

Thermodynamic Properties of Four Onion (*Allium cepa* L.) Varieties Produced in Senegal

Ngoné Fall Beye

Department of Food Technologies, UFR of Agronomic Sciences, Aquaculture and Food Technologies, Gaston Berger University, Saint-Louis, Senegal, Laboratory for Biological Sciences, Agronomy and Complex Systems Modeling (LaBAM) / Gaston Berger University, Saint-Louis, Senegal, Center for Studies on Food Safety and Functional Molecules- RESCIF, Polytechnic School (ESP), Dakar, Senegal and Water, Energy, Environment and Industrial Processes Laboratory (L3EPI), Polytechnic School (ESP), Dakar, Senegal

Cheikhou Kane

Center for Studies on Food Safety and Functional Molecules- RESCIF, Polytechnic School (ESP), Dakar, Senegal and Water, Energy, Environment and Industrial Processes Laboratory (L3EPI), Polytechnic School (ESP), Dakar, Senegal

Alioune Sow

Department of Food Technologies, UFR of Agronomic Sciences, Aquaculture and Food Technologies, Gaston Berger University, Saint-Louis, Senegal and Laboratory for Biological Sciences, Agronomy and Complex Systems Modeling (LaBAM) / Gaston Berger University, Saint-Louis, Senegal

Francisca Nadège Sètonndji Vodounnou

Department of Food Technologies, UFR of Agronomic Sciences, Aquaculture and Food Technologies, Gaston Berger University, Saint-Louis, Senegal

Nicolas Cyrille Ayessou

Center for Studies on Food Safety and Functional Molecules- RESCIF, Polytechnic School (ESP), Dakar, Senegal and Water, Energy, Environment and Industrial Processes Laboratory (L3EPI), Polytechnic School (ESP), Dakar, Senegal

Abdou Sene

Laboratory for Biological Sciences, Agronomy and Complex Systems Modeling (LaBAM) / Gaston Berger University, Saint-Louis, Senegal

Codou Mar Diop

Center for Studies on Food Safety and Functional Molecules- RESCIF, Polytechnic School (ESP), Dakar, Senegal and Water, Energy, Environment and Industrial Processes Laboratory (L3EPI), Polytechnic School (ESP), Dakar, Senegal

Highlights

- Net isosteric heat and entropy decrease with increasing equilibrium moisture content for Violet of Galmi, Safari, Gandiol F1, Orient F1, and the mixture of the four varieties.
- Gibbs free energy remains nearly constant for Safari, Gandiol F1, Orient F1, and the mixture.
- Gibbs free energy increases with increasing equilibrium moisture content (between 5 and 35 %) and decreases between 35 and 40 % for Violet of Galmi.
- A third-degree polynomial describes the variation of net isosteric heat of desorption as a function of equilibrium moisture content.
- Desorption is spontaneous and controlled by net isosteric heat (negative Gibbs free energy and isokinetic temperature higher than the harmonic temperature).

ABSTRACT

Thermodynamic data, essential for designing efficient dryers, depend on the physicochemical characteristics of products but remain unavailable for the Senegalese onion varieties Violet of Galmi, Safari, Gandiol F1, and Orient F1. This study determined the isosteric heat, desorption entropy, and Gibbs free energy of these varieties, individually and as a mixture, based on desorption isotherms modeled at 50, 55, 60, and 65 °C using the gravimetric method. Data analysis was performed with Matlab (version 6.0.0). Results show that net isosteric heat and entropy decrease with increasing equilibrium moisture content for all varieties and their mixture, whereas Gibbs free energy remains nearly constant, except for Violet of Galmi, which exhibits an increase between 5 and 35 % moisture content, followed by a slight decrease between 35 and 40 %. At 5 % equilibrium moisture content, the net isosteric heats of desorption were 156.92, 141.37, 115.89, 127.39, and 128.19 kJ·mol⁻¹ for Violet of Galmi, Safari, Gandiol F1, Orient F1, and their mixture, respectively approximately three times the latent heat of vaporization of water (42.52 kJ·mol⁻¹). The linear relationship between net isosteric heat and desorption entropy validates the enthalpy-entropy compensation theory. The isokinetic temperatures (385.04 - 398.37 K) exceed the harmonic mean temperature (329.95 K), indicating that desorption is controlled by net isosteric heat. Furthermore, negative Gibbs free energy values ($\Delta G < 0$) confirm that desorption is spontaneous. Energetically, although Violet of Galmi exhibits the highest isosteric heat, the mixture behaves similarly to Orient F1, likely due to interactions among constituents that facilitate water desorption. These findings provide a thermodynamic basis for optimizing dryer design and improving post-harvest management of onions, contributing to energy-efficient dehydration processes and the reduction of post-harvest losses in Senegal.

Keywords: *Allium cepa* L., Varieties, Net isosteric heat, Entropy, Gibbs free energy, Isokinetic temperature.

INTRODUCTION

Onion (*Allium cepa* L.), which is rich in polyphenols beneficial to human health, is a highly valued agricultural product in Senegal. It ranks first among horticultural crops, with a production volume of 435,000 tons during the 2021 growing season [1]. Between 2021 and 2023, a decline in production was observed approximately 3% between 2021 and 2022, and 5% between 2022 and 2023 [2]. In contrast, production increased slightly in 2024 and 2025,

reaching 412,000 tons and 450,000 tons, respectively. Despite this growth of onion, which can cover the annual national demand for onions (250,000 to 350,000 tons), Senegalese consumption remains partially dependent on imports. This situation can be attributed to the high moisture content of onions, ranging from 83% to 92% depending on the variety [3,4,5] which causes significant storage challenges for both producers and consumers.

To address these issues, the use of solar drying in Senegal has emerged as a key strategy to overcome storage and processing constraints affecting high-moisture agricultural products such as onions, where water content promotes degradation reactions. The adoption of solar energy for dehydration, a highly energy-intensive unit operation [6], is justified not only by Senegal's high solar potential due to its geographical location but also by promising results regarding both energy efficiency and preservation of product quality. Previous studies on solar dryers have reported satisfactory outcomes with various food products, including chili pepper and beef [7], okra, cassava, and banana [8], tomato [9], and roselle [10].

The selection of a solar dryer depends on several criteria that take into account the initial characteristics of the product, particularly its thermo-physical and thermodynamic properties [4,9,11,12,13]. Moreover, the performance of solar dryers is influenced by design parameters such as construction materials, type, size, and shape, which are determined according to product characteristics, quantity to be dried, and available solar potential [12,14]. Drying conditions including temperature, relative humidity, and air velocity also play a critical role in the dryer's thermal performance [7, 9,15].

In the scientific literature, studies addressing the thermodynamic properties of onions have been based on various mathematical sorption isotherm models, depending on product characteristics [16,17,18,19,20]. However, the lack of thermodynamic data for locally produced onion varieties, highlighted through a literature review, and the importance of these properties in assessing energy demand for the design and optimization of dryer performance, justify the present study [21,22,23].

The objective of this work is therefore to determine the thermodynamic properties of four onion varieties Violet of Galmi, Safari, Gandiol F1, and Orient F1 both individually and as a mixture, based on desorption isotherms modeled at different temperatures.

MATERIALS AND METHODS

Materials

Plant Material:

The onion varieties on which the thermodynamic properties were determined were Violet of Galmi, Safari, Gandiol F1, and Orient F1. They came from the RAO cooperative in the Saint-Louis region of Senegal. The onions were collected directly from the field and transported to the laboratory to avoid any source of mixing with other varieties. The initial moisture content (% wet basis) and water activity of the four varieties were as follows:

- Violet of Galmi: 85.56 ± 0.60 / 0.945 ± 0.01 .
- Safari 88.11 ± 0.61 / 0.950 ± 0.001
- Gandiol F1: 86.99 ± 0.10 / 0.940 ± 0.001 ;
- Orient F1 : 89.13 ± 0.69 / 0.947 ± 0.009 .

Statistical and Modeling Tools:

MATLAB software version 6.0.0 is used to model desorption isotherms and to determine isotheric heat of desorption at different temperatures (50°C, 55°C, 60°C and 65°C) for the four onion varieties, taken separately, and their mixture.

Methods

Determination and Modeling of Desorption Isotherms:

The desorption isotherms of onion varieties (Violet of Galmi, Safari, Gandiol F1, and Orient F1, grown in Senegal) taken separately, and of the varieties' mixture, are determined gravimetrically using seven saturated salt solution in an oven with temperature and relative humidity control. Three randomly selected onion bulbs are peeled, washed with 100 ppm chlorinated water, rinsed three times with clear water, wrung out, and chopped with a mincer (thickness of around 1.7 mm). From the prepared bulbs, the test sample consists of ten (10) grams (10 g of the same variety for separate monitoring and 2.5 g of each variety for the mixture). Moisture content and water activity are measured using the reference methods NF ISO 712 : 2009 and NF EN ISO 17025, respectively. Desorption isotherms (for onion varieties Violet of Galmi, Safari, Gandiol F1, and Orient F1, taken separately, and their mixture) at temperatures of 50, 55, 60, and 65 °C are obtained by plotting equilibrium content curves (X_{eq} in kg H₂O per kg d.b.) as a function of water activity. Among the eleven empirical mathematical models tested to model desorption isotherms at different temperatures for the four onion varieties, taken separately, and their mixture, the **Henderson model** provided the best overall fit for all varieties and their mixture (R^2 between 0.97 and 0.99, χ^2 between 0.0016 and 0.0079). The equation of Henderson model is :

$$X_{eq} = [-\ln(1 - a_w)/B]^{1/A} \quad \text{Equation 1}$$

The Henderson model parameters at different temperature are presented in *Table 1* [24]

Table 1 : Henderson Model Parameters of the Desorption Isotherms for Violet of Galmi, Safari, Gandiol F1, and Orient F1 Onion Varieties and Their Mixture at Various Temperatures [24]

	Varieties									
	Violet of Galmi		Safari		Gandiolf F1		Orient F1		Mixture of Variety	
	Henderson model Parameters									
T °C	B	A	B	A	B	A	B	A	B	A
50	0.178	1.705	0.093	1.736	0.166	1.491	0.091	1.635	0.1095	1.6639
55	0.256	1.523	0.142	1.547	0.219	1.372	0.136	1.482	0.1482	1.5819
60	0.367	1.302	0.196	1.401	0.301	1.218	0.198	1.337	0.2258	1.3882
65	0.468	1.175	0.249	1.292	0.365	1.124	0.245	1./275	0.2794	1.3011

Net Isotheric Heat and Isotheric Heat of Desorption of Onions

The Clausius–Clapeyron equation was applied to estimate the net isotheric heat of desorption ($Q_{n\ st}$) based on the desorption isotherms [16,20,25,26,27].

$$\frac{\partial \ln (aw)}{\partial (T)} = \frac{Q_{nst}}{R T^2} \quad \text{Equation 2}$$

For fixed equilibrium moisture contents ranging from 5% to 40%, the water activities at different temperatures (50°C, 55°C, 60°C, and 65°C) were calculated using the Henderson mathematical model, which provided the best fit to the experimental desorption isotherms of onions at the given temperatures [24].

Integration of **Equation 2**, allows the determination of the natural logarithm of water activity as a function of the inverse of absolute temperature. Assuming that the net isosteric heat remains constant with respect to temperature [28], the equation of these curves, referred to as isosteres, is expressed as follows:

$$\ln a_w = - \frac{Q_{nst}}{R} * \frac{1}{T} + b \quad \text{Equation 3}$$

The slopes of these isosteres are used to calculate the net isosteric heat of desorption (Q_{nst} , in $\text{kJ}\cdot\text{mol}^{-1}$). This parameter represents the energy required to release water molecules from the onion tissue. It thus provides insight into the degree of freedom of the water molecules and the nature of their binding interactions within the product. Consequently, the isosteric heat of desorption (Q_{st}) required to dehydrate the product is the sum of the net isosteric heat of desorption and the latent heat of vaporization of water, as expressed by the following equation:

$$Q_{st} = Q_{nst} + Lvap \quad \text{Equation 4}$$

Where $Lvap$ is the latent heat of vaporization of water, ranging from 42.20 to 42.84 $\text{kJ}\cdot\text{mol}^{-1}$ within the temperature range of 50 to 65°C. Since this variation is negligible, an average latent heat of vaporization of 42.52 $\text{kJ}\cdot\text{mol}^{-1}$ was used in this study [29].

The entropy of desorption (ΔS , in $\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) was calculated from the intercept values (b) of **Equation 3**, which correspond to the intersection points of the isosteres with the ordinate axis:

$$b = \frac{\Delta S}{R} \quad \text{Equation 5}$$

Enthalpy-Entropy compensation Theory and Gibbs Free Energy:

The enthalpy-entropy compensation theory indicates a compensation between the net isosteric heat and the entropy of desorption. This theory is based on the linear relationship between these two thermodynamic parameters [30], [31], [32], [33]. The slope of this line corresponds to the temperature at which all reactions proceed at the same rate, known as the isokinetic temperature (T_{iso}) :

$$Q_{nst} = T_{iso} \Delta S + \Delta G \quad \text{Equation 6}$$

The enthalpy–entropy compensation theory is valid only if, the isokinetic temperature (T_{iso}) differs from the harmonic mean temperature (T_{harm}). The harmonic mean temperature depends on the number of isotherms and is defined as follows:

$$T_{harm} = - \frac{n}{R \sum_{i=1}^n (1/T)} \quad \text{Equation 7}$$

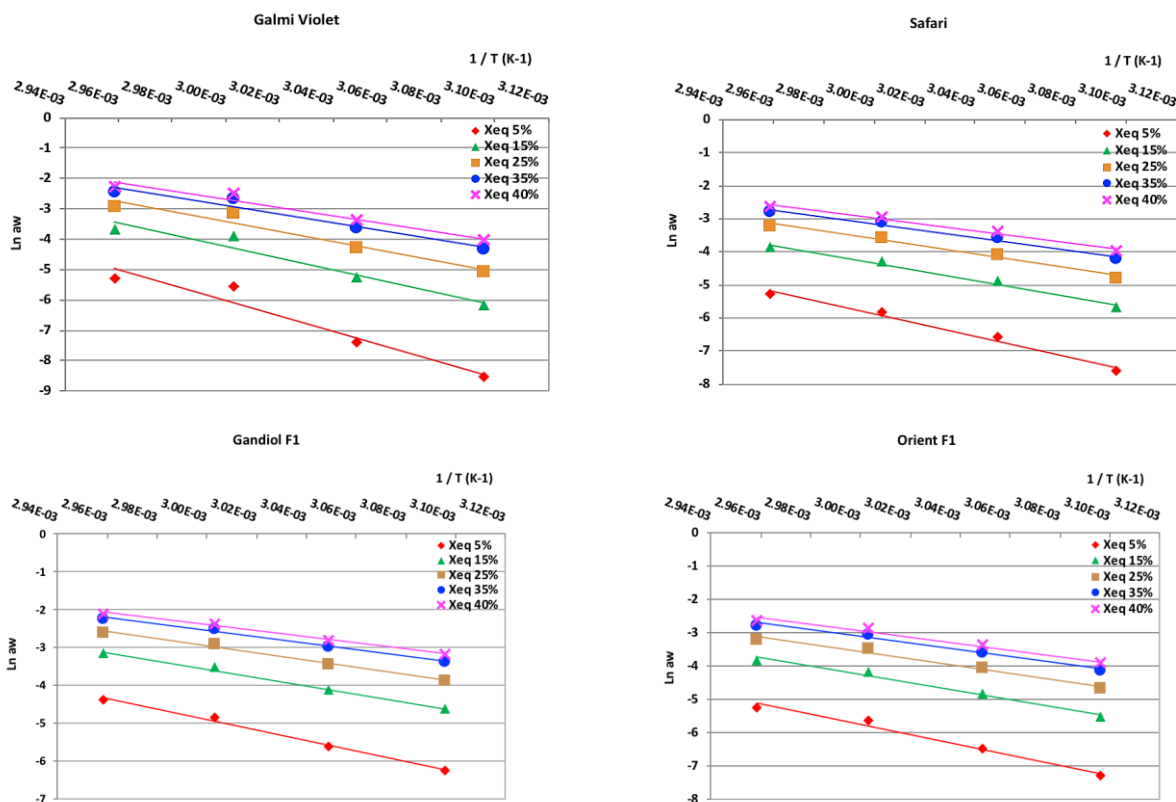
Where n is the number of desorption isotherms and T is the desorption temperature.

RESULTS AND DISCUSSION

Determination of Isosteric Heat of Desorption and Desorption Entropy

Determination of Isosteric Heat:

Figure 1 presents the curves of the natural logarithm of water activity ($\ln a_w$) plotted against the inverse of absolute temperature ($1/T$), which were used to determine the net isosteric heat of desorption for the four onion varieties. Water activity values were calculated at fixed equilibrium moisture contents of 5, 15, 25, 35, and 40%, based on Equation 1 and the corresponding A and B parameters obtained at the different temperatures (Table 1).



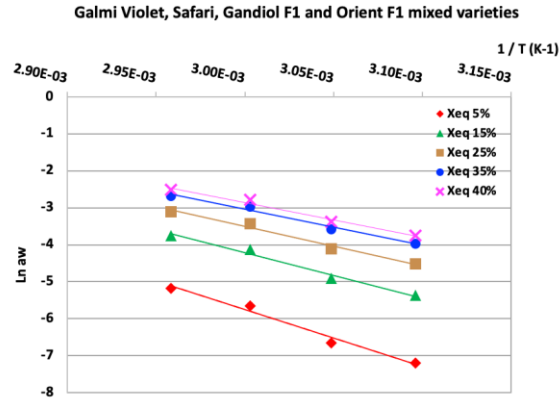


Figure 1: In Water Activity versus Inverse Temperature at Different Equilibrium Moisture Contents of 5, 15, 25, 35 and 40 % for Four Onion Varieties and Their Mixture

The trend lines obtained by linear regression Figure 1, are straight lines whose slopes increase (as the equilibrium moisture contents decrease. A strong correlation was observed for the four varieties individually as well as for their mixture, with R^2 values ranging from 0.982 to 0.994 (Table 2).

Table 2 : Regression lines of the curves $\ln(a_w)$ as a function of the inverse of temperature and Regression Coefficient for Violet of Galmi, Safari, Gandiol F1, and Orient F1 Onion Varieties and Their Mixture

	Regression lines and Coefficient at Different Xeq Values				
	Xeq (%)				
Varieties	5	15	25	35	40
Violet of Galmi	$Y = -18883x + 51.665$ $R^2 = 0.9933$	$Y = -14431x + 39.744$ $R^2 = 0.9929$	$Y = -12319x + 34.069$ $R^2 = 0.9933$	$Y = -10881x + 30.184$ $R^2 = 0.9929$	$Y = -10300x + 28.609$ $R^2 = 0.9927$
Safari	$Y = -17012x + 45.162$ $R^2 = 0.9872$	$Y = -13184x + 35.225$ $R^2 = 0.9870$	$Y = -11508x + 30.911$ $R^2 = 0.9866$	$Y = -10370x + 27.961$ $R^2 = 0.9863$	$Y = -9914.1x + 26.777$ $R^2 = 0.9865$
Gandiol F1	$Y = -13946x + 36.925$ $R^2 = 0.9939$	$Y = -10940x + 29.249$ $R^2 = 0.9934$	$Y = -9464.4x + 25.437$ $R^2 = 0.9932$	$Y = -8464.8x + 22.837$ $R^2 = 0.993$	$Y = -8061.6x + 21.783$ $R^2 = 0.9933$
Orient F1	$Y = -15330x + 40.24$ $R^2 = 0.9826$	$Y = -12425x + 33.019$ $R^2 = 0.9816$	$Y = -10946x + 29.273$ $R^2 = 0.9821$	$Y = -9963.7x + 26.776$ $R^2 = 0.9817$	$Y = -9608.2x + 25.886$ $R^2 = 0.9816$
Mixture of Varieties	$Y = -15426x + 40.52$ $R^2 = 0.9810$	$Y = -12298x + 32.679$ $R^2 = 0.9828$	$Y = -10808x + 28.92$ $R^2 = 0.9838$	$Y = -9802.5x + 26.368$ $R^2 = 0.9845$	$Y = -9396.2x + 25.332$ $R^2 = 0.9848$

Using the slopes of these trend lines and **Equation 3**, the net isosteric heat values were calculated for the four varieties and their mixture. The variation of these net isosteric heats as a function of equilibrium moisture content is presented in *figure 2*

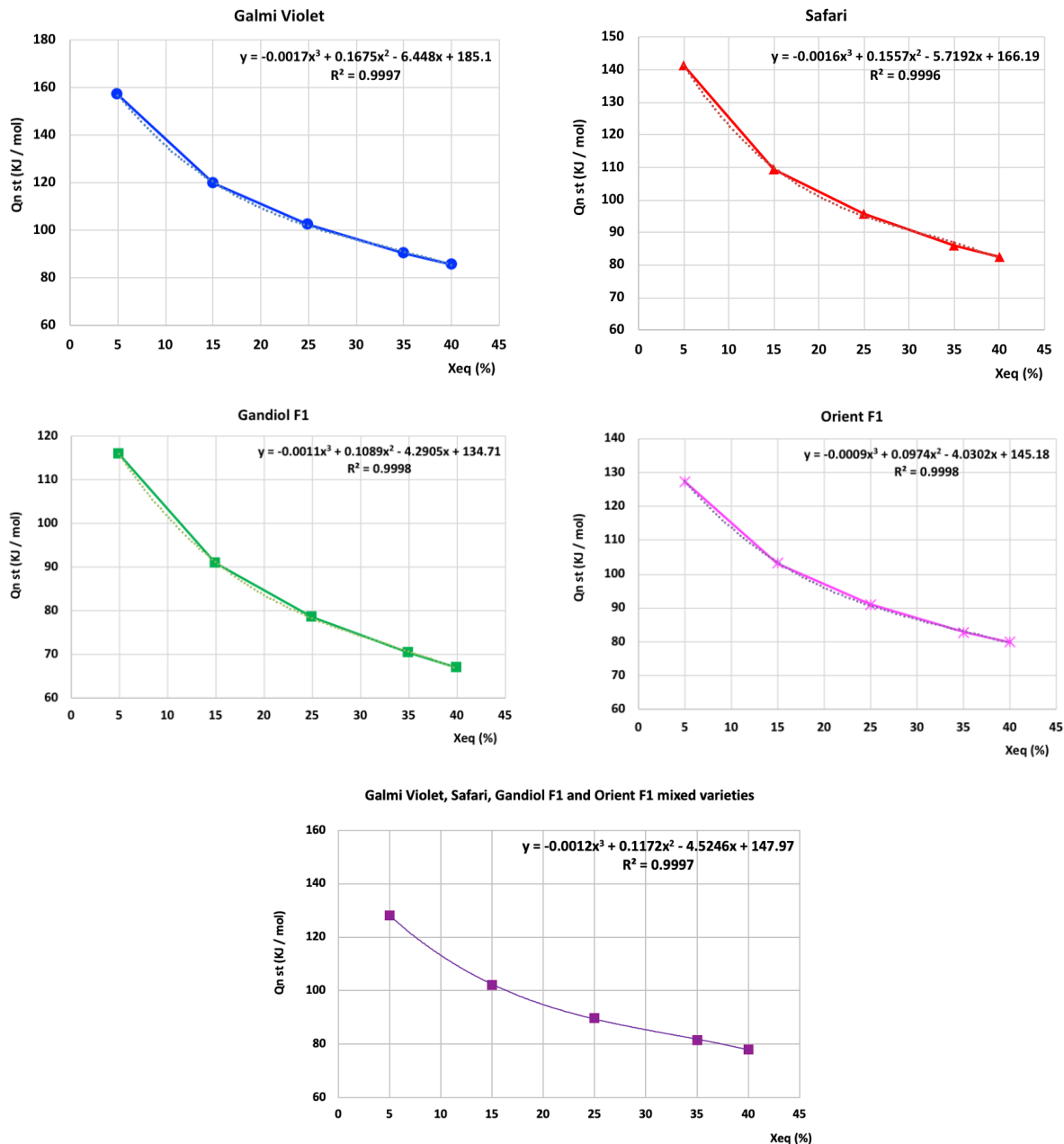


Figure 2 : Net Isosteric Heat of Desorption versus Equilibrium Moisture Content (5, 15, 25, 35 and 40 %) for Four Onion Varieties and Their Mixture

Figure 2 shows that the variation of the net isosteric heat of desorption with equilibrium moisture content is best described by a third-degree polynomial function, with correlation coefficients around 0.999 for both the individual varieties and their mixture [18, 26, 27, 34, 35].

As illustrated in figure 2, the net isosteric heat of desorption increases as the moisture content of the onions decreases. Indeed, the greater the number of hydrogen bonds, the higher the net isosteric heat of desorption. For an equilibrium moisture content of 5% (area 1, where $a_w < 0.2$), the net isosteric heat of desorption is approximately three times the latent heat of

vaporization of water ($42.52 \text{ kJ}\cdot\text{mol}^{-1}$), with values of $156.92 \text{ kJ}\cdot\text{mol}^{-1}$ for Violet of Galmi, $141.37 \text{ kJ}\cdot\text{mol}^{-1}$ for Safari, $115.89 \text{ kJ}\cdot\text{mol}^{-1}$ for Gandiol F1, $127.39 \text{ kJ}\cdot\text{mol}^{-1}$ for Orient F1, and $128.19 \text{ kJ}\cdot\text{mol}^{-1}$ for their mixture. However, in area 2 ($0.2 \leq a_w \leq 0.65$) and area 3 ($a_w > 0.65$), the net isosteric heat of desorption decreases with increasing equilibrium moisture content. These results are consistent with previous studies [17,21,25,27,36].

For every 10% decrease in equilibrium moisture content, the net isosteric heat of desorption increases by a factor ranging from 1.04 to 1.31 for the four varieties and their mixture. Areas 1, 2, and 3 are defined based on the research study on “Modeling Desorption Isotherms of Four Onion Varieties Related to Temperatures” [24]. The isosteric heat of desorption (calculated from) at different equilibrium moisture contents for the four varieties and their mixture is presented in Table 3.

Table 3 : Isosteric Heat of Desorption of Four Onion Varieties and Their Mixture at Different Equilibrium Moisture Contents of 5, 15, 25, 35 and 40 %

Isosteric Heat Qst (KJ / mol)					
Varieties					
Xeq (%)	Violet of Galmi	Safari	Gandiol F1	Orient F1	Mixture of Varieties
5	199.44	183.89	158.41	169.91	170.71
15	162.44	152.08	133.43	145.77	144.72
25	144.89	138.15	121.17	133.48	132.33
35	132.94	128.69	112.86	125.32	123.97
40	128.11	124.91	109.51	122.36	120.60

The variation of the isosteric heat of desorption for the four onion varieties as a function of equilibrium moisture content, as well as for their mixture, mirrors that of the net isosteric heat of desorption.

Regardless of the targeted equilibrium moisture content, the ranking of the varieties in descending order of net isosteric heat of desorption is Violet of Galmi, Safari, Orient F1, and Gandiol F1. The high net isosteric heat observed for Violet de Galmi corroborates previous findings by [37] which showed that this variety has the lowest effective diffusivity coefficient and requires more activation energy than the other three varieties, irrespective of maturity stage, suggesting that Violet de Galmi may be the limiting variety. However, the net isosteric heat trend of the mixture of the four varieties closely follows that of Orient F1, rather than Violet of Galmi. This behavior can likely be explained by the occurrence of multiple mechanisms among the four varieties, leading to modifications in the types of bonding within the poly-molecular layer, which in turn reduces the energy demand for the mixture. The difference in net isosteric heat between the individual varieties and the mixture can also be attributed to the higher content of soluble compounds in Violet de Galmi, followed by Safari, then Orient F1 (approximately equal to the mixture), and finally Gandiol F1[17,18,33,38,39].

Determination of Entropy:

The variation of entropy (calculated from the intercept values (b) obtained from figure 1 and equation 5 as a function of equilibrium moisture content for each variety and their mixture is presented in figure 3.

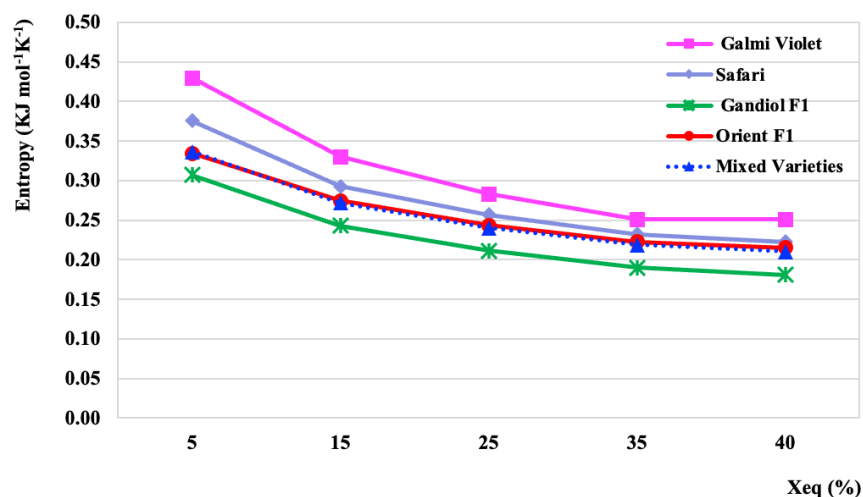


Figure 3 : Entropy versus Equilibrium Moisture Content (5, 15, 25, 35 and 40 %) for Four Onion Varieties and Their Mixture

The desorption entropy increases as the equilibrium moisture content decreases. For the different onion varieties, entropy ranged from 0.180 to 0.435 $\text{kJ}\cdot\text{mol}^{-1}$ for moisture contents between 5 and 40%. This result is consistent with the idea that internal transformations associated with microscopic changes in the system during moisture reduction are responsible for this increase [18,21,23,36,39].

The ranking of the varieties in descending order of entropy is the same as that observed for the net isosteric heat of desorption : Violet of Galmi, Safari, Orient F1, and Gandiol F1. The entropy of the mixture of the four varieties is approximately similar to that of Orient F1 and Safari. For three varieties (Gandiol F1, Orient F1, and Safari) and the mixture, entropy decreases until $X_{eq} \approx 20\%$ and tends to become asymptotic thereafter, whereas for Violet of Galmi, entropy also decreases but tends to become asymptotic only from $X_{eq} \approx 35\%$. According to [40, 41, 42], entropy variation plays a crucial role in the energetic analysis of food processing systems, as it is proportional to the number of sorption sites available at a given energy level. Moreover, the reduction of water content leads to the formation of a porous network in the matrix, increasing disorder. This disorder is not only related to the size of the food particles to be dried but also to the content of soluble compounds [11,18,43].

Enthalpy-Entropy Compensation and Gibbs Free Energy

A linear relationship was observed between the net isosteric heat of desorption and the desorption entropy (*Figure*). The trend lines established by linear regression (*Figure*) reveal an excellent correlation for the four varieties, with R^2 values ranging from 0.999 to 1. The linearity observed in the variation of the net isosteric heat of desorption with desorption entropy, along with the differences in isokinetic temperatures, confirms the enthalpy-entropy compensation theory during the drying of the four onion varieties individually as well as their mixture [21,22,23,36,38]. The isokinetic temperatures deduced from the slopes of these trend lines for Violet of Galmi, Safari, Gandiol F1, Orient F1, and their mixture are 385.04, 386.2, 388.7, 398.37, and 397.12 K, respectively. All of these isokinetic temperatures are higher than the

harmonic mean temperature (329.95 K), indicating that desorption is controlled by the net isosteric heat [27,30,31,32,33,38,44].

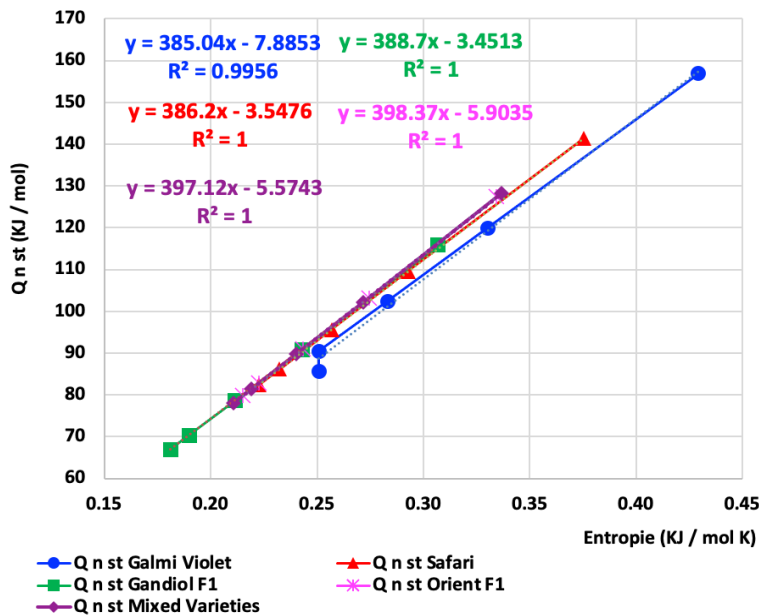


Figure 4: Net Isosteric Heat of Desorption versus Entropy for Four Onion Varieties and Their Mixture

Furthermore, these results suggest that the microstructure of these onion varieties remains stable and undergoes no significant changes during water desorption at temperatures between 50 and 65 °C [42,45, 46,47]. Therefore, the enthalpy-entropy compensation can be applied to the water desorption process in onions, which may occur via controlled mechanisms. The Gibbs free energy ($\Delta G < 0$, Table 5) for equilibrium moisture contents between 5 and 40% indicates that desorption is spontaneous. At the isokinetic temperature, the average free energy, corresponding to the intercept of the trend lines of net isosteric heat versus desorption entropy (Figure), is -7.89, -3.55, -3.45, -5.90, and -5.57 kJ·mol⁻¹ for Violet de Galmi, Safari, Gandiol F1, Orient F1, and their mixture, respectively.

Table 4 : Free energy at the isokinetic desorption temperature of onion varieties Violet de Galmi, Safari, Gandiol F1, and Orient F1 for equilibrium moisture contents of 5, 15, 25, 35, and 40%.

Free energy ΔG (KJ / mol)					
Varieties					
Xeq (%)	Violet of Galmi	Safari	Gandiol F1	Orient F1	Mixture of Varieties
5	-8.38	-3.57	-3.38	-5.82	-5.53
15	-7.23	-3.49	-3.57	-6.06	-5.65
25	-6.63	-3.57	-3.51	-5.95	-5.62
35	-6.15	-3.56	-3.42	-5.84	-5.56
40	-10.98	-3.55	-3.37	-5.85	-5.51

The Gibbs free energy values at the isokinetic desorption temperature for each variety (Table 4) are all negative, confirming the spontaneous nature of the desorption process. The Table 4

shows that the Gibbs free energy of the Safari, Gandiol F1, Orient F1 varieties and that of the mixture of the four varieties remain almost unchanged with equilibrium moisture content. In contrast, the Violet of Galmi variety exhibits a distinct trend, with an increase in free energy between 5 and 35% moisture content, followed by a slight decrease between 35 and 40%. This increase in Gibbs free energy reflects the need for additional activation energy to initiate the desorption process. Similar results were reported by Zhang *et al.* (2022) [36]. during the study of Tiger *nut*, suggesting a comparable energetic behavior related to the internal structure of the material and the nature of its water-binding sites.

CONCLUSION

This study focused on the determination of isosteric heat, entropy, and Gibbs free energy of four onion varieties (Violet of Galmi, Safari, Gandiol F1, and Orient F1), considered individually and as a mixture, based on the modeling of desorption isotherms at different temperatures (50, 55, 60, and 65 °C).

The net isosteric heats of desorption (156.92, 141.37, 115.89, 127.39, and 128.19 kJ·mol⁻¹ for Violet of Galmi, Safari, Gandiol F1, Orient F1, and their mixture, respectively) are higher at low equilibrium moisture contents, whereas the opposite trend is observed as the moisture content increases. Depending on the variety, the net isosteric heat ($Q_{n\ st}$) differs significantly due to variations in the types and strengths of water-matrix interactions. The mixture exhibits a net isosteric heat closer to that of Orient F1, despite the higher value observed for Violet of Galmi, likely due to interactive mechanisms between varieties that facilitate desorption. Furthermore, the variation of net isosteric heat as a function of equilibrium moisture content is well described by a third-degree polynomial with correlation coefficients around 0.999 for all individual varieties and their mixture.

The desorption entropy (ΔS) also decreases with increasing equilibrium moisture content, reaching an asymptotic value at $X_{eq} = 20\%$ for Gandiol F1, Orient F1, Safari, and the mixture, and at 35% for Violet of Galmi. The enthalpy-entropy compensation theory is validated for both the individual varieties and their mixture, as evidenced by the perfect linearity of $Q_{n\ st}$ versus ΔS (R^2 between 0.999 and 1) and the differences in isokinetic temperatures (385.04, 386.2, 388.7, 398.37, and 397.12 K for Violet of Galmi, Safari, Gandiol F1, Orient F1, and the mixture, respectively). These isokinetic temperatures, all higher than the harmonic mean temperature (329.95 K), indicate that water desorption in the 50 - 65 °C range is controlled by the net isosteric heat. Moreover, the negative Gibbs free energy values (average values of -7.89, -3.55, -3.45, -5.90, and -5.57 kJ·mol⁻¹ for Violet of Galmi, Safari, Gandiol F1, Orient F1, and the mixture, respectively) confirm that the desorption process is spontaneous. From a sustainable development perspective, these findings provide a scientific basis for the design of efficient dryers, representing a key strategy to reduce post-harvest losses and improve the valorization of onions in Senegal.

Acknowledgements : The authors thank the Center for Studies on Food Safety and Functional Molecules (CESAM-RESCIF) and the Laboratory of Water, Energy, Environment, and Industrial Processes (L3EPI) of the Polytechnic School (ESP) in Dakar for technical support during this research.

Authors' Contributions: **Ngoné Fall Beye:** Conceptualization, methodology, investigation, supervision, writing original draft, writing-review and editing, validation, and data curation. **Cheikhou Kane:** Writing original draft, statistical analyses and editing, and data curation. **Alioune Sow:** Writing original draft and editing. **Francisca Nadège Sètonджи Vodounnou:** Writing original draft, and writing-review. **Nicolas Cyrille Ayessou:** Resources and supervision. **Abdou Sene:** Statistical analyses. **Codou Mar Diop:** Resources and supervision.

Conflicts of Interest : The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this article.

References

- [1] ARM, « Agence de Régulation des Marchés (ARM) : Évolution de la Production des Produits Horticoles au Sénégal », Ministère du Commerce, de la Consommation et des PME / Agence de Régulation des Marchés, sept. 2021.
- [2] DAPSA, « Direction de l'Analyse, de la Prévision et des Statistiques Agricoles : Fiche d'information sur l'oignon », 2023.
- [3] CIQUAL, « Ciqua Table de composition nutritionnelle des aliments », <https://ciqua.anses.fr/>. Consulté le: 2 mars 2018. [En ligne]. Disponible sur: <https://ciqua.anses.fr/>
- [4] N. Albitar, S. Mounir, C. Besombes, et K. Allaf, « Improving the drying of onion using the instant controlled pressure drop technology », *Dry. Technol.*, vol. 29, n° 9, p. 993-1001, juill. 2011, doi: 10.1080/07373937.2010.507912.
- [5] M. K. Krokida, V. T. Karathanos, Z. B. Maroulis, et D. Marinou-Kouris, « Drying kinetics of some vegetables », *J. Food Eng.*, vol. 59, n° 4, p. 391-403, 2003.
- [6] ADEME, « Les procédés de séchage dans l'industrie », Agence de l'Environnement et de la Maîtrise de l'Energie (ADEME). CETIAT, 2017.
- [7] T. Lhendup, « Technical and financial feasibility of a solar dryer in Bhutan », *Energy Sustain. Dev.*, vol. 9, n° 4, p. 17-24, déc. 2005, doi: 10.1016/S0973-0826(08)60496-2.
- [8] P. Gbaha, H. Yobouet Andoh, J. Kouassi Saraka, B. Kaménan Koua, et S. Touré, « Experimental investigation of a solar dryer with natural convective heat flow », *Renew. Energy*, vol. 32, n° 11, p. 1817-1829, sept. 2007, doi: 10.1016/j.renene.2006.10.011.
- [9] S. Boughali, « Etude et optimisation du séchage solaire des Produits agro-alimentaires dans les zones Arides et désertiques », PhD Thesis, Université de Batna 2, 2010.
- [10] P. S. Chauhan et A. Kumar, « Thermal modeling and drying kinetics of gooseberry drying inside north wall insulated greenhouse dryer », *Appl. Therm. Eng.*, vol. 130, p. 587-597, févr. 2018, doi: 10.1016/j.applthermaleng.2017.11.028.
- [11] N. Allanic, « Optimisation sous contraintes d'une opération de séchage combinant la convection et les technologies rayonnantes infrarouges-application a un polymère en solution aqueuse », PhD Thesis, Université de Bretagne Sud, 2006.
- [12] O. Aumporn, *Contribution à l'étude des performances d'un séchoir serre avec stockage de chaleur dans des matériaux à changement de phase*. Perpignan, 2017. Consulté le: 22 juillet 2018. [En ligne]. Disponible sur: <http://www.theses.fr/2017PERP0032>
- [13] T. H. Nguyen, « Étude expérimentale et modélisation du procédé de séchage des végétaux », p. 243, 2015.
- [14] T. T. E. Boroze, « Outil d'aide à la conception de séchoirs pour les produits agricoles tropicaux », 2011.

- [15] ADEME, « Le séchage: de sa conception optimisée à une conduite performante », 2017. [En ligne]. Disponible sur: <https://www.ademe.fr/sites/default/files/assets/documents/sechage-conception-optimisee-energie.pdf>
- [16] M. M. Alam et M. N. Islam, « Study on water sorption isotherm of summer onion », *Bangladesh J. Agric. Res.*, vol. 40, n° 1, p. 35-51, 2015.
- [17] A. A. Bouba *et al.*, « Desorption isotherms, net isosteric heat and the effect of temperature and water activity on the antioxidant activity of two varieties of onion (*Allium cepa* L.) », *Int. J. Food Sci. Technol.*, vol. 49, n° 2, p. 444-452, févr. 2014, doi: 10.1111/ijfs.12321.
- [18] G. A. Collazos-Escobar, N. Gutiérrez-Guzmán, H. A. Váquiro-Herrera, J. Bon, et J. V. Garcia-Perez, « Thermodynamic analysis and modeling of water vapor adsorption isotherms of roasted specialty coffee (*Coffea arabica* L. cv. Colombia) », *LWT*, vol. 160, p. 113335, avr. 2022, doi: 10.1016/j.lwt.2022.113335.
- [19] G. Mazza et M. LeMaguer, « Water sorption properties of yellow globe onion (*Allium cepa* L.) », *Can. Inst. Food Sci. Technol. J.*, vol. 11, n° 4, p. 189-193, oct. 1978, doi: 10.1016/S0315-5463(78)73269-4.
- [20] R. Viswanathan, D. S. Jayas, et R. B. Hulasare, « Sorption isotherms of tomato slices and onion shreds », *Biosyst. Eng.*, vol. 86, n° 4, p. 465-472, déc. 2003, doi: 10.1016/j.biosystemseng.2003.08.013.
- [21] M. Karataş et N. Arslan, « Moisture sorption isotherms and thermodynamic properties of cowpea (*Vigna unguiculate* L. Walp) stored in a chamber under controlled humidity and temperature », *J. Food Process Eng.*, vol. 45, n° 9, p. e14101, sept. 2022, doi: 10.1111/jfpe.14101.
- [22] W. A. M. McMinn et T. R. A. Magee, « Thermodynamic properties of moisture sorption of potato », *J. Food Eng.*, vol. 60, n° 2, p. 157-165, nov. 2003, doi: 10.1016/S0260-8774(03)00036-0.
- [23] S. B. Santos et M. A. Martins, « Equilibrium moisture and thermodynamic properties on desorption process of jatropa seeds », *J. Chem. Eng. Process Technol.*, vol. 07, n° 05, 2016, doi: 10.4172/2157-7048.1000318.
- [24] N. F. BEYE *et al.*, « Modeling Desorption Isotherms of Four Onion Varieties Related to Temperatures », *Food Nutr. Sci.*, vol. 16, n° 9, p. 1332-1346, sept. 2025, doi: 10.4236/fns.2025.169076.
- [25] A. Benseddik, A. Azzi, et A. Allaf, « Modélisation des isothermes de désorption de la citrouille en vue de leur séchage solaire », *Revue des Energies Renouvelables (SIENR)*, n° 14, p. 173-182, 2014.
- [26] B. Touati, B. Lips, B. Benyoucef, J. Virgone, A. Jamali, et M. Kouhila, « Effet de la température sur les isothermes et la chaleur isostérique de sorption des feuilles de menthe (*mentha viridis*) », in *Congres Annuel de la Société Française de la Thermique (SFT'07)*, Ile des Embiez, 2007, p. 1-6.
- [27] A. Touil, J. Litaïem, et F. Zagrouba, « Isothermes de sorption et propriétés thermodynamique de l'*Allium sativum* », *J. Tunis. Chem. Soc.*, vol. 17, p. 105-114, 2015.
- [28] C. T. Kiranoudis, Z. B. Maroulis, E. Tsami, et D. Marinou-Kouris, « Equilibrium moisture content and heat of desorption of some vegetables », *J. Food Eng.*, vol. 20, n° 1, p. 55-74, janv. 1993, doi: 10.1016/0260-8774(93)90019-G.
- [29] R. Jeantet, T. Croguennec, P. Schuck, et G. Brulé, *Sciences des Aliments 1- Stabilisation biologique et physico-chimique*. Lavoisier - Tec & Doc, 2008. Consulté le: 2 mars 2018. [En ligne]. Disponible sur: <https://hal.archives-ouvertes.fr/hal-01454471>
- [30] F. Cladera-Olivera, L. D. F. Marczak, C. P. Z. Noreña, et A. C. Pettermann, « Modeling water adsorption isotherms of pinhão (*araucaria angustifolia* seeds) flour and thermodynamic analysis of the adsorption process: adsorption isotherms of pinhão flour », *J. Food Process Eng.*, vol. 34, n° 3, p. 826-843, juin 2011, doi: 10.1111/j.1745-4530.2009.00437.x.
- [31] C. F. García, P. C. Moyano, et F. Pedreschi, « Enthalpy-entropy compensation for water loss of vegetable tissues during air drying », *Dry. Technol.*, vol. 26, n° 12, p. 1563-1569, nov. 2008, doi: 10.1080/07373930802466997.
- [32] P. S. Madamba, R. H. Driscoll, et K. A. Buckle, « Enthalpy-entropy compensation models for sorption and browning of garlic », *J. Food Eng.*, vol. 28, n° 2, p. 109-119, mai 1996, doi: 10.1016/0260-8774(94)00072-7.

- [33] S. Simal, A. Femenia, Á. Castell-Palou, et C. Rosselló, « Water desorption thermodynamic properties of pineapple », *J. Food Eng.*, vol. 80, n° 4, p. 1293-1301, juin 2007, doi: 10.1016/j.jfoodeng.2006.10.001.
- [34] A. Jamali, M. Kouhila, L. A. Mohamed, A. Idlimam, et A. Lamharrar, « Moisture adsorption-desorption isotherms of Citrus reticulata leaves at three temperatures », *J. Food Eng.*, vol. 77, n° 1, p. 71-78, nov. 2006, doi: 10.1016/j.jfoodeng.2005.06.045.
- [35] N. E. Maati et K. Meghazi, « Détermination expérimentale et mathématique des isothermes de sorption des dattes de la variété Deglet-nour », Thesis, université Ghardaia, 2023. Consulté le: 30 septembre 2025. [En ligne]. Disponible sur: <https://dspace.univ-ghardaia.edu.dz/xmlui/handle/123456789/6665>
- [36] Z. Zhang, X. Li, H. Jia, et Y. Liu, « Moisture sorption isotherms and thermodynamic properties of tiger nuts: An oil-rich tuber », *LWT*, vol. 167, p. 113866, sept. 2022, doi: 10.1016/j.lwt.2022.113866.
- [37] N. F. Beye, C. Kane, N. C. Ayessou, C. Talla, A. Sene, et C. M. Diop, « Influence of variety and maturity level on natural convective heat drying of four onion varieties grown in Senegal », *Food Nutr. Sci.*, vol. 09, p. 997, août 2018, doi: 10.4236/fns.2018.98073.
- [38] P. C. Corrêa, M. F. T. Reis, G. H. H. de Oliveira, A. P. L. R. de Oliveira, et F. M. Botelho, « Moisture desorption isotherms of cucumber seeds: modeling and thermodynamic properties », *J. Seed Sci.*, vol. 37, n° 3, p. 218-225, sept. 2015, doi: 10.1590/2317-1545v37n3149549.
- [39] S. Ourouadi, « Valorisation de l'ail marocain (*Allium sativum* L.) : propriétés physico-chimiques et nutraceutiques ; étude expérimentale et modélisation du procédé de conservation par séchage solaire convectif », Université Sultan Moulay Slimane Faculté des Sciences et Techniques, Béni-Mellal -Maroc, 2019.
- [40] B. K. Koua, P. M. E. Koffi, P. Gbaha, et S. Toure, « Thermodynamic analysis of sorption isotherms of cassava (*Manihot esculenta*) », *J. Food Sci. Technol.*, vol. 51, n° 9, p. 1711-1723, sept. 2014, doi: 10.1007/s13197-012-0687-y.
- [41] P. Yogendrarajah, S. Samapundo, F. Devlieghere, S. De Saeger, et B. De Meulenaer, « Moisture sorption isotherms and thermodynamic properties of whole black peppercorns (*Piper nigrum* L.) », *LWT - Food Sci. Technol.*, vol. 64, n° 1, p. 177-188, nov. 2015, doi: 10.1016/j.lwt.2015.05.045.
- [42] K. S. Silva, T. C. Polachini, M. Luna-Flores, G. Luna-Solano, O. Resende, et J. Telis-Romero, « Sorption isotherms and thermodynamic properties of wheat malt under storage conditions », *J. Food Process Eng.*, vol. 44, n° 9, p. e13784, sept. 2021, doi: 10.1111/jfpe.13784.
- [43] L. E. Kurozawa, R. A. De Oliveira, M. D. Hubinger, et K. J. Park, « Thermodynamic Properties of Water Desorption of Papaya: Thermodynamic Properties of Desorption of Papaya », *J. Food Process. Preserv.*, vol. 39, n° 6, p. 2412-2420, déc. 2015, doi: 10.1111/jfpp.12491.
- [44] J. D. Bustos-Vanegas, P. C. Corrêa, J. S. Zeymer, F. M. Baptestini, et R. C. Campos, « Moisture sorption isotherms of quinoa seeds: thermodynamic analysis », *Eng. Agríc.*, vol. 38, n° 6, p. 941-950, déc. 2018, doi: 10.1590/1809-4430-eng.agric.v38n6p941-950/2018.
- [45] A. L. Gabas, F. C. Menegalli, et J. Telis-Romero, « Water Sorption Enthalpy-Entropy Compensation Based on Isotherms of Plum Skin and Pulp », *J. Food Sci.*, vol. 65, n° 4, p. 680-680, mai 2000, doi: 10.1111/j.1365-2621.2000.tb16072.x.
- [46] V. R. N. Telis, A. L. Gabas, F. C. Menegalli, et J. Telis-Romero, « Water sorption thermodynamic properties applied to persimmon skin and pulp », *Thermochim. Acta*, vol. 343, n° 1-2, p. 49-56, janv. 2000, doi: 10.1016/S0040-6031(99)00379-2.
- [47] J. Viganó, A. L. Gabas, et J. Telis-Romero, « Moisture Sorption Characteristics of Pineapple Processing Waste: Shell and Central Cylinder », *J. Food Process Eng.*, vol. 37, n° 2, p. 100-110, avr. 2014, doi: 10.1111/jfpe.12064.