activation (E_a) according to Equation 4.

$$\ln(D_{\text{eff}}) = \ln(D_0) - \frac{E_a}{R \cdot T_a} \quad \text{Eq. 4}$$

Adjustments to Mathematical Models

In predicting drying curves, mathematical adjustments of classical models that describe the kinetics of drying processes in foods were evaluated (Table I). These models describe the kinetics of the drying processes applied in the present work. The models

were adjusted by nonlinear regression to the results obtained in the drying experiments using the Statistica software (version 7.1, StatSoft Inc., USA). The Levenberg-Marquardt algorithm was used as a 10-6 12 convergence criterion¹⁵.

Table 1: Models used to describe the drying curves of different food matrices.

Model	Equation	Reference
Logarithmic	$Y = a \cdot \exp(k \cdot t^n) + c$	Togrul; Pehlivan ¹⁹
Diffusion Approximation	$Y = a \cdot e^{-k \cdot t} + (1a) \cdot e^{-k \cdot b \cdot t}$	Corrêa et al. ²⁰
Newton	$Y = e^{-k \cdot t}$	Faria et al. ²¹
Henderson & Pabis	$Y = a \cdot \exp(-k \cdot t)$	Henderson & Pabis (1974) ²²
Wang & Singh	$Y = 1 + a \cdot t + b \cdot t^2$	Wang; Singh (1978) ²³

Y = moisture rate (dimensionless), t = residence time (s), and a, b, c, and k are model constants.

The models were selected considering the magnitude of the estimate's standard deviation (SE). The values of the coefficient of determination (R^2) and chi-square (χ^2) were used to determine the model that best describes the drying curves according to Martins and Pena¹⁵. The SE and χ^2 values for each model were estimated by Equations 5 and 6, respectively.

$$SE = \sqrt{\frac{\sum(Y - \hat{Y})^2}{DF}} \quad \text{Eq. 5}$$

$$\chi^2 = \frac{\sum_{i=1}^n (Y - \hat{Y})^2}{DF} \quad \text{Eq. 6}$$

Where: Y = experimentally observed value; \hat{Y} = value estimated by the model; n = number of observed data; DF: degrees of freedom of the model.

For a model to have a good fit, it needs to obey the following metrics which are R^2 close to 1 and SE and χ^2 close to zero.

Calculation of thermodynamic parameters

The thermodynamic properties of enthalpy (Equation 7), entropy (Equation 8), and Gibbs free energy (Equation 9) in the drying process of cassava peels at different temperatures (50, 60, 70, and 80 °C) were determined using the method presented by Silva et al.²⁴

$$\Delta H = E_a - R(T + 273.15) \quad \text{Eq. 7}$$

$$\Delta S = R \left[\ln(D_0) - \ln\left(\frac{K_B}{h_p}\right) - \ln(T + 273.15) \right] \quad \text{Eq. 8}$$

$$\Delta G = \Delta H - (T + 273.15) \cdot \Delta S \quad \text{Eq. 9}$$

where: ΔH = specific enthalpy, J mol⁻¹; ΔS = specific entropy, J mol⁻¹ K⁻¹; ΔG = Gibbs free energy, J mol⁻¹; K_B = Boltzmann constant, 1.38×10^{-23} J K⁻¹; h_p = Planck constant, 6.626×10^{-34} J/s; T = temperature, °C.

Statistical analysis

For the physical-chemical, TPC, and ABTS determinations, averages, standard deviations, and the coefficient of variation were calculated (considering up to 10% for physical-chemical analyses and up to 15% for TPC and ABTS analyses).

ANOVA and Tukey analysis (after the data were analyzed by Shapiro-Wilk and presented as a normal distribution) were performed to compare the means of the TPC, AA, and starch analyses after drying the material at temperatures of 50, 60, 70, and 80°C and assess whether there was a significant difference between the treatments.

Results and discussion

Physicochemical characterization of the residue

Table 2 presents data on the centesimal and chemical composition (on a dry basis) of raw cassava peels (RCP).

Table 2: Centesimal and chemical composition of RCP.

Determination	RCP	Variation coefficient (%)
Moisture (g/ 100 g)	71.00±0.32	1.04
Ash (g/ 100 g)	8.15±0.41	4.58
Lipids (g/ 100 g)	0.29±0.01	3.45
Proteins (g/ 100 g)	4.70±0.05	1.22
Starch (g/ 100 g)	42.12±0.40	0.95
a_w	0.981±0.01	1.01
TSS (°Brix)	3.0±0.01	0.33
TTA (NaOH 1M/100 g)	4.13±0.24	5.81
pH	5.06±0.14	2.78
TPC (mg GAE/g)	12.50±1.80	14.4
ABTS (μmol TE/g)	150.00±18.33	12.22

According to Tapia et al.²⁵, a_w analysis is a determining factor in foods' microbiological stability and enzymatic activity. Therefore, controlling water activity and humidity are fundamental factors in preserving the quality of the product. The peels obtained a_w values from 0.981 to 0.9956, with an average of 0.996. These results demonstrate that the sample is perishable and that the probability of it undergoing chemical, physical, microbiological, or enzymatic reactions is much higher.

Souto²⁶ found the following compositions for cassava peel: 72.53 g/100 g of moisture, 1.63 ± 0.04 g/100 g of ash, 0.86 g/100 g of lipids, and 3.97 g/100 g of protein. Regarding pH, the author obtained a value of 4.85, while for Total Acid Titration (TTA), the value found was 5.18 mL of 1 M NaOH per 100 g. The starch content was 60.68 g/100 g. In the present research, the results obtained were close to those reported by Souta²⁶, although a considerably lower starch value was observed, as well as lipids. On the other hand, the protein content was slightly higher, while the moisture and ash values presented results close to those found by this author.

The values of the present research were also compared with those found by Batista et al.²⁷ for cassava peel, which were as follows: pH of 5.64, TTA of 4.13 mL of 1M NaOH (100 g), water activity of 0.996, moisture of 70.96 (g/100 g), ash of 8.95 (g/100 g), lipids of 0.26 (g/100 g), and protein of 4.08 (g/100 g).

The sample's total soluble solids (TSS) content shows

that cassava peel retains a low °Brix value. Pinto et al.²⁸ found a °Brix value varying from 2 to 3.9 for cassava flour.

The ash percentage of the sample had an average value of 8.15 g/ 100 g. This high ash value may indicate the presence of minerals in the roots, which is understandable, since this is in direct contact with the soil during its collection.

Regarding the TPC and AA by ABTS, it is important to highlight that these variations are common among vegetables and can be influenced by several factors, such as plant variety, soil type, climate, and growing conditions²⁹. Batista et al.²⁷ also measured TPC in cassava peel extracts (hot water extraction) and found values ranging from 10 to 15 mg GAE/g. These results are similar to those found in this work (12.50 ± 1.80).

Santos et al.³⁰ studied the extraction of phenolic compounds from cassava leaves in different extracting solutions (1: Methanol/water 50:50, (v/v); 2: Ethanol/water 50:50, (v/v); 3: Acetone/water 70:30, (v/v)). These authors performed chromatographic identification by HPLC, obtaining catechin, gallic acid, epigallocatechin, chlorogenic acid, and gallic acid as the major compounds. The authors also found 233.17 to 383.33 μmol trolox/g for AA by ABTS.

Mathematical modeling

The cassava peel was dried at four different temperatures, 50, 60, 70, and 80°C, until the final water contents in ds (dry basis) were 1.35, 1.23, 1.28, and 1.19, respectively. All four final water contents were obtained in an average of approximately 7 hours.

Figure 1 shows the profile of the drying kinetics curves at different temperatures (50, 60, 70, and 80°C). The results obtained in this analysis will be adjusted in mathematical models to verify which model best fits the drying conditions studied in this work.

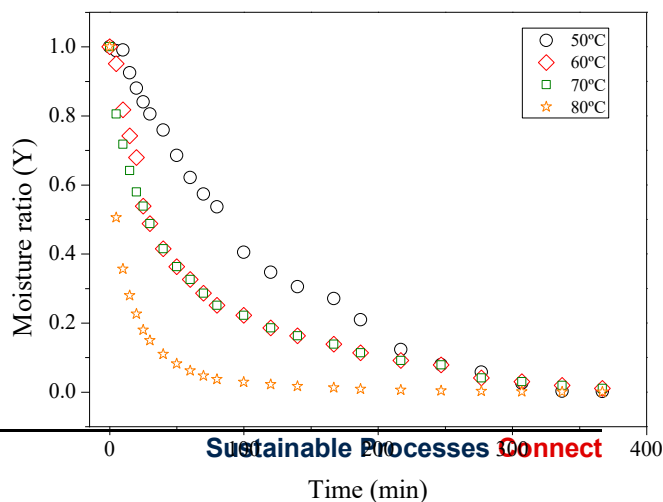


Figure 1: Drying kinetics curves at different temperatures.

Table 3 presents the values of the statistical parameters SE, R^2 , and the chi-square test (χ^2), which were used to compare the 5 mathematical models analyzed through nonlinear regression to describe the drying behavior of cassava peel at different temperatures.

Table 3: Values of the parameters of the adjustments of the mathematical models to the drying kinetics data of DCP.

Model	T (°C)	R^2	SE	χ^2
Logarithmic	50	0.99722	0.0189	$3.5738 \cdot 10^{-4}$
	60	0.98261	0.4005	0.0016
	70	0.97742	0.0418	0.0018
	80	0.96563	0.0427	0.0018
Diffusion Approximation	50	0.9958	0.0232	5.40×10^{-4}
	60	0.9679	0.0550	0.0030
	70	0.9824	0.0369	0.0013
	80	0.9947	0.0612	2.8×10^{-4}
Newton	50	0.9896	0.0364	0.0013
	60	0.9667	0.0561	0.0031
	70	0.9342	0.0713	0.0050
	80	0.9518	0.0505	0.0025
Henderson & Pabis	50	0.9941	0.0274	0.0157
	60	0.9676	0.0552	0.0641
	70	0.9631	0.0534	0.0599
	80	0.9567	0.0479	0.0482
Wang & Singh	50	0.9924	0.0312	9.7×10^{-4}
	60	0.7275	0.1604	0.0257
	70	0.5911	0.1780	0.0316
	80	-	-	-

Table 3 shows that the coefficient of determination (R^2) values were greater than 0.95 until the Henderson and Pabis model, evidencing a satisfactory representation of the drying process. But when we observe the Wang and Singh model, we can see that there was not a good fit for this experimental data at the temperatures of 60 and 70°C, and it did not fit at the temperature of 80°C, which is considered not an appropriate model for these data. According to Lopes de Menezes,⁹ the closer R^2 is to value 1, the better the model representation. However, when analyzed in isolation, the coefficient of determination (R^2) does not constitute a good selection criterion when dealing with nonlinear models.³¹ Analyzing the results, the estimated mean error (SE) values for all models at different temperatures were very low, with a maximum value of 0.0641 for the temperature of 60°C in the Henderson and Pabis models. For Draper and Smith,³² the lower the SE value, the better the fit of the model

and the better its ability to describe the dynamics of the drying process. In the chi-square test (χ^2), the values recorded for the different adjusted models presented very low results. Lima et al.³³ reported that the efficiency of a mathematical model for the drying process is related to the lowest chi-square value.

In the work of Modesto Junior et al.³⁴ for the mathematical modeling of the drying kinetics for cassava leaves, R^2 values were above 0.95 for the adjustments of all models to the experimental data, indicating that the mathematical models used by these authors described the drying processes studied by them well. Also, in this study, the authors reported χ^2 values lower than 0.005 and SE lower than 0.07, confirming that all models accurately described the drying kinetics in the experimental domain. The Logarithmic model (Figure 2 a) was chosen to calculate the value of the drying constant k (because this model had the best metric fit for all temperatures when compared to the other models tested), which was used to calculate D_{eff} to continue with the calculations of the thermodynamic parameters (Table 4).

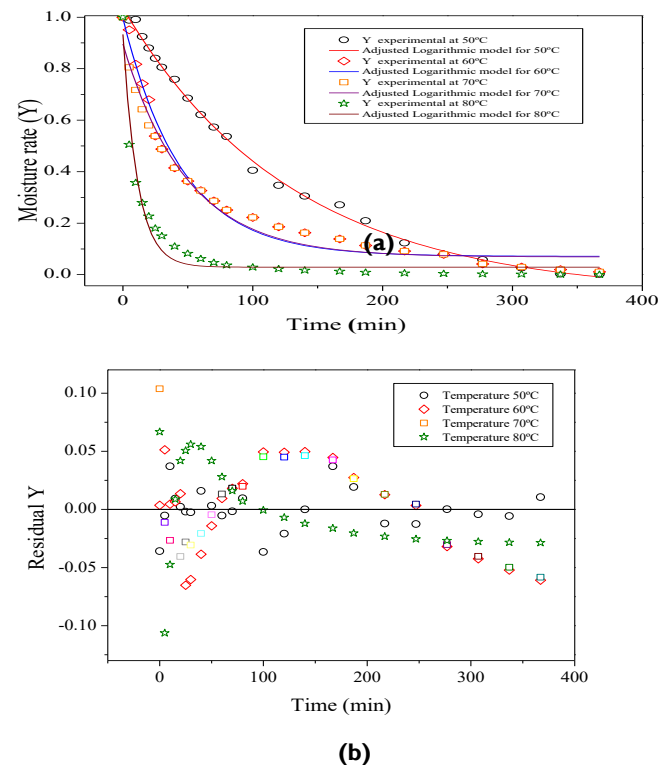


Figure 2: (a) Logarithmic model fit applied for all temperatures; (b) Graphical residual plot for the Logarithmic model fit.

The residual plot (Figure 2, b) in drying kinetics shows points were randomly distributed around zero, with no evident systematic trends, indicating that the logarithmic model adequately captured the drying kinetics. The residuals also showed approximate homoscedasticity, without strong signs of increasing or decreasing variance over time. In this analysis, there was no evidence of clustering or systematic deviations; the analysis of these residuals allows us to verify the adequacy of the model to describe the process, which is important in choosing the most appropriate model.

The logarithmic model was selected not only because it presented a better statistical fit but also because it reflects the expected behavior of the studied process. Furthermore, interpretation in terms of relative variations facilitates the practical application of the results and the definition of optimal conditions in the industrial context. Oliveira et al. (2015), in their study of strawberry drying using a forced air circulation oven, also found a better fit of their data with the logarithmic model. This type of model describes situations in which there are rapid initial gains, followed by stabilization, which is consistent with the dynamics of food systems.

Table 4: Thermodynamic properties for DCP at different temperatures with the Logarithmic model.

Thermodynamic properties	Temperature °C			
	50	60	70	80
K parameter	0.077	0.020	0.022	0.088
$D_{\text{eff}} \times 10^{-10} \text{ (m}^2/\text{s)}$	0.649	1.435	1.320	5.842
$\Delta H \text{ (kJ/mol)}$	66.64	66.55	66.47	66.39
$\Delta S \text{ (J/mol.K)}$	-276.01	-269.42	-270.12	-257.76
$\Delta G \text{ (kJ/mol)}$	137.82	137.74	134.25	137.72

Vilhava et al.³ found D_{eff} values ranged from 1.87 to $3.57 \times 10^{-9} \text{ m}^2/\text{s}$ for cassava peels at different conditions. According to Cuevas et al.³⁵, D_{eff} is an important parameter in the food drying process, as it helps in planning and modeling mass transfer. This value can vary depending on the thickness of the material and the external drying conditions. Santos et al.,³⁶ D_{eff} values ranged between 0.5666 and $1.4245 \times 10^{-10} \text{ m}^2/\text{s}$ for patuá (*Oenocarpus bataua*) pulp fruit.

As stated by Goneli et al.¹⁷ when the drying temperature is increased, it results in a decrease in water viscosity, a parameter used to measure fluid resistance. The reduction in viscosity facilitates the diffusion of water present in the leaf capillaries. The increase in D_{eff} with increasing temperature can be explained by the rise in vibrations of water molecules, which intensifies the diffusion of this water.

With the increase of temperature from 50 to 80

°C, the enthalpy decreased from 66.64 to 66.39 kJ/mol, indicating that less energy is required for drying at higher temperatures, a result like that found by Corrêa et al.²⁰ and by Silva et al.²⁴ for coffee drying. The entropy ranged from -276.01 to -257.76 J/mol.K, with lower values at higher temperatures, suggesting greater order in the arrangement of water molecules, which may be related to structural modifications in the product. The Gibbs free energy increased from 134.25 to 137.82 x kJ/mol, indicating that drying is a non-spontaneous process, requiring additional energy from the environment to occur, as also observed by Corrêa et al.²⁰ and Silva et al.²⁴

Silva et al.²⁴ found values of ΔH ranged from 33,323 to 32,991 kJ/mol, ΔS -295.7 to -296.7 Jmol/K, and ΔG of 131.85 to 143.70 kJ/mol for pepper species *Capsicum chinense* L.

Lower ΔS values at higher temperatures indicate greater order in the interaction between water molecules and the vegetable, suggesting less excitation of the molecules.³⁷ Furthermore, negative entropy values may reflect chemical or structural changes in the product during drying.

When the ΔG presents positive values, this indicates that drying is a non-spontaneous process; that is, it requires the supply of external energy from the environment for the reaction to occur.²⁰

Energy activation (E_a) represents the difficulty water molecules must overcome to overcome the energy barrier during their movement within the product. According to Kayacier and Singh,³⁸ this energy tends to decrease as the water content of the product increases. In drying processes, lower energy activation values are associated with greater water diffusivity within the material.³⁹ The energy activation (E_a) for the net diffusion of DCP, calculated as the slope of the line obtained from $\ln(D_{\text{eff}})$, was 69.32 kJ/K.mol; this result was considerably higher than the values reported by Kosasih et al.,¹⁶ who studied the drying of elephant cassava slices using natural convection in a moisture analyzer and forced convection at temperatures of 60°C, 80°C, 100°C the E_a found for them varied between 22.915 kJ/mol and 27.17 kJ/mol.

This discrepancy could be caused by experimental variables such measurement errors in moisture, increased internal barrier to water migration because cassava peel is fibrous, and potential physicochemical matrix transitions that prevent diffusion. Another factor that can be responsible for the higher energy need is the existence of competing reactions during drying. By reevaluating E_a at various temperature intervals and excluding locations outside of the linear Arrhenius regime, a sensitivity analysis was carried out (results not shown). However, even with these adjustments, it was not possible to obtain lower values than those originally estimated, which reinforces the robustness of the result.

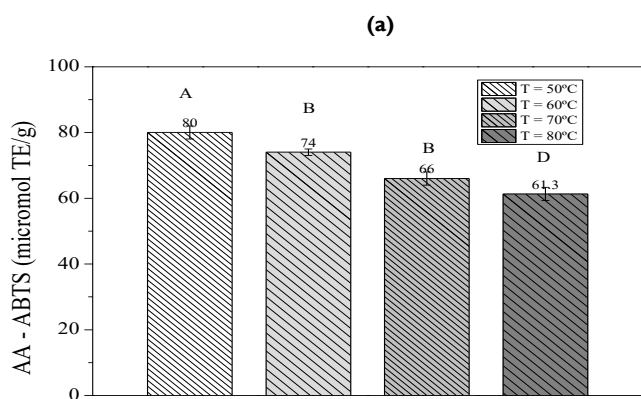
Further studies comparing different drying conditions and plant matrices are recommended to clarify these deviations.

These thermodynamic properties, primarily ΔH (kJ/mol), ΔS (J/mol.K), and ΔG (kJ/mol), have direct implications for scalability. The energy fluctuation that takes place during sorption processes when water molecules interact with product constituents is measured by enthalpy changes (ΔH). Entropy (ΔG) is related to the spatial arrangement of the water-product and can be linked to the binding or repulsion of water molecules from food components in the system.

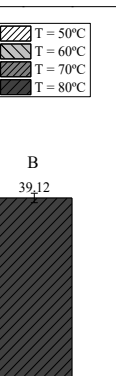
The degree of order or disorder in the water-product system is defined or characterized by entropy (ΔG). Conversely, Gibbs free energy serves as a criterion for assessing water desorption and is a measure of the product's attraction for water. The energy needed to move water molecules from the vapor state to a solid surface, or vice versa, is linked to changes in Gibbs free energy during the water exchange between the product and the environment [1].

Analysis performed at DCP

After the drying process was completed, analyses of TPC, AA, and starch were performed in DCP, as shown in Figure 3 (a, b, and c). The increase in temperature leads to the degradation of phenolic compounds (Figure 3a) and a decrease in AA (Figure 3b); therefore, to extract phenolic compounds from this residue, it is not advisable to work at temperatures above 60°C.



(b)



(c)

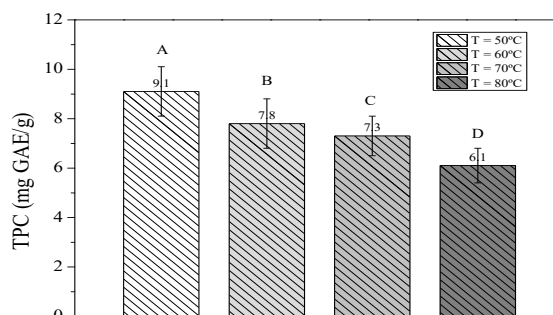


Figure 3: Drying kinetics effect on DCP: (a) total phenolic content (TPC), (b) antioxidant activity (AA), and (c) starch content. Columns marked with the same uppercase letter do not differ significantly from each other at the 95% confidence level ($p < 0.05$), according to analysis of variance (ANOVA) followed by Tukey's test. Different letters indicate statistically significant differences.

Conclusions

The physicochemical characterization confirmed the potential of cassava peel as a valuable by-product for the food industry. Studying its drying kinetics proved essential to extend shelf life, reduce microbial susceptibility, and enable broader applications. Among the mathematical models tested, the logarithmic model best described the drying behavior, while drying at 50 °C preserved phenolic compounds and antioxidant activity. Higher temperatures caused minimal starch losses, indicating their suitability for starch-focused applications. Although the study demonstrated the viability of drying cassava peel, it was limited to laboratory-scale hot air convection. Future research should address scale-up, evaluate alternative or hybrid drying technologies (e.g., vacuum, infrared, or freeze-drying), and investigate storage stability and practical applications to advance sustainable and efficient valorization strategies.

List of abbreviations

a_w : Water activity.
DCP: Dry Cassava Peels
 D_{eff} : Effective diffusivity.
 E_a : activation energy
RCP: Cassava Peels
TPC: Total phenolic compounds.
TSS: Total soluble solids.
TTA: Total titratable acidity.
 R^2 : Coefficient of determination.
 χ^2 : Chi-square.
 ΔH : Enthalpy variation (kJ/mol)
 ΔS : Entropy variation (J/mol.K)
 ΔG : Gibbs free energy (kJ/mol)
R: universal gas constant (8.314 kJ/mol.K)
 T_a : absolute temperature (K).

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Availability of Data and Materials

Data supporting the results of the current study are available within the article.

Consent for Publication

Not applicable

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Conflicts of Interest

The authors declare no conflicts of interest regarding this manuscript.

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References

1. Lobo, I. D., Júnior, C. F. dos S. & Nunes, A. Importância socioeconômica da mandioca (Manihot esculenta crantz) para a comunidade de Jaçapetuba, município de Cametá/PA. Multitemas 23, 195 (2018).
2. Cruz, I. A. et al. Valorization of cassava residues for biogas production in Brazil based on the circular economy: An updated and comprehensive review. Clean Eng Technol 4, 100196 (2021).
3. Vilhalva, D. A. A., Soares Júnior, M. S., Caliar, M. & Silva, F. A. da. Secagem convencional de casca de mandioca proveniente de resíduos de indústria de amido. Pesqui Agropecu Trop 42, 331–339 (2012).
4. Andrade, J. O. Aproveitamento do resíduo de manga no desenvolvimento de barra de cereal: atividade antioxidante in vitro e avaliação sensorial. (Universidade Federal de Campina Grande, Cuité-PB, 2019).
5. Olmedo, Z. R., J. et al. Análise Preliminar do potencial energético da casca de mandioca para formação de Biochar. Engineering & Technology Scientific Journal 1, (2023).
6. de Campos Cuchi, M. M., & Galão, O. F. (2022). Obtenção de etanol a partir de resíduos de mandioca (manihot esculenta crantz). Semina: Ciências Exatas e Tecnológicas, 43(1), 85-94.
7. Arlindo, J. et al. Chemical Composition and Profile of the Fermentation of Cassava Starch By-Products Silage. Original Article Biosci. J vol. 30 (2014).
8. Barros, S. L. et al. Modelagem matemática da cinética de secagem de cascas do kino (Cucumis metuliferus). Research, Society and Development 9, e60911608 (2020).

9. Lopes De Menezes, M., Ströher, A. P., Pereira, N. C. & Davantel De Barros, S. T. ANÁLISE DA CINÉTICA E AJUSTES DE MODELOS MATEMÁTICOS AOS DADOS DE SECAGEM DO BAGAÇO DO MARACUJÁ-AMARELO.
10. IAL. Normas Analíticas Do Instituto Lutz: . vol. 1 (São Paulo, 1985).
11. Azzini, A. & Arruda, M. C. Q. Sacarificação da serragem de bambu visando ao estabelecimento de um método de determinação de amido. *Bragantia* 45, 15–22 (1986).
12. Guindani, M. et al. Estudo do processo de extração dos compostos fenólicos e antocianinas totais do hibiscus Sabdariffa. in *Anais do XX Congresso Brasileiro de Engenharia Química* 4496–4502 (Editora Edgard Blücher, São Paulo, 2015). doi:10.5151/chemeng-cobeq2014-1245-20276-155624.
13. Singleton, V. L. & Rossi, J. A. Colorimetry of Total Phenolics with Phosphomolybdic-Phosphotungstic Acid Reagents. *Am J Enol Vitic* 16, 144–158 (1965).
14. Rufino, M. S. M., Alves, R. E., Fernandes, F. A. N. & Brito, E. S. Free radical scavenging behavior of ten exotic tropical fruits extracts. *Food Research International* 44, 2072–2075 (2011).
15. Martins, M. G. & da Silva Pena, R. Combined osmotic dehydration and drying process of pirarucu (*Arapaima gigas*) fillets. *J Food Sci Technol* 54, 3170–3179 (2017).
16. Kosasih, E. A., Zikri, A. & Dzaky, M. I. Effects of drying temperature, airflow, and cut segment on drying rate and activation energy of elephant cassava. *Case Studies in Thermal Engineering* 19, 100633 (2020).
17. Goneli, A. L. D., Vieira, M. do C., Vilhasanti, H. da C. B. & Gonçalves, A. A. Modelagem matemática e difusividade efetiva de folhas de aroeira durante a secagem. *Pesqui Agropecu Trop* 44, 56–64 (2014).
18. Crank, J. *The Mathematics of Diffusion*, 21–24 Oxford University Press. vol. 1 (1975).
19. Toğrul, İ. T. & Pehlivan, D. Mathematical modelling of solar drying of apricots in thin layers. *J Food Eng* 55, 209–216 (2002).
20. Corrêa, P. C., Oliveira, G. H. H., Botelho, F. M., Goneli, A. L. D. & Carvalho, F. M. Modelagem matemática e determinação das propriedades termodinâmicas do café (*Coffea arabica* L.) durante o processo de secagem. *Revista Ceres* 57, 595–601 (2010).
21. Faria, R. Q. de, Teixeira, I. R., Devilla, I. A., Ascheri, D. P. R. & Resende, O. Cinética de secagem de sementes de crambe. *Revista Brasileira de Engenharia Agrícola e Ambiental* 16, 573–583 (2012).
22. Henderson, S. M. & Pabis, S. Grain drying theory. 1. Temperature effect on drying coefficient. *Journal of Agricultural Engineering Research* 6, 169–164 (1961).
23. Wang, C. Y. & Singh, R. P. Use of variable equilibrium moisture content in modeling rice drying. *Transactions of American Society of Agricultural Engineers*, 11, 668–672 (1978).
24. Silva, H. W. da, Rodovalho, R. S., Velasco, M. F., Silva, C. F. & Vale, L. S. R. Kinetics and thermodynamic properties related to the drying of ‘Cabacinha’ pepper fruits. *Revista Brasileira de Engenharia Agrícola e Ambiental* 20, 174–180 (2016).
25. Tapia, M. S., Alzamora, S. M. & Chirife, J. Effects of Water Activity (a_w) on Microbial Stability as a Hurdle in Food Preservation. in *Water Activity in Foods* 323–355 (Wiley, 2020). doi:10.1002/9781118765982.ch14.
26. Souto, L. R. F. Utilização do amido da casca de mandioca na produção de vinagre: características físico-químicas e funcionais. (Universidade Federal de Goiás, Goiás, 2011).
27. Batista Pinheiro, S. et al. Caracterização físico-química e análise de compostos fenólicos em cascas de mandioca in natura e submetidas a tratamento Hidrotérmico. in *Anais do II conecta UFRA: bioeconomia* (2022).
28. Pinto, C. C. et al. Parâmetros físico químicos e resíduos cianogênicos em farinhas de mandioca de diferentes casas de e um município do estado do Pará, Brasil. *Brazilian Journal of Development* 6, 43459–43473 (2020).
29. Biondi, F. et al. Environmental Conditions and Agronomical Factors Influencing the Levels of Phytochemicals in Brassica Vegetables Responsible for Nutritional and Sensorial Properties. *Applied Sciences* 11, 1927 (2021).
30. Santos, M. A. I., Simão, A. A., Marques, T. R., Sackz, A. A. & Corrêa, A. D. Efeito de diferentes métodos de extração sobre a atividade antioxidante e o perfil de compostos fenólicos da folha de mandioca. *Brazilian Journal of Food Technology* 19, (2016).
31. Madamba, P. S., Driscoll, R. H. & Buckle, K. A. Enthalpy-entropy compensation models for sorption and browning of garlic. *J Food Eng* 28, 109–119 (1996).
32. Draper, N. R. & Smith, H. *Applied Regression Analysis*. Vol. 1 (John Wiley & Sons, New York, 1998).
33. Lima, N. C. R., Junior, J. M. dos S., Filho, E. E. X. G., Costa, R. M. M. & Santana, A. A. Cinética de secagem e difusividade efetiva do Abiu (*Pouteria caimito*)/Abiu (*Pouteria caimito*) drying and effective diffusivity Kinesy. *Brazilian Applied Science Review* 5, 02–10 (2021).
34. Modesto Junior, E. N., Carmo, J. R., Chisté, R. C. & Pena, R. S. Cinética de secagem das folhas de mandioca (*Manihot esculenta* Crantz). In *XXVI Congresso Brasileiro de Ciência dos Alimentos* (Belém-PA, 2018).

35. Cuevas, M. et al. Drying kinetics and effective water diffusivities in olive stone and olive-tree pruning. *Renew Energy* 132, 911–920 (2019).
36. Santos, D. da C. et al. Cinética de secagem e propriedades termodinâmicas da polpa de patauá (*Oenocarpus bataua* Mart.). *Brazilian Journal of Food Technology* 22, (2019).
37. Jideani, V. A. & Mpotokwana, S. M. Modeling of water absorption of Botswana bambara varieties using Peleg's equation. *J Food Eng* 92, 182–188 (2009).
38. Kayacier, A. & Singh, R. K. Application of effective diffusivity approach for the moisture content prediction of tortilla chips during baking. *LWT - Food Science and Technology* 37, 275–281 (2004).
39. Morais, S. J. da S., Devilla, I. A., Ferreira, D. A. & Teixeira, I. R. Modelagem matemática das curvas de secagem e coeficiente de difusão de grãos de feijão-caupi (*Vigna unguiculata* (L.) Walp.). *Revista Ciência Agronômica* 44, 455–463 (2013).
40. Oliveira, Gabriel Henrique Horta de et al. Modelagem e propriedades termodinâmicas na secagem de morangos. *Brazilian Journal of Food Technology*, v. 18, n. 4, p. 314–321, 2015. <https://doi.org/10.1590/1981-6723.5315>
41. Oliveira, G. H. H.; Corrêa, P. C.; Santos, E. S.; Treto, P. C.; Diniz, M. D. M. S. Evaluation of thermodynamic properties using GAB model to describe the desorption process of cocoa beans. , *International Journal of Food Science and Technology*, Londres, v. 46, n. 10, p. 2077–2084, 2011. <http://dx.doi.org/10.1111/j.1365-2621.2011.02719.x>.