



## Drying kinetics and thermodynamic properties of guava peel

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**ABSTRACT:** The drying agroindustrial products is used to preserve the sensory and nutritional quality and to reduce the biological activity, preventing deterioration and loss of commercial value. The objective was to study the mathematical modeling Guava bark drying to obtain flour and to determine and evaluate the effective diffusion coefficient, get the activation energy and the thermodynamic properties in drying temperatures of 45, 55, 65 and 75 °C. The experiment was conducted Instituto Federal Goiano - Campus Rio Verde, the guava was purchased in local shops in the city of Rio Verde Goiás, in the commercial maturity. Among the analyzed models, Midilli was the best to represent the drying phenomenon. The effective diffusion coefficient increased with increasing temperature and the activation energy for liquid diffusion drying was 37,207 kJ mol<sup>-1</sup>. The enthalpy and entropy increased with increasing drying temperature. While the Gibbs free energy increased with increasing drying temperature.

**Key words:** *Psidium guajava*, mathematical modeling, activation energy, Midilli model.

## Cinética da secagem e propriedades termodinâmicas da casca de goiaba

**RESUMO:** A secagem de produtos agroindustriais é utilizada visando preservar as qualidades sensoriais e nutricionais, bem como reduzir a atividade biológica que impede a deterioração e a perda do valor comercial. Assim, objetivou-se neste trabalho estudar a modelagem matemática da secagem da casca de goiaba para obtenção de farinha, bem como determinar o coeficiente de difusão efetivo, a energia de ativação e as propriedades termodinâmicas nas temperaturas de secagem de 45, 55, 65 e 75 °C. O experimento foi realizado no Instituto Federal Goiano - Campus Rio Verde, e as goiabas foram adquiridas no comércio local do município de Rio Verde, GO, no estádio de maturação comercial. Dentre os modelos analisados, Midilli foi selecionado para representar a cinética de secagem da casca de goiaba. O coeficiente de difusão efetivo aumentou com a elevação da temperatura e a energia de ativação para a difusão líquida na secagem foi de 37,207 kJ mol<sup>-1</sup>. A entalpia e a entropia diminuíram com a elevação da temperatura de secagem, enquanto a energia livre de Gibbs aumentou com o incremento da temperatura de secagem.

**Palavras-chave:** *Psidium guajava*, modelagem matemática, energia de ativação, modelo de Midilli.

## INTRODUCTION

Guava is a native fruit of tropical America, and the most cultivated species in the *Myrtaceae* family, it is a source of vitamin C and minerals such as calcium, phosphorus, and iron (ALI & LAZAN, 2001). Tropical fruits such as guava (*Psidium guajava*) are commonly consumed *in natura*, however, as they are extremely perishable, they are mostly processed in the form of juices, nectars, pulps, jellies, and sweets (INFANTE et al., 2013).

The drying of fruit residues aims to reduce waste in addition to being an alternative for the

processing of new food products with high nutritional value (SOUSA et al., 2015). The reuse of residues has aroused growing interest, giving rise to studies which aim to study the drying of various by-products generated by the agribusiness, including residues of jaboticaba peel (COSTA et al., 2016), grapefruit peel (*Citrus paradisi* Macf.) (SANTOS et al., 2019) and pineapple peel (SANTOS et al., 2020).

The drying process reduces water activity, inhibits microbial deterioration and chemical reactions that lead to food deterioration, in addition to increasing the shelf life of the food during storage (SURIYA et al., 2016). The drying kinetics, is

understood as the speed with which a given product loses water, is influenced by the intrinsic peculiarities, ambient temperature, relative humidity and air velocity (SILVA et al., 2015).

Through mathematical modeling of drying kinetics, it is possible to describe the process of mass transfer between the product and the drying agent, which add to information about its behavior during the process (SANTOS et al., 2017). In this context, this study dried the kinetics of guava peel to obtain flour, as well as to set the effective diffusion coefficient, activation energy, and thermodynamic properties at drying temperatures of 45, 55, 65, and 75 °C.

## MATERIALS AND METHODS

Guava fruits were purchased from local businesses in the municipality of Rio Verde, GO, at the commercial maturation stage. They were washed in running water followed by rinsing, sanitized with sodium hypochlorite solution at 100 ppm for 10 minutes, and manually peeled with previously sanitized stainless steel knives. The residues (guava peel) were cut evenly to obtain a standard size approximately  $17.20 \pm 0.28$  mm long,  $12.10 \pm 1.66$  mm wide and  $2.30 \pm 0.28$  mm thick, and frozen at  $-18$  °C until drying. The guava shells were thawed in a refrigerated temperature at  $5$  °C before drying started.

The guava shells were dried in an oven with forced air ventilation at the Post-Harvest Laboratory of Vegetable Products of the Federal Goiano Institute - Rio Verde Campus, where the initial moisture content of  $6.89 \pm 0.11$  decimal dry basis (d.b) determined aoven and dry at  $105 \pm 3$  °C until constant mass.

The shells were packed in stainless steel trays, with approximately 150 g samples perforated, evenly spread out to make a 6 cm layer. The samples were submitted to drying in an oven with forced air ventilation, in four temperature conditions 45, 55, 65, and 75 °C that promoted the average relative humidity of 23.3%; 14.2%; 8.9% and 5.8%, respectively. The monitoring of mass reduction during drying was carried out with the aid of a scale with a resolution of 0.01 g by means of weighing in regular periods.

The reduction of the moisture content during drying was accompanied by the gravimetric method (loss of mass), knowing the initial moisture content of the product until reaching the constant mass, which was considered after three consecutives equal weighings.

The temperature and relative humidity of the ambient air was monitored by means of a data logger

and the relative humidity inside the greenhouse was obtained using the basic principles of psychrometry.

For the determination of the moisture content ratios of the guava peels during drying, the following expression was used:

$$RX = \frac{X - X_e}{X_i - X_e} \quad (1)$$

where in: RX: moisture content ratio of the product, dimensionless; X: moisture content of the product (d.b.);  $X_i$ : initial moisture content of the product (d.b.); and  $X_e$ : equilibrium moisture content of the product (d.b.).

The mathematical models frequently used to represent the drying of vegetable products, table 1, were adjusted to the experimental data on the drying of guava peels. The mathematical models were adjusted by means of non-linear regression analysis by the Gauss-Newton method and, for the degree of adjustment, the magnitude of the coefficient of determination ( $R^2$ ), the Chi-square test ( $\chi^2$ ), of the relative mean error (P) and standard deviation of the estimate (SE).

The liquid diffusion model for the geometric shape of a flat plate, with an approximation of eight terms (Equation 4), was adjusted to the experimental data of guava peel drying, considering the surface area and volume, according to the following expression:

$$RX = \frac{8}{\pi^2} \sum_{i=0}^{\infty} \frac{1}{(2i+1)^2} \exp \left[ -\frac{(2i+1)^2 \pi^2 D \cdot t}{4} \cdot \left( \frac{S}{V} \right)^2 \right] \quad (2)$$

where in: RX: product moisture content ratio, dimensionless; nt: number of terms; S: product surface area,  $m^2$ ; and V: product volume,  $m^3$ .

The surface area (S) of the guava peels was calculated according to the expression:

$$S = \pi \cdot D_g \quad (3)$$

$$D_g = (A \cdot B \cdot C)^{1/3} \quad (4)$$

where in:  $D_g$ : average geometric diameter; A: length, mm; B: width, mm; and C: thickness, mm.

The volume of the guava sheels was obtained according to the expression proposed by MOHSENIN, (1986):

$$V = \frac{\pi \cdot A \cdot B \cdot C}{6} \quad (5)$$

The relationship between the effective diffusion coefficient and the elevation of the drying air temperature was described using the Arrhenius equation:

Table 1 - Mathematical models used to predict drying of plant products.

Model designation	Model	
$RX = 1 + a \cdot t + b \cdot t^2$	Wang & Sing	(2)
$RX = a \cdot \exp(-k \cdot t) + (1 - a) \exp(-k_1 \cdot t)$	Verma	(3)
$RX = \exp\left(\frac{-a \cdot (a^2 + 4 \cdot b \cdot t)^{0.5}}{2 \cdot b}\right)$	Thompson	(4)
$RX = \exp(-k \cdot t^n)$	Page	(5)
$RX = \exp(-k \cdot t)$	Newton	(6)
$RX = a \cdot \exp(-k \cdot t^n) + b \cdot t$	Midilli	(7)
$RX = a \cdot \exp(-k \cdot t) + c$	Logarithmic	(8)
$RX = a \cdot \exp(-k \cdot t)$	Henderson & Pabis	(9)
$RX = a \cdot \exp(-k \cdot t) + (1 - a) \exp(-k \cdot a \cdot t)$	Two-Term Exponential	(10)
$RX = a \cdot \exp(-k_o \cdot t) + b \cdot \exp(-k_1 \cdot t)$	Two Terms	(11)
$RX = a \cdot \exp(-k \cdot t) + (1 - a) \cdot \exp(-k \cdot b \cdot t)$	Approximation of Diffusion	(12)

Where: t: drying time, h,  $k_o$ ,  $k_1$ : drying constants  $h^{-1}$ ; a, b, c, n: parameters of the models.

$$D = D_o \cdot \exp\left(\frac{-E_a}{R \cdot T_{abs}}\right) \quad (6)$$

where:  $D_o$ : pre-exponential factor;  $E_a$ : activation energy,  $kJ \cdot mol^{-1}$ ;  $R$ : universal gas constant,  $8,134 \text{ kJ} \cdot mol^{-1} \cdot K^{-1}$ ; and  $T_{abs}$ : absolute temperature,  $K$ .

The coefficients of the Arrhenius expression were linearized with the application of the logarithm in the following form:

$$\ln D = \ln D_o - \frac{E_a}{R} \cdot \frac{1}{T_{abs}} \quad (7)$$

The thermodynamic properties of the guava peel drying process were obtained by the equation:

$$H = E_a - R \cdot T \quad (8)$$

$$S = R \cdot \left( \ln k - \ln \frac{k_B}{h_p} \right) - \ln T_{abs} \quad (9)$$

$$G = H - T_{abs} \cdot S \quad (10)$$

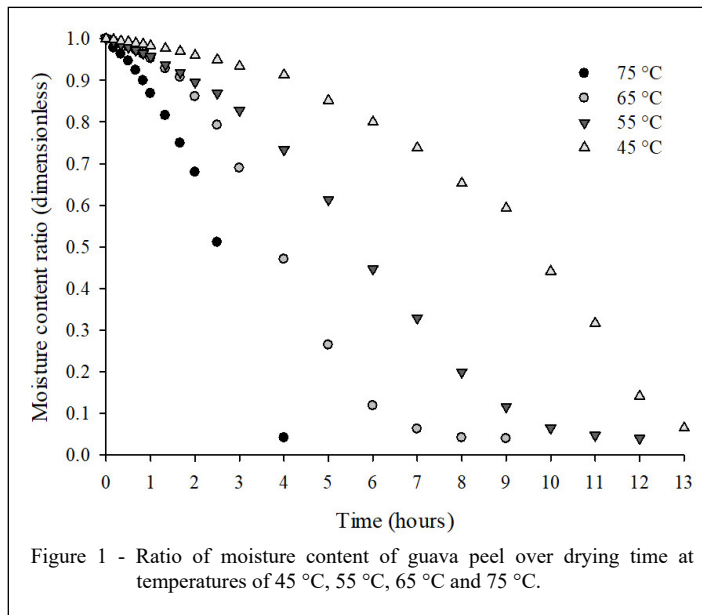
where in:  $H$  = enthalpy,  $J \cdot mol^{-1}$ ;  $S$  = entropy,  $J \cdot mol^{-1}$ ;  $G$  = Gibbs free energy,  $J \cdot mol^{-1}$ ;  $k_B$  = Boltzmann constant,  $1,38 \times 10^{-23} \text{ J} \cdot K^{-1}$ ; and  $h_p$  = Planck's constant,  $6,626 \times 10^{-34} \text{ J} \cdot s^{-1}$ .

## RESULTS AND DISCUSSION

The time required for guava shells to reduce the moisture content  $0.167 \pm 0.012$  dry bases (decimal, d.b.) was 13; 12; 9 and 4 h for drying temperatures of 45, 55, 65 and 75 °C, respectively, showing that the increase in air temperature promoted a reduction in the drying time of the guava peels (Figure 1).

The temperature of 75 °C showed a shorter dehydration time, compared to other temperatures. The increase in the temperature of the drying air resulted in a higher rate of moisture removal from the product due to a greater moisture gradient between the product and the air, decreasing the time needed to reduce the moisture content to constant mass (SOUSA et al., 2011). The same phenomenon was observed by GONÇALVES et al. (2016) when studying the drying of banana peel, SANTOS et al. (2019) with grapefruit peel (*Citrus paradisi* Macf.) when under the evaluated temperature conditions, with a difference only in the drying times.

Among the models fitted to the experimental data, Midilli model reached convergence of fitness in the iterative process (Table 2). Regarding the Chi-square test ( $\chi^2$ ), the eleven models analyzed are in the 95% confidence interval. However, the Midilli model showed satisfactory fit to the experimental data.



The determination coefficients ( $R^2$ ) of the Wang & Singh, Page, Midilli, Logarithmic, and Diffusion Approximation models presented values above 98% for all drying temperatures (Table 3), indicating, according to ARAÚJO et al. (2017), a satisfactory representation of the drying process. The Midilli model showed the highest  $R^2$  value for the experimental data on guava peel drying, because of the higher the  $R^2$ , satisfactory fit.

Analyzing the values of the relative average error (P), it was observed that only the Midilli model presented values below 10% for the four drying conditions, indicating that it is the appropriate model to predict the phenomenon.

According to the estimated mean error (SE), chi-square ( $\chi^2$ ), determination coefficients ( $R^2$ )

and relative mean error (P), Midilli equation was the one that best represented the experimental data to predict drying curve of guava sheels (Figure 2). Note that the curves estimated by the model followed the experimental points with small deviations, presenting less final moisture and less drying time, a process similar to that found by MENEZES et al. (2013) when drying passion fruit bagasse in a convective dryer at temperatures of 55 and 65 °C. Similar results were observed by SOUZA et al. (2016) in the evaluation of mathematical modeling of bagasse at temperatures of 50, 60 and 70 °C. The researchers concluded that the Midilli model was the one that best represented the drying kinetics, as well as SOUSA et al. (2015) in a kinetic study of drying leaves of *Ziziphus joazeiro*.

Table 2 - Values for the Chi-square test ( $\chi^2$ , decimal) and estimated average error (SE, decimal) for the models used in the representation of the kinetics of guava peel drying.

Models	-----45 °C-----		-----55 °C-----		-----65 °C-----		-----75 °C-----	
	SE	$\chi^2$	SE	$\chi^2$	SE	$\chi^2$	SE	$\chi^2$
Wang & Singh	0.0187	0.0003	0.0627	0.0039	0.0885	0.0078	0.0099	0.0001
Verma	0.1394	0.0194	0.0528	0.0028	0.0539	0.0029	0.1327	0.0176
Thompson	0.1356	0.0184	0.1243	0.0155	0.1421	0.0202	0.1259	0.0158
Page	0.0363	0.0013	0.0215	0.0005	0.0156	0.0002	0.0405	0.0016
Newton	0.1323	0.0175	0.1212	0.0147	0.1378	0.0190	0.1200	0.0144
Midilli	0.0137	0.0002	0.0162	0.0003	0.0093	0.0001	0.0078	0.0001
Logarithmic	0.0873	0.0076	0.0567	0.0032	0.0777	0.0060	0.0610	0.0037
Henderson & Pabis	0.1222	0.0149	0.1047	0.0110	0.1161	0.0135	0.1110	0.0123
Two-Term Exponential	0.1356	0.0184	0.1243	0.0155	0.1421	0.0202	0.1259	0.0158
Two Terms	0.1288	0.0166	0.0501	0.0025	0.1241	0.0154	0.1241	0.0154
Approximation of Diffusion	0.1046	0.0109	0.0528	0.0028	0.0915	0.0084	0.0721	0.0052

Table 3 - Mean relative error and coefficient of determination (P, R<sup>2</sup>, %) during drying of the guava peels at 45 °C, 55 °C, 65 °C and 75 °C.

Models	-----45 °C-----		-----55 °C-----		-----65 °C-----		-----75 °C-----	
	P	R <sup>2</sup>	P	R <sup>2</sup>	P	R <sup>2</sup>	P	R <sup>2</sup>
Wang & Singh	3.86	99.61	32.51	97.30	44.45	95.02	1.88	99.88
Verma	43.07	79.50	25.48	98.19	24.32	98.27	72.53	80.73
Thompson	42.13	79.56	65.88	89.41	79.80	87.17	72.53	80.73
Page	9.32	98.54	6.44	99.68	9.93	99.84	17.37	98.01
Newton	42.13	79.56	65.86	89.41	79.80	87.17	72.53	80.73
Midilli	3.30	99.81	5.83	99.84	2.31	99.95	0.96	99.94
Logarithmic	23.24	91.96	27.82	97.91	37.70	96.40	24.82	95.92
Henderson & Pabis	38.09	83.42	54.61	92.49	63.15	91.43	62.92	85.01
Two-Term Exponential	42.13	79.56	65.86	89.41	79.80	87.17	72.53	80.73
Two Terms	38.09	83.42	23.31	98.46	63.16	91.43	62.92	85.01
Approximation of Diffusion	28.30	88.46	25.48	98.19	43.00	95.01	39.00	94.31

According to GONELI et al. (2014b), the best fit of the Midilli model to the experimental data of drying is probably associated with the fast loss of water in the initial stages of the process in these materials, generating a drying curve that is sharper and best characterized mathematically by this model.

Regarding the values of the “a”, “k”, “n” and “b” coefficients of the Midilli model adjusted to the experimental data on guava bark drying (Table 4), it is observed that the “a” coefficients, “N” and “b” did not show a definite trend of values in relation to drying temperature, in this case, they can be treated as empirical variables. Only the drying constant “k” for the midilli model, increased with the increase in the drying air temperature (Table 4).

According to MARTINS et al. (2015), the k parameter represents the effective diffusivity in the drying process and shows an increasing trend with increasing temperature.

The constant k is related to the effect of temperature on the effective diffusivity in the drying process, and the liquid diffusion controls the process (BABALIS & BELESSIOTIS, 2004), that is, as the magnitude of this constant increases due to the increase in drying temperature, there is an increase in the effective diffusivity.

The determination of the effective diffusion coefficient for the different drying air temperatures of the guava peels (Figure 3A) showed an increasing linear behavior in which the values of the effective diffusion

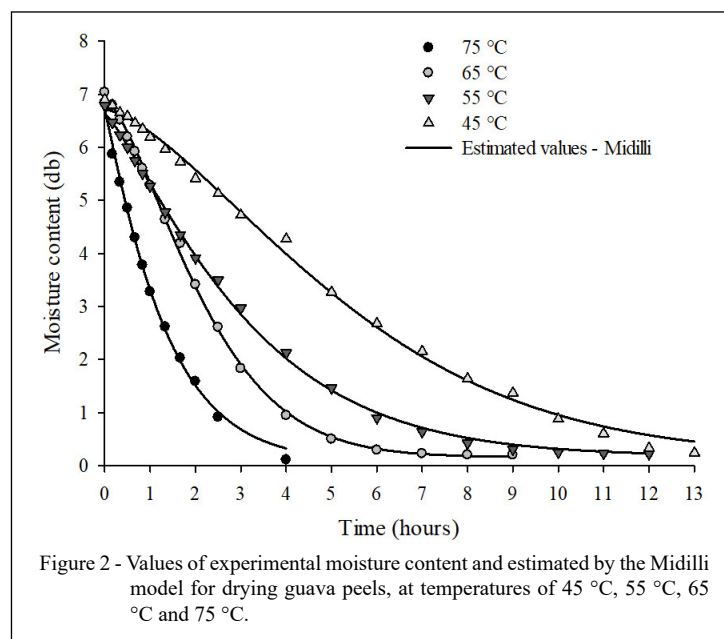


Figure 2 - Values of experimental moisture content and estimated by the Midilli model for drying guava peels, at temperatures of 45 °C, 55 °C, 65 °C and 75 °C.

Table 4 - Parameters of the Midilli model adjusted for the different drying conditions of the guava peels, with the respective equation as a function of temperature.

Parameters	Temperature (°C)			
	45	55	65	75
	-----Midilli-----			
a	1.3669**	0.975186**	0.982641**	0.9953939**
k	0.000075*	0.011808**	0.022718**	0.029091**
n	3.742882**	2.339413**	2.552831**	2.477962**
b	-0.02207**	0.000211 <sup>ns</sup>	0.003536**	-0.091031**

\*\*Significant at 1% by t test. \* Significant at 5% by t test. ns Not significant by t test.

coefficient increased in response to the elevation of the drying air temperature, varying from  $0.85 \times 10^{-9}$  to  $2.92 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  for the temperature range of 45 to 75 °C.

This phenomenon indicated a greater magnitude of water transport from the interior to the exterior of the product, corroborating with SILVA et al. (2015) on drying kinetics and effective diffusivity in genipap leaves. MENEZES et al. (2013) pointed out that the effective diffusion coefficients are in the range of  $10^{-10}$  to  $10^{-9} \text{ m}^2 \text{ s}^{-1}$  for drying yellow passion fruit bagasse.

The effective diffusion coefficient of the guava peel in relation to the drying air temperature was represented by the Arrhenius expression, as shown in figure 3 B. The activation energy for the effective diffusion of the guava peel was approximately  $37.207 \text{ kJ mol}^{-1}$  for the studied temperature range (Figure 3 B). SILVA et al. (2014) reported that the activation

energy was  $34.51 \text{ kJ mol}^{-1}$  for drying pigeon pea for the temperature range of 40 to 70 °C.

As the activation energy is considered a barrier to be crossed so that the water diffusion process in the product can occur (KASHANINEJAD et al., 2007), the lower the activation energy, the greater the water diffusivity in the product per unit of time. Such different values of activation energy for agricultural products can be attributed to their physical and biological characteristics (MARTINS et al., 2015)

Enthalpy (H) decreased with increasing temperature (Table 5). This indicated the need for less energy to remove the water bound to the material during drying, as found by CORRÊA et al. (2010) because enthalpy is related to the energy needed to remove the water attached to the product during the drying process.

Low enthalpy values at lower temperatures indicated a greater amount of energy

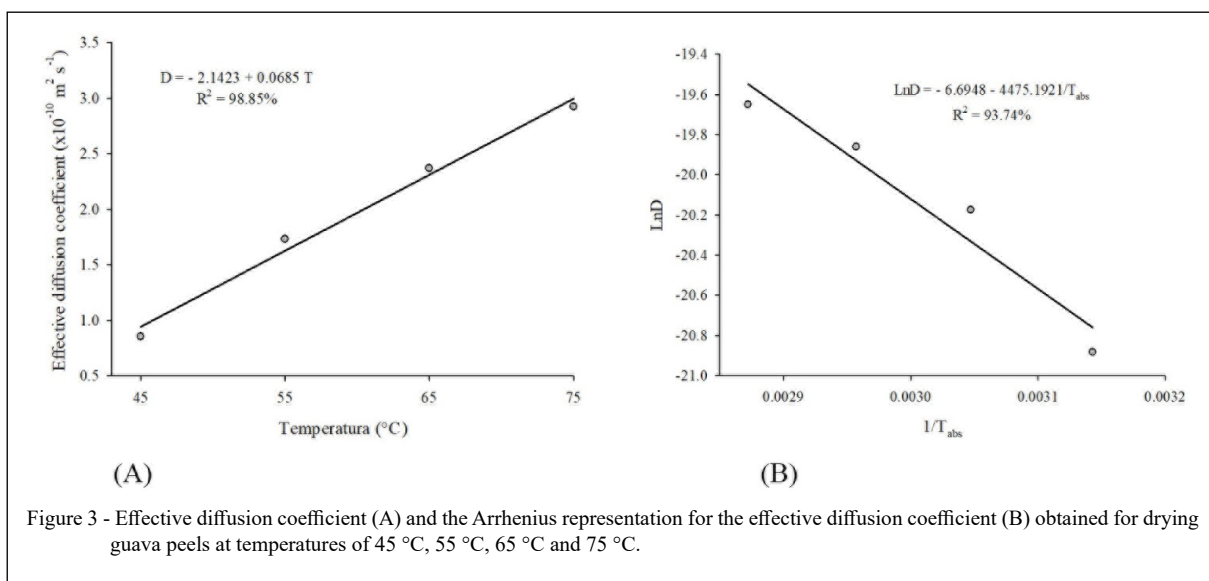


Table 5 - Enthalpy values (H, J mol<sup>-1</sup>), entropy (S, J mol<sup>-1</sup> K<sup>-1</sup>) and Gibbs free energy (G, J mol<sup>-1</sup>) for different drying air conditions of the husks of guava.

Temperature (°C)	Thermodynamic properties		
	H	S	G
45	34561.71	-229.64	107,621.23
55	34478.57	-229.90	109,918.91
65	34395.43	-230.15	112,219.12
75	34312.29	-230.39	114,521.79

required to promote the drying of guava peel; similar behavior was observed in the drying processes of 'baru' fruits (*Dipteryx alata* Vog.) studied by RESENDE et al. (2018).

Entropy decreases with increasing drying temperature. According to CORRÊA et al. (2010), entropy tends to decrease, with an increase in temperature, because when the temperature decreases, less excitation of water molecules occurs, and the degree of order between the water system and the product increases. Negative entropy values are attributed to the existence of chemical adsorption and/or structural modifications of the adsorbent (MOREIRA et al., 2008).

Gibbs free energy increased with increasing temperature, being positive for all studied drying conditions. Positive Gibbs free energy values are characteristic of an exogenous reaction, that is, when there is a need for an external agent to supply energy to the environment. MARTINS et al. (2015) studying the drying of timbó leaf for temperatures from 40 to 70 °C, found the same phenomenon.

## CONCLUSION

To represent the drying of guava peel the Midilli model was selected for the range from 45 to 75 °C. The effective diffusion coefficient increased with increasing drying temperature, with activation energy of 37.207 kJ mol<sup>-1</sup>. Enthalpy and entropy decreased with increasing temperature and Gibbs free energy was positive and increased with increasing temperature.

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## DECLARATION OF CONFLICT OF INTEREST

The authors declare no conflict of interest.

## AUTHORS' CONTRIBUTIONS

The authors contributed equally to the manuscript.

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