Desorption and thermophysical properties of feijoa pulp as affected by temperature and moisture content

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ABSTRACT
Feijoa has a high nutraceutical and agro-industrial potential, an attractive opportunity for Colombia to enter new markets with innovative products. However, there is little knowledge about its behavior and requirements for its proper industrial processing. The studies of thermophysical and sorption properties are fundamental for analyzing and optimizing the different unit operations, evaluation, and product quality control. This study aimed to determine and mathematically model the physical, thermal, and water desorption properties of feijoa pulp in the physiological ripening stage. The desorption isotherms were determined using the gravimetric method, based on saturated salts’ solutions to create atmospheres of controlled relative humidity (RH, %), in this case, at temperatures (T) of 8°C, 23°C, and 38°C and water activities (a_w) between 0.07 and 0.98. From the isotherms model that best fits the experimental data, the isosteric heat of sorption (Q_s), differential entropy (ΔS_dry), and Gibbs free energy (ΔG) were calculated. The density (ρ), thermal conductivity (κ), and specific heat capacity (c_p) properties were determined and modeled at different moisture contents (H: 75%, 80%, 85%, and 90%) in the temperature range (T) 20 to 80°C, using the pycnometer method, concentric cylinder method, and differential scanning spectrophotometry (DSC), respectively. The desorption isotherms of the feijoa pulp were type III with equilibrium moisture contents (X_e) between 0.1246 and 5.5135 kg/kg (dry basis, d.b.), a monolayer moisture content of 0.2 kg/kg (d.b.); and spontaneity of the sorption phenomenon. Both c_p and κ depended more on H than on T; while ρ showed an equal relationship with both factors; these behaviors are characteristic of high humidity foods. The mathematical models obtained in this study are a valuable contribution for the food industry for an effective agro-industrialization, use, and added value of feijoa pulp through the design, control, and optimization of processes and equipment that involve the transfer of heat and matter.

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Introduction

The feijoa (*Acca sellowiana* (O. Berg) Burret) is an exotic Myrtaceae native to the South American subtropics (Brazil, Uruguay, Paraguay, and Argentina).\(^1\) It is a climacteric berry with a sweet-acidulous taste and peculiar floral aroma, predominantly oval, with a diameter of 3–5 cm, and weighing between 40 and 100 g. It has a rough or smooth green-gray skin throughout its development; a whitish-beige-colored pulp with pink tones in advanced degrees of maturity, and tiny ellipsoid seeds.\(^2\) Depending on genetic, nutritional, and edaphology factors, the Colombian varieties of the fruit have simple, sigmoidal growth curves, taking between 120 and 150 days post-anthesis to reach physiological maturity, sometimes even as long as 154 days.\(^3\)

Feijoa stands out as a promising nutritional, bioactive source rich in vitamins, sugars, minerals, organic acids, dietary fiber, and iodine, as well as flavonoids, tannins, tocoherols, polyphenols, phenolic acids, pectins, saponins, and volatile-aromatic compounds.\(^4\) These compounds are responsible for biological activities of nutraceutical, pharmacological, and cosmetic interest detected in this fruit, including antioxidant, antimicrobial, analgesic, gastroprotective, anti-cancer, and anti-inflammatory actions.\(^2\)

A nutraceutical and agroindustrial potential is thus envisioned for feijoa along with a socio-economic and commercial opportunity for Colombia to enter new markets with innovative products because this country has a growing production of 2,408 t/year of feijoa\(^5\) and edaphoclimatic conditions between 1,800 and 2,700 m a.s.l. that are conducive to crop expansion.\(^3\) It is worth bearing in mind the great demand for this fruit for the potential processing of different products (sweets, ice cream, desserts, concentrates, eggnog, fermented, and other beverages), and that only 10%
of feijoa production in Colombia is marketed internationally, but processed,\textsuperscript{[6,7]} an opportunity already noted for feijoa with its inclusion within the 2006–2020 Colombian export bet.\textsuperscript{[1]}

However, a limitation for effective agro-industrialization is the scarce knowledge about its behavior and requirements when subjecting it to the different industrial processes. Considering that most food processing and conservation methods involve processes of material and energy transfer, a study of the thermophysical and sorption properties is essential for the analysis and optimization of the different unitary operations, evaluation and control of product quality, and prediction of the behavior of its properties during processing within the food industry.\textsuperscript{[8]} Studies on the mathematical modeling of sorption isotherms, convection drying, and refractance window of feijoa slices have been published.\textsuperscript{[9,10]}

Evaluation of water sorption properties in food is critical due to the direct influence of water on physicochemical, biochemical, and microbiological qualities.\textsuperscript{[11]} The adsorption/desorption isotherms describe the relationship between the water activity ($a_w$) and the equilibrium moisture content ($X_e$) at a constant temperature. Isotherms describe how water molecules are absorbed by a specific material, useful in predicting the shelf life and conditions of storage, transport, and processing of the material.\textsuperscript{[12]} The gravimetric method allows determining the sorption experimentally in a sample, bringing it to a condition of equilibrium when it reaches constant weight at a determined temperature and relative humidity using saturated salts’ solutions to create controlled atmospheres.\textsuperscript{[13]}

For the prediction of sorption isotherms in food, various empirical and theoretical models have been proposed, prominent among them Guggenheim, Anderson and De Boer (GAB), Brunauer, Emmett and Teller (BET), Iglesias and Chirife, Halsey, Henderson, and Oswin.\textsuperscript{[14,15]} The GAB model is primarily used in foods due to its wide $a_w$ range (0 to 0.95) and its better fit to the experimental data.\textsuperscript{[14]} Once the isotherm model has been determined, it is possible to estimate sorption properties such as the isosteric heat of sorption ($Q_s$), Gibbs free energy ($\Delta G$), and the differential and integral entropies ($\Delta S_{diff}, \Delta S_{int}$) and enthalpies ($\Delta H_{diff}, \Delta H_{int}$). These properties describe the relationship between water and food structures and provide relevant information about energy requirements, optimal processing conditions (concentration and drying), handling, and equipment design.\textsuperscript{[16,17]}

Regarding the density ($\rho$) and thermal properties of food, knowledge of these is useful for designing, controlling, and optimizing any process involving heat transfer. Properties such as specific heat capacity ($cp$), thermal conductivity ($k$), and thermal diffusivity ($\alpha$) allow evaluating aspects such as the capacity of the food to maintain and store heat, the flow of heat during processing, speed of propagation, and its ability to store heat, while determining $\rho$ is indispensable to estimate $\alpha$ and the description of the phenomenon of heat transfer in a steady and transient state.\textsuperscript{[18,19]} The chemical composition and physical structure of the food material, and the temperature and the type of processing influence these properties.\textsuperscript{[20]} with their study commonly depending on the concentration of the material (moisture or total soluble solids) and the temperature of the process.\textsuperscript{[21–23]}

Under conditions of the steady state and transient state, heat conduction through the material can be described mathematically through the first and second Fourier Law, respectively.\textsuperscript{[20]} Of the most common methods used for measuring thermal properties, the concentric cylinder method stands out for its practicality, simplicity, and the possibility of studying both states (Figure 1).\textsuperscript{[24,25]}

This study aimed to determine and model the physical, thermal, and water desorption properties of feijoa pulp at the physiological ripening stage. So far, there are no reports available on these properties of feijoa pulp. This study contains relevant information for the use and optimization of industrial processes of this food matrix.

**Material and methods**

**Collection and conditioning of vegetable material**

Feijoa fruit in the physiological ripening stage\textsuperscript{[1]} was harvested at 2,050 m a.s.l. (4°55’51.4” N and 74°19’25.5” W) and average temperature 18°C, on the “La Cascada” farm, in La Vega, region Cundinamarca (Colombia). The fruit (about 3 kg) was disinfected (sodium hypochlorite at 200 mg/
L) and then peeled and de-pulped. Peel and seeds were discarded, while the pulp, homogenized and with preservative (sodium benzoate, 3,000 mg/L: purchased of Merck, Darmstadt, Germany), was used for the study. Table 1 shows the physicochemical analysis of feijoa pulp.

A part of the fresh pulp was destined for the desorption isotherm test. The remaining sample was concentrated in a rotary evaporator (RV 10 control, IKA, Staufen, Germany) to the point where the pulp’s characteristics would be preserved without subjecting it to de-pectination. Samples were prepared from the concentrated pulp (75% moisture content) at moisture contents of 80%, 85%, and 90% by the addition of distilled water. All samples were stored hermetically in glass jars at 2°C until analysis. Some pulp was lyophilized (model 7758020, LABCONCO, Kansas, USA) and used to determine the specific heat capacity of the dry matter.

**Desorption isotherms**

The gravimetric method was used to determine the equilibrium moisture content at temperatures of 8, 23, and 38°C, and water activities between 0.07 and 0.98. For each temperature, seven hermetic plastic containers containing saturated saline solutions (salts: KOH; CH₃CO₂K; MgCl₂; Mg(NO₃)₂; NaNO₃; KBr, and K₂SO₄, purchased of Merck and Sigma-Aldrich, Darmstadt, Germany) were arranged according to the range of water activities to be evaluated. The relative vapor pressures of the saturated saline solutions are shown in Table 2. For each determination, three replicas of the sample (1.674 ± 0.237 g) were deposited in small plastic containers placed on a support inside each hermetic plastic container, thus avoiding direct contact between the sample and the saline solution. The closed containers were placed under controlled temperature experimental conditions. The samples’ mass was checked weekly until their variation did not exceed 0.1%. The initial moisture content previously determined by the AOAC method 934.01 was used to establish Xₑ for each experiment. The values of Xₑ, aₑ, and T were used to construct the desorption isotherms.

**Thermal properties**

The density (ρ), specific heat of dry (cpₘ₀) and wet (cp) matter, and thermal conductivity (k) of the feijoa pulp were determined under the same conditions of moisture content (H) (75%, 80%, 85%, and 90%) and T (20–80°C).
Table 1. Physicochemical analysis of feijoa pulp.

| Physical                  | Diameter (Longitudinal (cm)) | 5.72 ± 0.60 |
|---------------------------|------------------------------|-------------|
|                           | Transversal (cm)             | 3.48 ± 0.56 |
| Fresh Weight (g)          |                              |             |
| Firmness (Kgf)            |                              |             |
| Dry Matter (%)            |                              |             |
| SST (°Brix)               |                              |             |
| pH                        |                              |             |
| Acidity (% Ac. Citric)    |                              |             |
| Moisture (%)              |                              |             |
| Ether extract (%)         |                              |             |
| Crude fiber (%)           |                              |             |
| Ash (%)                   |                              |             |
| Nitrogen (%)              |                              |             |
| Protein (%)               |                              |             |
| Total C.H. (mg/g dry sample) |                          | 338.75 ± 4.25 |
| Reducing C.H. (mg/g dry sample) |                        | 15.65 ± 0.12 |
| Non Reducing C.H. (mg/g dry sample) |                    | 84.35 ± 0.12 |
| Nitrogen Free Extract (%) |                              | 70.55 ± 0.69 |
| Organic Matter (%)        |                              | 97.64 ± 0.00 |
| Gross Energy (kCal/100 g) |                              | 362.97 ± 5.96 |
| Acid Detergent Fiber (%)  |                              | 14.95 ± 1.40 |
| Neutral Detergent Fiber (%) |                            | 17.62 ± 0.11 |
| Vitamin C (mg ascorbic acid/g freeze-dried sample) | 25.73 ± 2.06 |
| Vitamin A (mg β-carotene/g lyophilized sample) | 10.76 ± 0.46 |

| Micronutrients and macronutrients | Cu (mg/g dry sample) | 0.01 ± 0.00 |
|                                  | Zn (mg/g dry sample) | 0.01 ± 0.00 |
|                                  | Fe (mg/g dry sample) | 0.03 ± 0.00 |
|                                  | Mn (mg/g dry sample) | 0.00 ± 0.00 |
|                                  | B (mg/g dry sample)  | 0.18 ± 0.01 |
|                                  | Na (mg/g dry sample) | 0.11 ± 0.06 |
|                                  | Ca (mg/g dry sample) | 5.77 ± 0.61 |
|                                  | Mg (mg/g dry sample) | 0.63 ± 0.06 |
|                                  | K (mg/g dry sample)  | 14.30 ± 0.10 |
|                                  | P (mg/g dry sample)  | 1.25 ± 0.08 |
|                                  | S (mg/g dry sample)  | 0.77 ± 0.21 |

Table 2. Relative vapor pressures of the saturated salt solution at 8, 23 and 38°C (*Relative vapor pressures calculated from Fontana[26]).

| Saturated salt solution | Temperature (°C) | 8  | 23  | 38 |
|-------------------------|------------------|----|-----|----|
| KOH                     |                  | 0.133 | 0.085 | 0.063 |
| CH₃CO₂K                 |                  | 0.233 | 0.228 | 0.195 |
| MgCl₂                   |                  | 0.336 | 0.330 | 0.319 |
| Mg(NO₃)₂                |                  | 0.580 | 0.535 | 0.490 |
| NaNO₃                  |                  | 0.780 | 0.747 | 0.714 |
| KBr                     |                  | 0.846 | 0.812 | 0.796 |
| K₂SO₄                  |                  | 0.983 | 0.974 | 0.964 |

Density: The sample density (5 g) at different concentrations was determined in triplicate using a previously calibrated 50 mL volumetric pycnometer and an analytical balance (PA214, Ohaus, NJ, USA). The sample temperature was controlled using a thermostatic bath with water (WCR-P22, Dahian, Gangwon-do, Korea).[28]

Specific heat capacity: The experiments to determine the $c_p$ of the feijoa pulp were carried out in a calorimeter (DSC 8000, Perkin Elmer, Waltham, MA, USA), using aluminum capsules (ref 0219–0041, Perkin Elmer, Waltham, MA, USA). The equipment was calibrated with indium (melting point = 156.6°C; enthalpy of fusion = 28.45 J/g) at a heat flow of 2°C/min and a temperature range of 20–80°C. The measurements were made using the step-response analysis method[29] in a nitrogen atmosphere (99.5% purity, ~20 mL/min of gas flow) at a heating rate of 2°C/min from 0°C to 90°C.
The $cp_m$ of the pulp was determined as a function of temperature using the software Pyris 10.1 (Perkin Elmer, Waltham, MA, USA). [30]

Thermal conductivity: This property was determined at different heat fluxes following the method described by Sánchez et al. [31] using a previously constructed and calibrated cell to measure the heat transmitted by conduction through the sample that occupies the annular space between two concentric bronze cylinders (Figure 1). [24] The cell was immersed in a thermostated bath and stirred with distilled water to keep constant the external temperature. Likewise, the intensity of current supplied from a regulator to an electrical resistance located in the axial direction of the inner cylinder was controlled during the experiment. The external and internal temperatures and the temperature differential were monitored with two type-J thermocouples and a data logger (421509 model, Extech Instruments, Waltham, MA, USA).

Modeling of desorption and thermophysical properties

Desorption properties of water

The desorption isotherms were simulated using the GAB (Eq. 1), and BET (Eq. 2), theoretical models, and the empirical models of Iglesias and Chirife (Eq. 3), Halsey (Eq. 4), Henderson (Eq. 5), and Oswin (Eq. 6). [13,32,33] In the models, $X_e$ was described as a function of temperature and $a_w$. For the BET and GAB models, the constants $C_g$ and $K_g$ were determined using Eq. 7 and 8, respectively. ASAE Standards D271.2 DEC99 [34] were used to estimate the latent heat of vaporization ($\lambda$, in kJ/kg) as a temperature function. The computational software Matlab® R2019a (The Mathworks Inc., Natick, MA, USA) was used for modeling.

$$X_e = \left( \frac{X_m C_g K_g a_w}{(1 - K_g a_w) [1 + (C_g - 1) K_g a_w]} \right)$$  \hspace{1cm} (1)

$$X_e = \left( \frac{X_m C_b a_w}{(1 - a_w) [1 + (C_b - 1) a_w]} \right)$$  \hspace{1cm} (2)

$$X_e = C + \left( \frac{a_w}{1 - a_w} \right) \times (A + BT_{abs})$$  \hspace{1cm} (3)

$$X_e = \left( - \frac{\exp(A + BT_{abs})}{\log a_w} \right)^{1/C}$$  \hspace{1cm} (4)

$$X_e = \left( - \frac{\log(1 - a_w)}{A(T_{abs} + B)} \right)^{1/C}$$  \hspace{1cm} (5)

$$X_e = (A + BT_{abs}) \times \left( \frac{a_w}{1 - a_w} \right)^{1/C}$$  \hspace{1cm} (6)

$$C_g = C_0 \exp \left( \frac{H_m - H_n}{RT_{abs}} \right)$$  \hspace{1cm} (7)

$$K_g = K_0 \exp \left( \frac{\lambda - H_n}{RT_{abs}} \right)$$  \hspace{1cm} (8)
For Eq. 1 to 8: \( X_e \) and \( X_m \) are the equilibrium, and monolayer moisture content, respectively (kg/kg, d. b.), \( C_gK_g \) and \( C_g \) are constants of the theoretical models of GAB and BET (dimensionless), \( A, B, \) and \( C \) are constants of the empirical models, \( a_w \) is the water activity (dimensionless), \( H_m \) and \( H_n \) is the heat of sorption of water in the monolayer and multilayer, respectively (kJ/mol), \( \lambda \) is the latent heat of vaporization of pure water (kJ/mol), \( R \) is the universal constant of ideal gases \( (8.314472 \times 10^{-3} \text{kJ/mol-K}) \) and \( T_{abs} \) the absolute temperature (K).

From the desorption isotherm model that best fits the experimental data, \( Q_s \) (kJ/mol), \( \Delta S_{diff} \) (J/mol-K) and \( \Delta G \) (kJ/mol) were calculated. \( Q_s \) was calculated by the Clausius-Clapeyron equation Eq. 9, as the sum of the net isosteric of heat sorption \( (q_\text{iso} \text{ in kJ/mol}) \) and \( \lambda \) (in kJ/mol), whereas \( \Delta S_{diff} \) and \( \Delta G \) through Eq. 10 and 11, respectively. \(^{[13]}\)

\[
Q_s = \lambda - R \frac{\partial (\ln a_w)}{\partial (1/T_{abs})}
\]  
Eq. 9

\[
\ln a_w = - \frac{q_s}{R T_{abs}} - \frac{\Delta S_{diff}}{R}
\]  
Eq. 10

\[
\Delta G = R T_{abs} \ln a_w
\]  
Eq. 11

**Thermophysical properties**

The experimental data of \( \rho, \ cp, \) and \( k \) of the feijoa pulp were correlated with \( H \) and \( T \) using non-linear regression models, testing the fit of all possible combinations of the independent variables and selecting the best-fit model according to the goodness-of-fit statistics. Because the \( cp \) of the wet matter is an additive property, it can be calculated using a predictive model (Eq. 12), where the water and the pulp (dry matter) is its main components. The specific heat of water \( (cp_w) \) can be estimated as a function of \( T \), according to Eq. 13. \(^{[16]}\)

\[
cp = \left(1 - \frac{H}{100}\right) \text{cp}_{ms} + \left(\frac{H}{100}\right) \text{cp}_w
\]  
Eq. 12

\[
cp_w = 4.1726 - 9.09 \times 10^{-5} T + 5.4731 \times 10^{-6} T^2
\]  
Eq. 13

where \( cp, cp_{ms}, \) and \( cp_w \) are the specific heat (in kJ/kg-K) of the wet and dry matter of the feijoa pulp and the water, respectively; \( H \) is the moisture content of the pulp (%); and \( T \) is the temperature (°C). Fourier’s second law, \(^{[20]}\) in cylindrical coordinates, was used to calculate \( k \) by describing the one-dimensional heat transfer by conduction through the cell (Eq. 14) and considering the assumptions expressed in Eq. 15\(^{[31]}\) and the initial and boundary conditions in Eq. 16.

\[
\rho cp \frac{\partial T}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left[rk \frac{\partial T}{\partial r}\right]
\]  
Eq. 14

If \( R_1 < r < R_2, \) \( v, \) \( R_2 < r < R_2' \) (Figure 1) \( \rightarrow \rho = \rho', \ k = k', \ cp = cp' \)

\[
T|_{t=0} = T_0; \quad -k \frac{\partial T}{\partial r}|_{r=R_1'} = q; \quad T|_{r=R_2'} = T_{\infty}
\]  
Eq. 15

In Eq. 14, 15 and 16, \( T, T_0, \) and \( T_{\infty} \) are the local, initial and water temperatures (°C), respectively; \( t \) is the time (s); \( k', \rho' \) and \( cp' \) are the thermal conductivity (W/m-K), density (kg/m³) and specific heat (J/kg-K) of bronze, respectively; and \( q \) is the heat flux per unit area (W/m²) emitted by the electrical resistance. The mathematical model (Eq.14) was solved numerically using the *pdepe* function of Matlab. An optimization algorithm was used to estimate the values of the properties that minimize the deviation between the experimental and simulated temperature profiles.
Statistical analysis

The experimental data in triplicate (n = 3) or duplicate (n = 2, for \( \epsilon_p \)) were subjected to a non-linear regression analysis to determine the mathematical models and their respective parameters in each of the properties evaluated. The goodness-of-fit of the models was verified through their fitted correlation coefficient values (\( R_{adj}^2 \)) and their mean relative error (MRE), complemented by Lilliefors’s test and determination of confidence intervals for the different parameters. Moreover, the selected models were subjected to a residual analysis to assess the adequacy of the estimations. All analyzes were carried out with a confidence level of 95% using the software Matlab\textsuperscript{*} R2019a (The Mathworks Inc., Natick, MA, USA).\textsuperscript{[35]}

Results and discussion

Desorption isotherms

The \( X_c \) (0.1246 to 5.5135 kg/kg, d.b.) of the feijoa pulp in the physiological ripening stage decreased as \( T \) increased and increased as \( a_w \) increased in the conditions studied (Figure 2a). The feijoa pulp showed \( X_c \) values similar to those reported in banana, apple, tomato, and rosehip pulps.\textsuperscript{[36,37]} It likewise was found to have type III desorption isotherms, typical of food systems rich in crystalline compounds such as sugars and highly water-soluble salts,\textsuperscript{[14]} a characteristic evidenced in feijoa.\textsuperscript{[2]} These isotherms occur when the binding energy of the first layer is less than the energy between the water molecules.\textsuperscript{[33]}

Considering the division of the isotherm into three regions,\textsuperscript{[32]} for feijoa pulp in region C (\( a_w: 0.983–0.680 \)) where free water predominates, a more influential role of \( T \) is observed in the desorption phenomenon, where its increment together with the decrease of \( a_w \) produced the significant decrease of \( X_c \), an effect attributable to the substantial presence of free water in materials with high humidity, whose water molecules, weakly bound to the food, are activated on increasing \( T \) at energy levels that allow them to detach from their sorption sites.\textsuperscript{[38]} In region B (\( a_w: 0.680–0.230 \)), it was observed that the available water (retained by condensation in the solid matrix) could be in a low proportion, or its extraction could be limited by the dissolution of sugars, a behavior that is typical in type III isotherms,\textsuperscript{[15]} which explains the slight effect of \( T \) and gradual decrease of \( X_c \) in this region. Values of \( a_w < 0.230 \) in the feijoa pulp are dominated by region A containing bound water, which is difficult to extract and is composed of structural and monolayer water.\textsuperscript{[32]} Considering the relationship between \( a_w \) and the quality-stability of the food, around 23°C, the control of the proliferation of microorganisms (\( X_c \leq 0.35 \) kg/kg, d.b.), of enzymatic reactions (Maillard) and lipid oxidation could be expected for the pulp of feijoa (\( X_c \) between 0.16 and 0.24 kg/kg, d.b.).\textsuperscript{[14]} Table 3 contains the results of the modeling of the desorption isotherms of the feijoa pulp. All the mathematical models tested showed a good fit (\( R_{adj}^2: 0.983–0.991 \)). However, Iglesias & Chirife presented the best fit, followed by GAB (MRE: 14.5% and 17.8%, respectively), where Iglesias & Chirife is the model that best represents the phenomenon of desorption in the feijoa pulp, with higher \( R_{adj}^2 \) (0.991), lower MRE and a statistically significant incidence of all its parameters at a confidence level of 95%. The GAB model has been used mainly for the modeling of sorption isotherms due to its goodness-of-fit\textsuperscript{[12]}, however, the Iglesias & Chirife model\textsuperscript{[39]} was proposed for foods with type III isotherms,\textsuperscript{[40]} such as feijoa pulp. This model has been used in several desorption processes in various plant products.\textsuperscript{[39,41,42]} The model of Iglesias and Chirife showed absolute residuals lower than 0.62 kg/kg (d.b.) (Figure 2b). However, the Lilliefors test shows that the residuals do not follow a normal distribution (p < .01), 84.1% of the absolute residuals were lower than 0.24 kg/kg (d.b.).

Sorption isotherms of gases by solid materials have five basic types. Consequently, water sorption isotherms of biological and food materials usually follow the form of the sigmoid isotherm, type II. Consequently, some crystalline materials, including sugars, may have rather low water adsorption until the aqueous activity becomes sufficient for deliquescence and water sorption increases. Such water sorption follows the type III isotherm, as discussed above for feijoa pulp. Consequently,
Deliquescence is a moisture-induced phase transformation from solid to solution. A deliquescent material interacts with water vapor in the atmosphere and, at the deliquescence point or critical relative humidity (RH₀), dissolution of the solid occurs, leading to the presence of bulk water with a water activity (aw) less than 1. RH₀ is different from the caking point, which is the minimum relative humidity at which a powder cakes, i.e., vapor absorption in amorphous regions of the solid or deliquescence (regardless of the water absorption mechanism). Deliquescent materials are solids of crystalline character that are highly soluble in water and capable of reducing the colligative properties. As a result, this phenomenon can lead to significant changes in the physicochemical properties of fruit pulp, including feijoa. The relative humidity at which deliquescence occurs depends on the intrinsic properties of the substance, the presence of other deliquescent compounds and temperature. Due to the fact that deliquescence involves the formation of a solution, its occurrence can be very detrimental to physical and chemical stability in the development of new products. Therefore, for susceptible raw materials, such as fruit pulps, it is essential to establish conditions under which deliquescence can occur for both a pulp and the final formulation and product, and thus avoid exposure to these conditions.

Figure 2. A) Experimental desorption isotherms of feijoa pulp at the physiological ripening stage and calculated values using Iglesias and Chirife model. b) Residual analysis of the model.
Table 3. Identified parameters and goodness-of-fit statistics of the models used to describe the desorption isotherms of feijoa pulp at the physiological ripening stage.

| Model          | Parameters                                                                 | 95% Confidence intervals | $R^2_{adj}$ | MRE (%) |
|----------------|-----------------------------------------------------------------------------|---------------------------|-------------|---------|
| Iglesias & Chirife | $A = 0.17347$                                                                 | 0.20712, 0.26995          | 0.991       | 14.5    |
|                | $B = -2.6988 \times 10^{-5}$/K                                              | $-6.1304 \times 10^{-5}$, $-3.9527 \times 10^{-4}$ |             |         |
|                | $C = 0.14361$                                                                | 0.14377, 0.1872           |             |         |
| GAB            | $X_m = 0.13052$ kg/kg (d.b.)                                                | 0.10567, 0.13027          | 0.988       | 17.8    |
|                | $C_P = 2767.2$                                                              | $-3.93761 \times 10^{11}$, $9.3761 \times 10^{11}$ |             |         |
|                | $K_Q = 156.81$                                                               | 145.48, 168.18            |             |         |
|                | $H_m = 3046$ kJ/mol                                                          | $-1.0472 \times 10^{14}$, $1.0472 \times 10^{14}$ |             |         |
|                | $H_m = 3140.7$ kJ/mol                                                        | 3130.5, 3150.4            |             |         |
| Halsey         | $A = 1.3527$                                                                 | $-0.63336$, 2.6083        | 0.989       | 21.7    |
|                | $B = (-1.1478 \times 10^{-5})$/K                                            | $-0.019575$, $-0.0084606$ |             |         |
|                | $C = 1.2542$                                                                 | 2.0889, 2.2949            |             |         |
| BET            | $X_m = 9.8371 \times 10^{-2}$ kg/kg (d.b.)                                  | 9.5039 $\times 10^{-2}$, $-0.10229$ | 0.989       | 22.2    |
|                | $C_P = -510.3$                                                               | $-8.1196 \times 10^{11}$, $-8.1196 \times 10^{11}$ |             |         |
|                | $H_m = 5203.6$                                                               | $-1.3667 \times 10^{13}$, $-1.3667 \times 10^{13}$ |             |         |
| Oswin          | $A = 0.6158$                                                                 | 0.46083, 0.91355          | 0.989       | 36.5    |
|                | $B = (-1.3758 \times 10^{-5})$/K                                            | $-0.0022803$, $-0.00091598$ |             |         |
|                | $C = 1.2595$                                                                 | 1.2028, 1.3435            |             |         |
| Henderson      | $A = (9.3845 \times 10^{-4})$/K                                             | 0.0069123, 0.012908       | 0.983       | 36.5    |
|                | $B = -71.994$ K                                                              | $-156.89$, $-26.551$      |             |         |
|                | $C = 0.41738$                                                                | 0.40639, 0.47908          |             |         |

**Thermodynamic properties of water sorption**

From the Iglesias & Chirife isotherm, the properties of $Q_s$, $\Delta S_{s,hg}$, and $\Delta G$ of the feijoa pulp were estimated as a function of the moisture content ($X$, kg/kg) at the minimum and maximum temperature levels studied (8°C and 38°C).

$Q_s$ represents the minimum amount of heat required to remove water, making it a relevant parameter in food dehydration processes.\(^{[38]}\) In the desorption of the feijoa pulp, it is clear that for $X$ values between 5.5 and 1.5 kg/kg (d.b.), $Q_s$ remains almost constant (Figure 3a), with any differences due to the effect of $T$ (8°C: 44.8 kJ/mol, 38°C: 43.5 kJ/mol). The energy demand in this process increases with $T$ decrease, in which a drop of 30°C demands an additional 72.2 kJ to remove 1 kg of water. However, considering the low variation in $Q_s$ between the two temperatures (2.1%), drying of feijoa pulp at room temperature might be convenient for the process and energy levels.

Likewise, in this desorption process, a more significant increase in $Q_s$ for both temperatures is observed at values of $X \leq 1.0$, reaching a moment where $X$ tends to be constant despite the increase in $Q_s$. This behavior is attributable to the fact that $q_i$ in the food matrix at a determined $X$ approaches or exceeds $\lambda\(^{[17]}\)$ suggesting that the interaction energy between the sorbate and the sorption sites is greater than the energy that holds together the molecules of sorbate in the liquid state. This $X$ value is comparable to the moisture content of the monolayer.\(^{[38]}\)

![Figure 3](image-url) A), b) and c): $Q_s$, $\Delta S_{s,hg}$ and $\Delta G$ of feijoa pulp as a function of moisture content at $T = 8°C$ and 38°C, respectively.
The $\Delta S_{\text{diff}}$ property, proportional to the number of adsorption sites available at a specific energy level, defines the change in order or randomness in the water-sorbent system when new water molecules are adsorbed to a certain level of hydration.\cite{13} On drying the feijoa pulp, it was observed that at high values of $X$, $\Delta S_{\text{diff}}$ remains almost constant ($= 0$ J/mol-K), showing its gradual decrease at the maximum experimental temperature (38°C). This tendency is prominent at dry matter moisture contents of $X < 1$ kg/kg (d.b.) to a minimum peak of $-0.5$ J/(mol-K) around $X = 0.3$ kg/kg (d.b.) (Figure 3b), while at 8°C there is a slight decrease to a minimum peak of $-0.1$ J/(mol-K) around $X = 0.4$ kg/kg (d.b.). From these peaks, it is observed that $\Delta S_{\text{diff}}$ tends to increase, and $X$ reaches a constant value ($X = 0.2$ kg/kg, d.b.) identical for both temperatures. Similar behavior for $\Delta S_{\text{diff}}$ was reported in mango pulp formulations with maltodextrin and skimmed milk.\cite{43}

These points of minimum entropy correspond to the moisture content required to form a monolayer; in this area, the water-matrix bond is the strongest and maximum stability for food is achieved due to the better organization of water molecules and less availability for deterioration reactions.\cite{44} These points also indicate water sorption at accessible points on the surface before forming a monolayer that causes the material surface to be hydrated.\cite{45}

It is possible to infer that the increase of $\Delta S_{\text{diff}}$ at a constant $X$ is due to a higher concentration of available sorption sites. In contrast, $\Delta S_{\text{diff}}$ presents lower results when the product has a higher $X$ because the molecular movement is more limited. Consequently, a constant $\Delta S_{\text{diff}}$ at the beginning of the process, ($X > 1$ at 8°C and $X > 2$ at 38°C), can be attributed to the lower mobility of the water molecules at higher values of aw, because the available sorption sites are covered with water molecules.\cite{46} In effect, the water molecules saturate the system and they cannot interact with the sorption sites of the material, causing a constant $\Delta S_{\text{diff}}$. This additional water corresponds to “free water” which has the same properties as pure water. The behavior of the process at 38°C reveals a more remarkable change in the water-sorbent system order and a greater fraction of available sorption sites compared to 8°C as $X$ decreases, which would suggest a greater efficiency in the desorption of the feijoa pulp at 38°C.\cite{9}

$\Delta G$ is indicative of the amount of water bound to the product and is an evaluation criterion for the removal of the water. Based on its positive or negative sign, it reveals the affinity of the water-food matrix and makes it possible to define if the water sorption process is spontaneous ($\Delta G < 0$) or not ($\Delta G > 0$).\cite{47,48} $\Delta G$ showed negative values (Figure 3c), indicating that all physicochemical reactions of sorption in the microstructure of the material occur spontaneously. These reactions could demonstrate a similar behavior in the range between 8°C and 38°C due to the minimal temperature effect. Cano et al.\cite{43} conclude that the tendency of $\Delta G$ to 0 with the increase of $X$ is the response to the decrease in the availability of sorption sites to high values of $X$. Results similar to those evidenced in feijoa pulp have been reported on other food matrices.\cite{13,22,43}

**Density**

The results of the modelization of $\rho$ of feijoa pulp are shown in Figure 4a. An increase in $\rho$ as $H$ and $T$ decreased, yielding values between 994 and 1094 kg/m$^3$, in the range of $H$ and $T$ studied. This behavior is comparable to that shown by banana puree and jackfruit pulp.\cite{21,49} Changes in $T$ and $H$ can influence $\rho$ by the thermal expansion of the components and the concentration of solids present in the food matrix, respectively.\cite{21} The effect of $T$ and $H$ on $\rho$ was modeled satisfactorily using a second-order polynomial ($R^2_{\text{adj}} = 0.979$, MRE = 0.257%), Eq. 17. All parameters of the model were statistically significant at a confidence level of 95%. The residual analysis of the model (Figure 4b) showed absolute residuals less than 10 kg/m$^3$, which follow a normal distribution ($p > .01$) according to the Lilliefors test, with 83.3% of the absolute residuals less than 4.6 kg/m$^3$.

where $\rho$ is expressed in kg/m$^3$, $H$ is the moisture content of feijoa pulp in (% d.b.), and $T$ is the sample temperature in °C.
Specific heat capacity (cp)

The $cp_{ms}$ of the feijoa pulp as a function of $T$ yielded experimental data between 1.82 and 2.05 kJ/kg·K between 20°C and 80°C. This property was $T$ dependent (Figure 5a), a behavior satisfactorily fitted and described ($R^2_{adj}$ 0.971; MRE 0.443%) through a second-order polynomial function (Eq. 18). According to experimental data, $cp_{ms}$ remained almost constant between 44°C and 48°C, whereas between 56°C and 80°C $cp_{ms}$ showed a wide variability between replicates. These phenomena can be attributed to interaction in the water molecules and the food structure. The changes in the conformation of components also can explain this behavior, since $cp$ is related to the ability of water molecules to form hydrogen bridges and the strength of these bonds\[^{50}\] and that the physicochemical composition of the food has a marked influence on this property.\[^{16}\] The residual analysis for the $cp_{ms}$ model (Fig. 5b) yielded absolute residuals of 0.033 kJ/kg·K, which follow a normal distribution ($p > .01$) according to the Lilliefors test, with 82% of the absolute residuals less than 0.023 kJ/kg·K. (where $cp_{ms}$ is expressed in kJ/(kg·K), and $T$ is the temperature in °C.

The values of $cp$ obtained for the feijoa pulp (3.59–3.99 kJ/kg·K) are similar to the value reported by Castellanos et al.\[^{51}\] (3.6 kJ/kg·°C), also in the physiological state of the fruit. The $cp$ showed greater

![Figure 4. A) Density of feijoa pulp as a function of T and H; b) Residual analysis of the model.](image-url)
dependence with $H$ than with $T$, and a direct relationship with both variables, in the conditions studied (Figure 6). In foods such as feijoa with high $H$ values, water – as a significant component due to its high specific heat – predominantly influences the $cp$ of the material, whereas the effect of $T$ is low at values above the freezing point. Values and behavior similar to $cp$ of feijoa pulp have been reported in other food matrices.

The fact that there is a substantial difference between the thermal properties of water and those of other food constituents has suggested many possibilities for estimating the specific heat of foods mainly from its moisture content. The trend of experiments may present a reduction in the specific heat of carbohydrate solutions with increasing solute concentration as a result of the lower heat capacity of carbohydrates compared to water, i.e., specific heat values are influenced by solute concentration rather than by the effects of temperature itself, since an increase in the latter usually causes the $C_p$ to increase. It has been shown that density, specific heat, and thermal conductivity are more affected by increasing solute concentration at higher temperatures than by temperature itself. Therefore, specific heat and thermal conductivity are intrinsic properties of the material. It represents the ability of the material to accumulate and transport heat, respectively. It is evident that both properties are strongly related to the water content. Furthermore, analysis of the data shows that the less water there is in the material, the larger the discrepancies between the

![Figure 5](image-url)
Figure 6. Influence of $H$ and $T$ on the specific heat of the feijoa pulp.

Figure 7. a) Thermal conductivity of feijoa pulp as a function of $T$ and $H$; b) Residual analysis of the model.
predicted and measured values. It is reasonable to assume that the discrepancies arise from the treatment of the whole water in the food as bulk water. Interactions between water and food components affect the properties of water. Therefore, it is rather difficult to accept that the interactions do not affect the thermal properties. However, water has a high specific heat compared to other food components, even a small amount of water in food significantly affects its specific heat. Therefore, the specific heat, as a physical property, is equal to the sum of the fractional specific heats of the main constituents of the food.

However, the equilibrium water content may increase with decreasing solids content in the pulp, i.e., the equilibrium water content of feijoa pulp may decrease with increasing temperature at different levels of water activity, which is an already expected behavior. The higher equilibrium water content in the pulp is probably due to the content of solids present in the pulp, which can affect the behavior of the thermophysical properties.

In contrast, when measurements are performed in the low aw range (>0.6), there is a slow increase in the equilibrium water content, followed by a strong increase in intermediate values up to higher aw values (>0.6), being sorption measurements that show the typical behavior of foods rich in sugars. Behavior that has been attributed to the predominant effect of solute-solvent interactions associated with sugar dissolution. Consequently, the interactions between water and solute molecules are called hydration. Consequently, in the presence of polar molecules these interactions are dominated by hydrogen bonds. This water called hydration water it is evident that the interactions between water and macromolecules create and stabilize the spatial conformation of the biopolymers present in the food (pulp fruit). Therefore, the number of water molecules in the hydration layer depends on the nature of the macromolecule and its ionization energy and ionization state.

**Thermal conductivity (k)**

In the feijoa pulp, k increases with H and T. However, H showed a more significant effect on k than T (Fig. 7a). In foods, k depends mainly on their chemical composition, while at values of T above their freezing point, the increase in k is slight despite the increase in T. This behavior observed in the feijoa pulp can be attributed mainly to the effect of the water content on k, where the k of water, as a prominent thermal conductor, affects and increases the k of the feijoa pulp at higher values of H. In the feijoa pulp, k ranged from 0.51 to 0.68 W/m-K in the studied H and T ranges. The behavior and values of k shown by the feijoa pulp are similar to those reported in other pulps and fruit juices.

The relationship of k with H and T obtained by multiple linear regression analysis can be expressed with Eq. 19, according to the fit of the experimental data ($R^2_{adj} = 0.998$ and MRE = 1.202%) at a confidence level of 95%. The residual analysis of the obtained mathematical model (Fig. 7b) showed absolute residuals lower than 2.1°C, and although they do not follow a normal distribution (p < .01), 78.9% of them were below 0.97°C.

$$k = -0.2706 + 1.0267 \times 10^{-2}H + 2.9656 \times 10^{-6}HT$$

where k is expressed in W/(m K), H is moisture content of feijoa pulp in (% d.b.), and T is the temperature in °C.

**Thermal diffusivity (α)**

Another important property of feijoa pulp that defines the rate of heat diffuses through the material, α, was determined from the previous mathematical models dividing k by ρ, and cp.

Using a second-order polynomial function, the relationship of α (m²/s) with H and T can be expressed as Eq. 20, according to the fitting results of estimated data ($R^2_{adj} = 1$ and MRE = 0.0096%).
\[
\alpha = -4.611 \times 10^{-8} + 2.543 \times 10^{-9}H - 3.064 \times 10^{-10}T - 2.661 \times 10^{-12}H^2 + 3.103 \times 10^{-12}HT + 1.837 \times 10^{-12}T^2
\]  

(20)

**Conclusion**

The sorption isotherms of feijoa pulp are typical of sugar-rich foods (Type III) with only a slight dependence on \(T\) in the studied conditions. The Iglesias and Chirife model showed the best goodness-of-fit. The sorption properties (\(Q_s\), \(\Delta S_{d,hg}\), and \(\Delta G\)) showed strong interactions between the water and the food matrix components, the spontaneity of the sorption reactions, and the maximum stability of the product at moisture contents between 0.16 and 0.24 kg/kg (d.b.). The thermal properties \(c_p\) and \(k\) showed greater dependence on \(H\) than on \(T\). In contrast, \(\rho\) showed equal dependence on both variables, the sorption process being governed by the physicochemical composition and the matrix structure of the food, the interaction between components, and alterations on these by the heating effect. The mathematical models obtained are a valuable contribution for an effective agro-industrialization, and added value on feijoa through the design, control, and optimization of processes and equipment that involve heat and matter transfer.

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**Disclosure statement**

No potential conflict of interest was reported by the author(s).

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