

Modelling the Desorption Isotherms of Chestnuts

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Abstract

The sorption isotherm of food material is pertinent in the processing and storage of food products. Desorption isotherms for peeled and unpeeled chestnuts were investigated using the hygrometric technique at 60 °C and water activity (*aw*) ranged between 0.989 and 0.23.

The experimental data were compared with four widely recommended models in the literature for food sorption isotherms (GAB, Freundlich, Henderson, and Smith). A non-linear least square regression program was used to evaluate the models constants. The four models were found to be acceptable for predicting the moisture sorption isotherms for chestnut cultivars. However, the empirical Smith model followed by the kinetic GAB was found to better represent the experimental data in the water activity range. Overall, the Smith model appears to be most suitable for fitting the desorption moisture isotherms data for the chestnut.

Key Words: Chestnut, Model, Desorption, Isotherm.

1. Introduction

The European chestnut (*Castanea sativa* Mill.) is a traditional product with an important role in the economy of the Mediterranean countries, where it is mainly consumed unprocessed [1]. Although it is a seasonal nut (autumn and winter), it is nowadays consumed in many different forms such as marron glace, purees, flours, as pre-cooked products, and even as frozen products [2]. In recent years, it has been observed an increased interest of the consumers in chestnut fruits because of their nutritional qualities and potential beneficial health effects. In fact, the chemical composition of sweet Portuguese chestnut cultivars from three protected designation of origin (PDO) areas in the Trás-os-Montes reveals that nuts were characterized by high moisture content (50 %), high levels of starch (43 % (dry matter)) and low fat content (3 % (dry matter)). In addition, chestnuts contain significant amounts of fibre (3 % d.m.), are rich in minerals, such as K, P, and Mg, and are a good source of total amino acids [3].

The worldwide production (around 250 000 ton/year) is concentrated basically in regions of Middle East and Europe. In Portugal, the main production area is located in the Trás-os-Montes region (Northeast of Portugal), with an important role in the economy and landscape patrimony, contributing with 84 % of the total of Portuguese's production [3],[4].

The knowledge of the sorption characteristics is essential with respect to stability in storage and acceptability of food products, drying process modelling, design and optimization of drying equipment, aeration, calculation of moisture changes which may occur during storage, and for selecting appropriate packaging materials [5],[6].

Despite the availability of a variety of water-based criteria, which can give indications of food's stability, water activity is one of the most effective and useful measurements of water in food, with particular emphasis to microbial growth and enzyme activity [7]. In fact, the stability is mainly a consequence of the relationship between the equilibrium moisture content of the food material and its correspondence water activity at a given temperature and it gives an insight into the moisture-binding characteristic of a food.

Although several mathematical models exist to describe water sorption isotherms of food materials none of the equations typically tested gives accurate results throughout the whole range of water activities, or for all types of foods. Labuza (1975) [8] attributed this to the fact that the water is associated with the food matrix by different mechanisms in different water activity regions.

Many models have been previously proposed to describe the relationship between equilibrium moisture content and water activity [9]. However, following the insights of Al-Muhtaseb et al.

(2004) [10] these models can be divided into several categories, namely: kinetic models based on a mono-layer (Mod-BET model); kinetic models based on a multi-layer and condensed film (GAB model); semi-empirical (Ferro-Fontan, Henderson and Halsey models); and empirical models (Smith and Oswin models). The GAB model is considered to be the most versatile sorption model available in the literature [11]. Food systems typically exhibit type II and III isotherms according to the BET classification [12].

The evaluation of moisture desorption behaviour of chestnut is important for selecting more adequately the drying and storage conditions. The preservation of foods with high starch content depends essentially on its sorption parameters. However, information on water sorption isotherm of chestnut is scarce [13], [14].

Since the processes of conservation of this product involves dehydration and storage steps, the main aim of this work is to determine desorption isotherms for three Portuguese chestnuts over a wide range of water activities. To accomplish this purpose, the experimental data were fitted using four widely recommended isotherm models.

2. Experimental

Chestnut of the cultivars Judia, Longal, and Martainha used in this study were collected in the North of Portugal. The average initial moisture content of Judia, Longal, and Martainha varieties were, respectively, 49.8 %, 51.1 %, and 41.71 % (wet basis). The study used both chestnuts with the pericarp (external shell) and endocarp (internal skin), and chestnuts without these two natural resistances (previous careful peeling). When the pericarp and endocarp is present the chestnut is named as unpeeled while when both skins are removed the chestnut is denoted as peeled.

Desorption experiments were carried out at a temperature of 60 °C, to unpeeled and to peeled (without pericarp and endocarp) chestnuts. The chestnuts were dried in a convective drier that was designed and built in the laboratory for the drying of food products. The moisture content was continuously measured and recorded on a computer and the corresponding water activity was measured with a Rotronic Hygroskop BT-RS1. All determinations were done in duplicate in each chestnut sample.

The experimental points for the equilibrium moisture content, expressed in dry basis (W_e) and the corresponding water activity (a_w) were plotted, thus giving the adsorption isotherms. The results obtained were then fitted to different models available in the literature.

3. Mathematical Modelling

Moisture sorption isotherms of foodstuffs can be described by several mathematical models. As usual (e.g. [15]), the criteria that have been used to select the most appropriate model is based on the degree of fit to the experimental data and its simplicity to use. The sorption isotherm models used to fit the data are presented in Table 1. In the Henderson model the variable temperature (T) is expressed in Kelvin.

Table 1 - Some models found in literature to describe sorption isotherms.

Model	Equation	Parameters
GAB (Guggenheim-Andersen-deBoer) [16]	$W_e = \frac{W_m C K a_w}{(1 - K a_w) (1 - K a_w + C K a_w)}$	$W_m, C(T), K(T)$
Freundlich [17]	$W_e = K a_w^{1/n}$	K, n
Henderson [18]	$W_e = \left[\frac{\ln(1 - a_w)}{-A T} \right]^{1/B}$	A, B
Smith [19]	$W_e = A - B \ln(1 - a_w)$	A, B

The model coefficients and statistical parameters were obtained through a non-linear regression analysis performed in SigmaPlot V11.0 (Systat Software, Inc.). For evaluating the

most appropriate model to describe the desorption behavior of chestnut, some statistical indicators were used as highlighted by the following equations:

$$\text{Mean absolute error: } MAE = \frac{1}{N} \sum_{i=1}^N |V_{\text{exp},i} - V_{\text{pred},i}| \quad (1)$$

$$\text{Root mean square error: } RMSE = \sqrt{\frac{1}{N} \sum_{i=1}^N (V_{\text{exp},i} - V_{\text{pred},i})^2} \quad (2)$$

$$\text{Standard error: } SE = \frac{\sqrt{\sum_{i=1}^N (V_{\text{exp},i} - V_{\text{pred},i})^2}}{N - 1} \quad (3)$$

$$\text{Sum of square errors: } SSE = \frac{1}{N} \sum_{i=1}^N (V_{\text{exp},i} - V_{\text{pred},i})^2 \quad (4)$$

$$\text{Relative percent deviation: } RPD = \frac{100}{N} \sum_{i=1}^N \frac{|V_{\text{exp},i} - V_{\text{pred},i}|}{V_{\text{exp},i}} \quad (5)$$

In the above equations N is the number of observations and n_p is the number of parameters, while $V_{\text{exp},i}$ and $V_{\text{pred},i}$ are the experimental and predicted values for the dependent variable at any observation i . RMSE aim at comparing the differences between the experimental and predicted values, and when they approach zero it indicates that the prediction is closer to the experimental data. On the other hand, the relative percent error compares the absolute differences between those values, and for RPD under 10 % the fit is considered to be good. RMSE provides information on the short-term performance of the correlations by allowing a term by term comparison of the actual deviation between the calculated value and the measured value [20]. Other statistical information provided is the correlation coefficient, the standard error of estimate and the normality test (Shapiro-Wilk).

4. Results and Discussion

The equilibrium moisture content at different water activity (Figure 1) was used for plotting desorption isotherms for the three varieties of unpeeled chestnut. According to the classification of five general types of sorption isotherms proposed by Brunauer et al. (1940) [12], sorption curves obtained for unpeeled fruits were of type III isotherms, at least in the range of a_w studied.

For the unpeeled fruits of the three cultivars under analysis, the equilibrium moisture content increased as the water activity rises, and thus at high a_w the soluble component absorbs more water. A more detailed data analysis led to the identification of two different regions in the isotherm. At low and intermediate water activities (< 0.85), the so-called multilayer sorption region, moisture content increased nonlinearly with water activity, whereas at high water activity levels water content increased sharply and linearly with water activities due to capillarity, independently of chestnut cultivar. However, Vázquez et al. (2001) [14] identify a lower value of water activity (approximately 0.5) to the transition of the regions of adsorption bound and capillarity to desorption of chestnuts in the range of 5 °C to 50 °C.

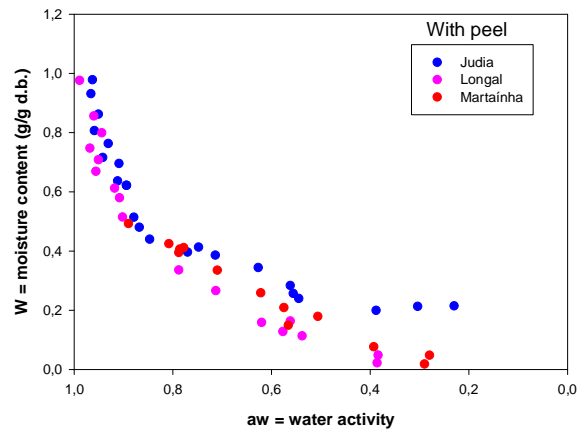


Figure 1 - Desorption for peeled chestnuts of Judia, Longal and Martainha cultivars.

As referred above, the main component of chestnut is starch, which comprises crystalline and amorphous regions. The starch sorption isotherms are attributable to hydrogen bonding of water molecules to the available hydroxyl groups of the substrate. As the crystalline regions typically exhibit resistance to solvent penetration, the water effect is very small and the mobility is restricted to the amorphous regions. However, the increase of water activity causes a subsequent swelling of the biopolymer. As a result, the degree of crystallinity decreased and augmented the availability of the polar groups to water molecules [21]. These experimental data were fitted with four models using a non-linear regression program, which calculated the fitting constants and the statistic parameters listed in Table 2.

Table 2 - Estimated values of models parameters and the corresponding statistic parameters to unpeeled chestnuts.

Model / Parameters	Judia	Longal	Martainha
GAB			
Wm	0,1258	0,0855	0,0959
C	448861,93	2211,39	2853707,63
K	0,8913	0,9256	0,9323
R	0,9812	0,9883	0,9821
MAE	0,038361	0,034829	0,0247
RMSE	0,046261	0,046551	0,028969
SSE	0,00214	0,002167	0,000839
RPD	8,49	17,16	34,43
SE	0,0101	0,0120	0,0087
Normality test: Shapiro-Wilk	Passed (P = 0,0736)	Passed (P = 0,7550)	Passed (P = 0,0925)
Freundlich			
k	0,8601	0,9023	0,6651
n	0,4388	0,2578	0,4688
R	0,9150	0,9821	0,9906
MAE	0,078325	0,048353	0,017062
RMSE	0,096619	0,057578	0,021049
SSE	0,009335	0,003315	0,000443
RPD	20,17	14,87	19,81
SE	0,0211	0,0148	0,0063
Normality test: Shapiro-Wilk	Passed (P = 0,6212)	Passed (P = 0,7408)	Passed (P = 0,2632)
Hendersen			
A	0,0116	0,0127	0,0115
B	1,1491	0,9258	0,9396
R	0,9719	0,9794	0,9724
MAE	0,044654	0,049176	0,031477
RMSE	0,056333	0,061731	0,035921
SSE	0,003173	0,003811	0,00129
RPD	11,04	36,36	39,64
SE	0,0123	0,0159	0,0108
Normality test: Shapiro-Wilk	Passed (P = 0,7683)	Passed (P = 0,0875)	Passed (P = 0,0864)
Smith			
A	0,0774	0,010	0,0315
B	0,2416	0,2267	0,2233
R	0,9786	0,9831	0,9771
MAE	0,039213	0,042065	0,027692
RMSE	0,049243	0,055964	0,032751
SSE	0,002425	0,003132	0,001073
RPD	8,75	20,25	26,81
SE	0,0107	0,0144	0,0098
Normality test: Shapiro-Wilk	Passed (P = 0,9047)	Passed (P = 0,4649)	Passed (P = 0,1295)

Figures 2, 3, and 4 show the curves obtained by fitting the experimental moisture content versus water activity data for all trials done with the three cultivars with peel.

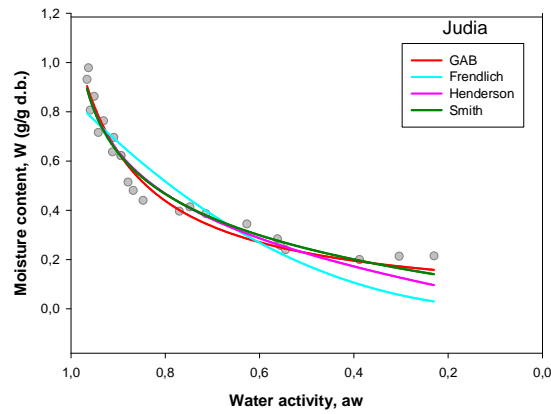


Figure 2 - Experimental points of Judia chestnut cultivar and fits obtained with the four models.

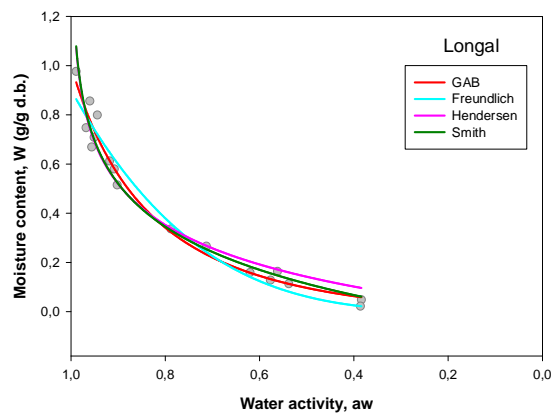


Figure 3 - Experimental points of Longal chestnut cultivar and fits obtained with the four models.

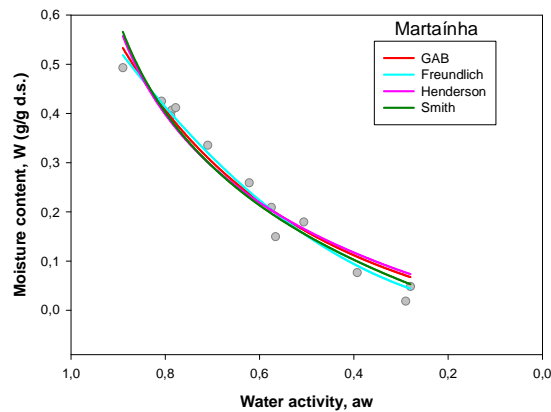


Figure 4 - Experimental points of Martainha chestnut cultivar and fits obtained with the four models.

In summary, all the four tested models were generally suitable for predicting desorption isotherms for chestnut, with their correlation coefficient ranging from 0.9150 to 0.9906. However, the Smith equation and the kinetic GAB showed the higher values of determination coefficient (R) and low statistic parameters to the three chestnut varieties. Nevertheless, the Smith model reports systematically better values of statistical parameters and it is applicable satisfactorily in all the experimental range.

In the case of the GAB model, however, the monolayer moisture content (parameter W_m of GAB model, Table 1) ranged between 0.086 and 0.126 g water/g dry basis), corresponding to a water activity of around 0.4. The monolayer moisture content is especially important, because it is considered to be the optimal moisture content for storage of a dried foodstuff. Vázquez et al 2001 [14] predicted a slight lower value of moisture content around 0.06 g water/g dry basis for peeled and fragmented chestnut.

To analyse the effect of the natural skins of chestnut (endocarp and pericarp), that protect the fruit from the external environment, samples of Judia and Longal cultivars were peeled. Figure 5 shows the desorption isotherms (Judia and Longal cultivars) for unpeeled chestnut (presence of endocarp and pericarp) and peeled chestnuts (removal of both skins).

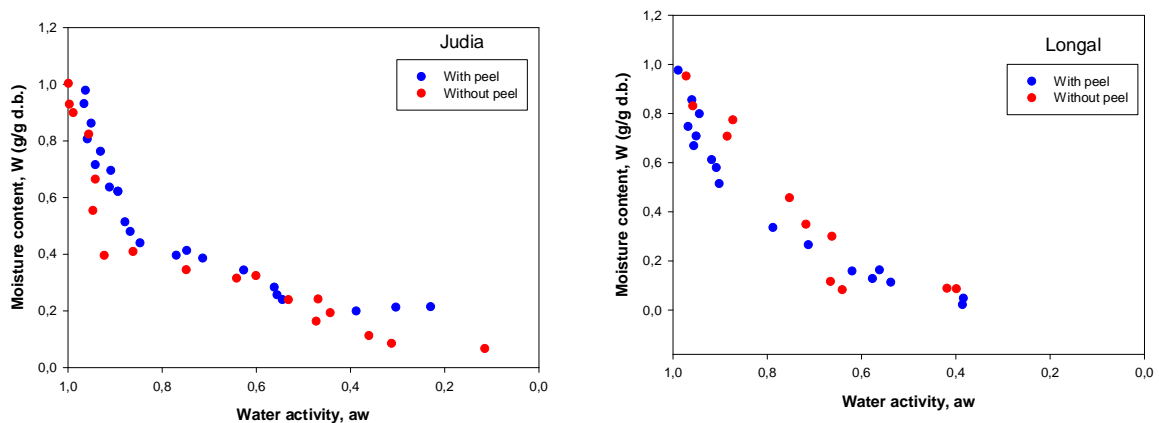


Figure 5 - Effect of peeling influence on desorption isotherms.

The Figure reveals that the chestnut barriers has a small effect on the desorption isotherms to the both varieties of chestnut.

5. Conclusions

From the results obtained it was possible to conclude that although all models tested to describe the desorption of three varieties of chestnuts at 60 °C showed some degree of adequacy, the empirical Smith model and the GAB model were found to perform a good fit of experimental desorption isotherms and both reported better values of statistical parameters. The average monolayer moisture content (grams per gram d.b.) calculated by the GAB model was 0.1 for the three varieties of chestnut.

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