



Experimental Determination of Desorption Isotherms and Isotheric Heat of Smoked Sardinella

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Abstract The determination of desorption isotherms is an indispensable step in a drying process. In our study we made the hygroscopic characterization of the smoked sardinella by the determination of the desorption isotherms. These isotherms were determined experimentally for three different temperatures (40°C, 50°C and 60°C). This determination was carried out by the static gravimetric method of the five saturated salt solutions (KOH, K₂CO₃, NaBr, KCl and NaCl). The experimental results were then smoothed by six models (GAB, BET, HENDERSON, OSWIN, PELEG) to describe the steady state of this product. The modelling allowed us to conclude that the PELEG model is the best model for the description of the desorption isotherms of smoked sardinella. From the results obtained, we determined the isosteric heat of desorption of smoked sardinella.

Keywords smoked sardinella, desorption isotherm, isosteric heat, hygroscopic characterisation, modelling

1. Introduction

Dried smoked sardinella is increasingly consumed in Senegal. Experimental determination of desorption curves and the development and use of mathematical models can facilitate the improvement of the processing quality of this product. In drying processes, desorption isotherms make it possible to determine the equilibrium water content of the product with its environment, which is the limit of water content at the end of drying. The value of the equilibrium moisture content is also an important parameter appearing in models that predict the evolution of the moisture content of the product during drying and storage [1].

The objective of this study is to determine the desorption isotherms of smoked sardinella. The static gravimetric method is used for this purpose. The desorption isotherms are also used to calculate the amount of heat required to evaporate the water molecules to the equilibrium water content. The knowledge of this total heat quantity is important for the dimensioning of drying and storage equipment to a lesser extent [2].

2. Materials and methods

The experimental device used is composed of:

- An oven filled with ten jars, each containing a different saline solution.
- A desiccator to dehydrate the samples.
- Porcelain capsules to put the product in.
- An electronic balance with an accuracy of 1/10 000.
- Une balance électronique avec une précision 1/10000





Figure 1: Experimental device

The static gravimetric method was used to determine the desorption curves of the smoked sardinella. This method ensures the regulation of humidity by contact with aqueous salt solutions above which the water vapour pressure at a given temperature is perfectly known. We used five saturated salt solutions: KOH, K_2CO_3 , NaBr, NaCl, KCl. These solutions make it possible to obtain relative humidities varying from 0.05 to 0.9. They are prepared in hermetically sealed jars and are kept in a temperature-controlled oven. The sample is suspended in the jar, above the salts, and thus remains in a temperature and humidity stabilized environment. The experiment is carried out at three temperatures: 40, 50 and 60 °C.

Table 1 below gives the water activity values of the different solutions used at different temperatures [3].

Table 1: Water activity values of the different solutions used

Salt solutions used	Water activities		
	40°C	50°C	60°C
KOH	0.063	0.057	0.056
K_2CO_3	0.422	0.456	0.45
NaBr	0.532	0.509	0.497
NaCl	0.747	0.744	0.745
KCl	0.823	0.812	0.803



The mass of the product used for desorption is 7.0000 ± 0.0001 g. The loss of mass is monitored by a balance with a precision of ± 0.0001 g. Hygroscopic equilibrium is obtained when the exchange between the product and the ambient air is complete. As soon as the wet masses have been determined, the samples are placed in an oven at 105°C for 24 hours to determine their dry masses.

3. Modelling of the desorption isotherms of smoked sardinella

Several mathematical models describe the relationship between equilibrium water content, equilibrium relative humidity and temperature. In our study; we used five models to smooth the desorption isotherms of our product: BET, ATM, Henderson, Oswin and Peleg. The goal is to determine the most suitable model(s) for the description of the desorption isotherms of our product [4].

Table 2 shows the five models studied [5].

Table 2: Mathematical models of sorption isotherms

Auteurs	Modèles	Paramètres	Domaine
BET	$X_{eq} = \frac{ACa_w}{(1-a_w)(1-a_w+Ca_w)}$	A, C	Monocouche
GAB	$X_{eq} = \frac{ABCa_w}{(1-Ka_w)(1-Kaw+CKa_w)}$	A, B, C	Courbe complète
Oswin	$X_{eq} = A \left[\frac{a_w}{1-a_w} \right]^B$	A, B	Courbe complète
Henderson	$X_{eq} = \left[\frac{\ln(1-a_w)}{-A} \right]^{1/B}$	A, B	Courbe complète
Peleg	$X_{eq} = Aa_w^{K_1} + Ba_w^{K_2}$	K_1, K_2	Courbe complète

Where A, B, C, K1, K2 are model constants and T is the temperature in degrees Kelvin. The parameters of these models vary as a function of temperature.

The models are compared based on the correlation coefficient (R^2), the relative error (P), the root mean square error (RMSE) and the average of the sum of the root mean square errors (RMSE) and the chi-2 reduced chi-2 (χ^2) obtained from the Origin Pro.8 software where RMSE and χ^2 give the difference between the experimental and modelled values. The best model will be the one with the highest correlation coefficient (almost equal to 1) and the smallest values of P, RMSE and χ^2 . These parameters can be calculated by the following equations 1; 2 and 3

$$RMSE = \left[\frac{1}{N} \sum_{i=1}^N (X_{exp,i} - X_{mod,i})^2 \right]^{\frac{1}{2}} \quad (\text{Error! Bookmark not defined.})$$

$$\chi^2 = \frac{\sum_{i=1}^N (X_{exp,i} - X_{mod,i})^2}{N-n} \quad (2)$$

$$P(\%) = \frac{100}{n} \sum_{i=1}^N \frac{X_{exp} - X_{mod}}{X_{exp}} \quad (3)$$

X_{exp, i}: i-th experimentally obtained reduced water content

X_{exp, i}: i-th reduced water content obtained with the model studied

N: number of measuring points

n : number of parameters



4. Results and Discussions

Experimental Results

Experimental results of desorption of smoked sardinella at different temperatures (40, 50 and 60°C) are presented in figures (2), (3) and (4). These represent the evolution of the Xeq equilibrium water content as a function of the water activity of the medium for the temperatures studied. This is observed for activities that vary between 0.05 < Aw < 0.9.

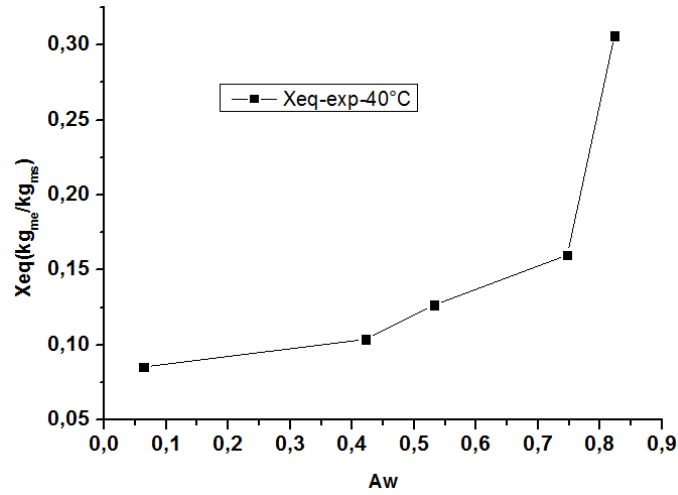


Figure 2 : Isothermal desorption of sardinella smoked at 40°C

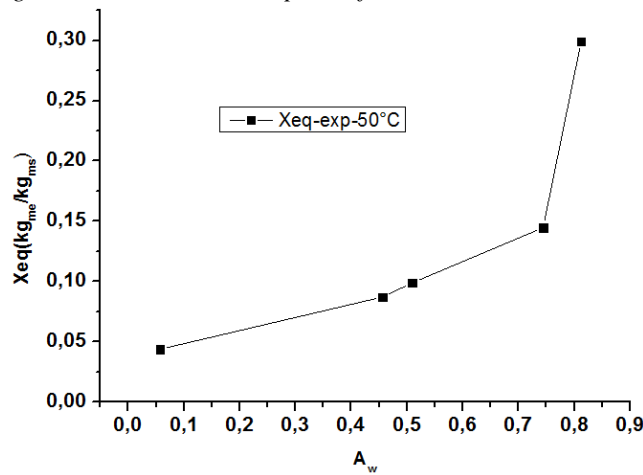


Figure 3 : Isothermal desorption of sardinella smoked at 50°C

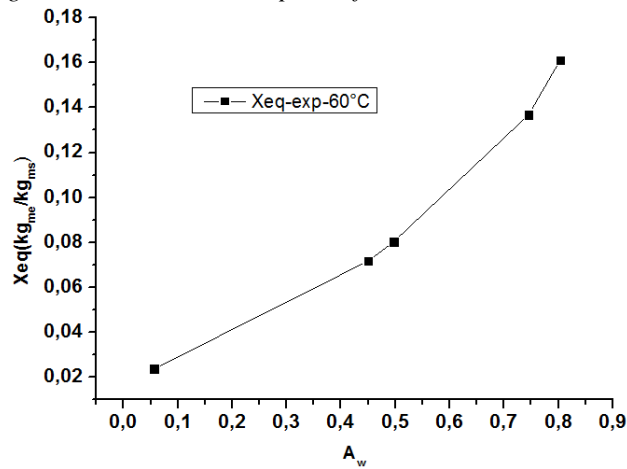


Figure 4 : Isothermal desorption of sardinella smoked at 60°C

The curves have a sigmoidal shape similar to those commonly presented by several products [6]. It can be seen that the water content increases with water activity. We also note that an increase in temperature is accompanied by an increase in water activity for a constant water content.

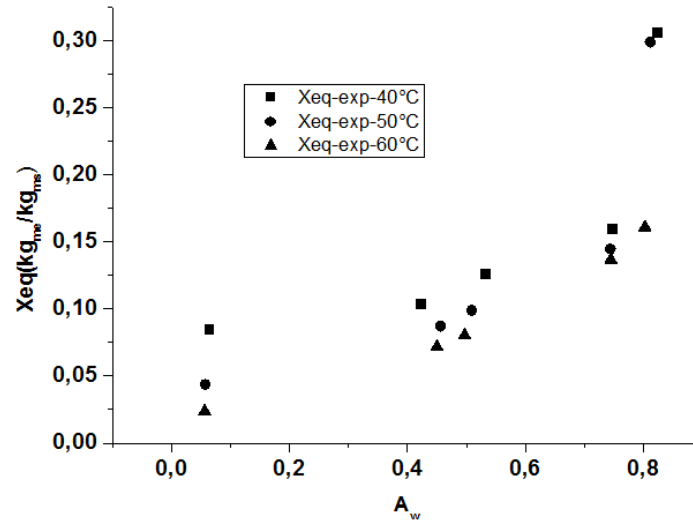


Figure 5 : Influence of temperature on desorption isotherms

For a given water activity, the equilibrium water content of smoked sardinella decreases with increasing temperature, which is consistent with the results obtained by many authors for high-protein products [7]. At higher temperatures the excitation state of the molecules is higher, leading to a decrease in the attraction forces of the water molecules to each other. At constant temperatures, water activity (A_w) increases with the equilibrium water content (X_{eq}).

To ensure the microbiological quality of the product and its preservation, the water activity (A_w) must be less than 0.6. This activity value corresponds to equilibrium water contents between $0.10 < X_{eq} < 0.13$ in desorption for air temperatures between 40°C .50°C and 60°C.

Modelling Results

The following Table 3 gives us the adjustment parameters on the experimental results.

Table 3: Values of the coefficients determined for the desorption isotherms

	Modèles	RMSE	χ^2	R ²	P(%)
40°C	BET	0.03444	0.00119	0.88582	19.7916
	GAB	0.04177	0.00174	0.88799	5.839871
	Oswin	0.04896	0.0024	0.76914	15.16156
	Henderson	0.05868	0.00344	0.66846	42.99626
	Peleg	0.001313	$1.72285 \cdot 10^{-4}$	0.99447	0.27551
50°C	Modèles	RMSE	χ^2	R ²	P(%)
	BET	0.03469	0.0012	0.90719	9.50483
	GAB	0.03264	0.00107	0.94523	12.62525
	Oswin	0.00568	0.0012	0.86877	37.36473
	Henderson	0.04892	0.00239	0.81544	22.93572
Peleg	0.00568	$3.22715 \cdot 10^{-5}$	0.99917	0.01917	
60°C	Modèles	RMSE	χ^2	R ²	P(%)
	BET	0.01253	$1.57099 \cdot 10^{-4}$	0.9605	5.790517
	GAB	0.01384	$1.915 \cdot 10^{-4}$	0.96794	19.4199
	Oswin	0.00212	$4.49586 \cdot 10^{-6}$	0.99887	5.082849
	Henderson	0.01372	$1.88354 \cdot 10^{-4}$	0.95271	43.83319
Peleg	0.00156	$2.42488 \cdot 10^{-6}$	0.9998	0.019911	

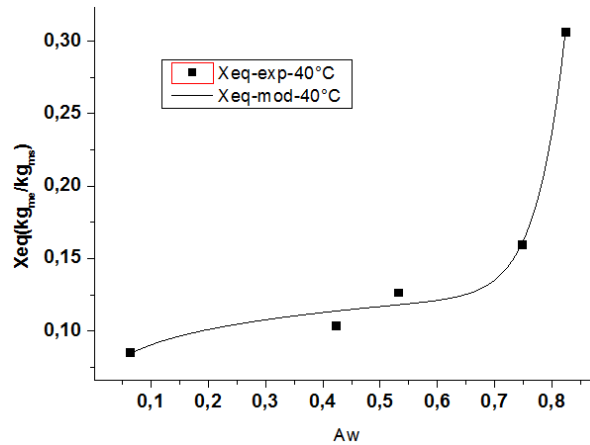


Figure 6: Desorption isotherm of sardinella smoked at 40°C obtained from modelling.

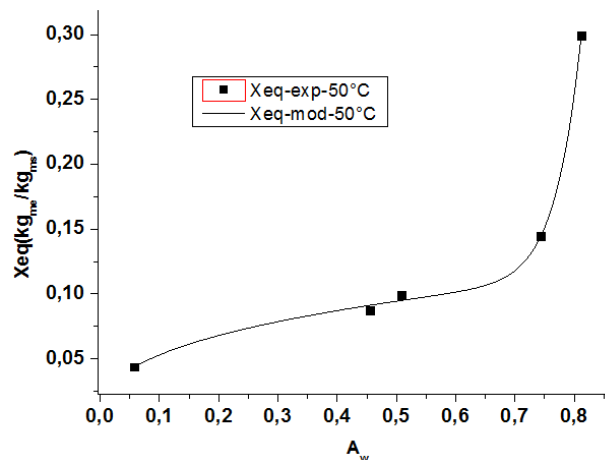


Figure 7: Desorption isotherm of sardinella smoked at 50°C obtained from modelling

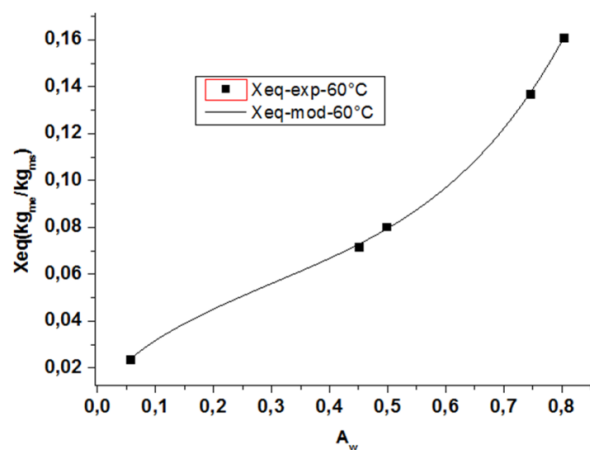


Figure 8: Desorption isotherm of sardinella smoked at 60°C obtained from modelling

Contrary to some authors who claim that the BET model is more efficient for water activities between 0.05 and 0.45 and that the GAB model is better for products with high water content [7], whatever the range of activity considered and temperature, the Peleg model is the best to describe the desorption isotherms of our product. Among the models tested, the Peleg model provides the best fit for the experimental desorption isotherms of smoked sardinella. The desorption isotherms of the smoked sardinella measured and calculated for the Peleg model for the different temperatures studied are shown in figure 3. These isotherms are in agreement with the analysis of the calculated R², P, RMSE and χ^2 values.

The values of the coefficients A, B, K1 and K2 of the Peleg model are obtained from the software by setting initial values at the beginning of the program. These values are given in table 3 below.

Table 4: Peleg model parameter values

Peleg	A	B	K1	K2
40°C	4.67122	0.13047	16.72165	0.15915
50°C	0.12107	9.44519	0.35844	18.84288
60°C	0.19007	0.1015	0.5053	2.42488.10 ⁻⁶

Determination of the isosteric heat of desorption of smoked sardinella

The isosteric heat is equal to the sum of the latent heat of vaporization of water (L_{vap}) and the net isosteric heat of desorption (Q_{st}). It is given by equation (4). The isosteric heats are calculated from the desorption isosteres, i.e. the curve giving $\ln(Aw)$ as a function of $1/T$ at a constant water content (Figure 9) according to equation (5) [8].

$$Q_s = Q_{st} + L_{vap} \tag{4}$$

$$\ln(Aw) = -\left(\frac{Q_{st}}{R}\right)\frac{1}{T} + K \tag{5}$$

This isosteric heat is calculated from the desorption isosteres.

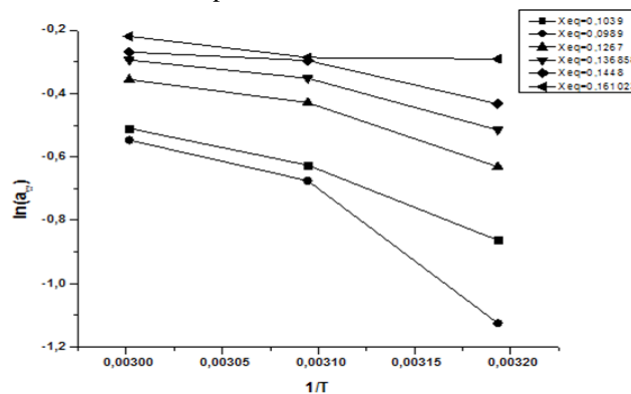


Figure 9: Desorption isostere of smoked fish as a function of the inverse of the temperature for different water contents

Figure 10 shows that the isosteric heat of desorption decreases as the equilibrium water content increases. High isosteric heat values for low water contents indicate a strong binding of water in the product to be dried. The isosteric heat of desorption decreases continuously with increasing water content, moving towards the latent heat of vaporization of pure water (0.13338 kJ/mol). This indicates that the vapour of the adsorbed water can behave like pure water when the water content is high.

The rapid decrease in isosteric heat for low water contents in the product is due to the existence of the highly active polar sites in the product which are covered with water molecules forming the molecular monolayer [8]. Other authors ([9],[10]) have explained this phenomenon by the fact that in a very restricted range of humidity, when the water content increases, some products swell and promote the opening of new adsorption sites of strong bonds, thus increasing the isosteric heat.

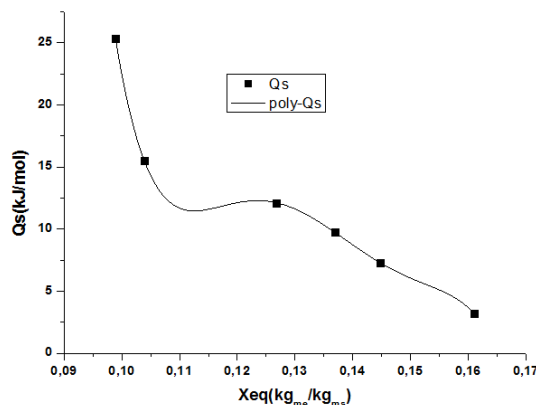


Figure 10: Isosteric heat of desorption as a function of water content

These results are consistent with those generally observed for most food products (such as spearmint leaves). The knowledge of isosteric heat of desorption is therefore very important for a good design of drying equipment. Indeed, for example, it turns out that in order to reach the water activity values that ensure the stability of the smoked sardinella ($A_w < 0.6$), i.e. equilibrium water content values between 0.10 (dry basis) and 0.13 (dry basis) depending on the temperature of the drying air, an energy of at least 10 kJ/mol is required.

5. Conclusion

The determination and modelling of sorption isotherms is an essential step in any drying process. Their knowledge is an essential step to better understand and apprehend the problems related to conservation, experimentation and modeling of drying processes. From the results obtained, we can conclude that the sorption isotherms of smoked sardinella follow the general shape of the sorption curve and that Peleg's model describes well the sorption isotherms for different temperatures. It is also noted that the net isosteric heat of smoked fish decreases with increasing water content. Finally, knowing the equilibrium moisture content of the smoked sardinella, we can now consider determining its behaviour in a solar dryer operating under forced convection.

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