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SORPTION ISOTHERMS OF PORTUGUESE VARIETIES OF PEARS

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Abstract
In this study the desorption isotherms of fresh pears were investigated at 30 ºC for fruits of the varieties *Amêndoa*, *Amorim*, *Carapinheira Branca* and *S. Bartolomeu*, all original from Portugal. This value of temperature was established to represent the summer average daily temperatures in Portugal, where the solar dried of pears is carried out. From the results obtained it was possible to verify that the behaviour of the equilibrium moisture content against the corresponding water activity is very similar for the four varieties of pears, and is of type III according to the Brunauer *et al.* (1940) classification of isotherms, very characteristic of products rich in carbohydrates (Vásquez-Uña, 2001; Rizvi, 1986).
The experimental data were fitted to the Guggenheim-Anderson-deBoer (GAB), Halsey, Hendersen and Oswin models found in literature (Viswanathan, 2003). The performance of these models was evaluated by comparing the coefficient of correlation (R), the residuals of moisture content and the prediction capabilities.
From the results obtained it was possible to conclude that the Oswin model is less appropriate for describing the process at study, and that the Chen and Halsey models are also not very adequate. The Henderson and GAB models, and this last in particular, was the one that allowed the best prediction capabilities for the isotherms of the varieties of pears studied.

Keywords: sorption isotherms, solar drying, dried pears, water activity.

1. Introduction

The equilibrium moisture content of a product, obtained by sorption isotherms, is very important for the determination of the optimal storage and package conditions as well as for the prediction of thermodynamic equilibrium models. Besides, such isotherms also give information on how strongly the water is bounded to the material and thus are essential for the prediction of the drying and rehydratation rates (Guiné, 2002a; Vázquez-Uña, 2001). The sorption isotherms can also be used for selecting appropriate storage conditions and packaging systems that optimise or maximise retention of aroma, colour, texture, nutrients and biological stability (Labuza *et al.*, 1985; Okos *et al.*, 1992).
The moisture sorption isotherms, characteristic of each product, correlate, at a constant temperature, the equilibrium water content of a food (W_e) and the its water activity (a_w) or relative humidity of the surrounding atmosphere ($HR=100*a_w$) (Park, 2001). Therefore, the knowledge of such relations is of unquestionable importance for food industry. For most foods, isotherms are nonlinear, generally sigmoidal in shape. However, for foods rich in soluble components, such as sugars, it exhibits an increasing exponential behaviour (Rizvi, 1986; Vázquez-Uña, 2001).

The preservation of fruits in the dried form is commonly practised for easy transportation and to reduce the bulk handling, and also to allow their use during the off-season. Many countries produce large quantities of the most common dried fruits, such as grapes, plums, figs or apricots, about which a large quantity of information can be found in scientific literature (Matteo, 2003). Dried fruits like apples, bananas and pears, that are produced in small quantities and by a restricted number of countries, have more recently gained increased importance, but the scientific literature published information is very scarce (Chiang, 1987; Park, 2002). In Portugal dried pears are produced in the summer almost exclusively after pears of the variety *S. Bartolomeu.* The traditional solar drying method consists of different phases described elsewhere (Ferreira, 1997; Guiné 2003). Although it is a much appreciated food product its production is very small due to the complexity and slowness of the processing method, to the intensive handwork and space requirements and to the shortcomings associated to the natural sun drying (Ferreira, 1997; Guiné and Castro, 2002b). When dried, these small sun-dried pears are highly valued for their quality, with a reddish brown colour and peculiar elastic properties (Ferreira, 2003).
The traditional open-air sun drying is being replaced by a solar stove drying process in order to reduce the drying time and to obtain a safer sun-dried product, maintaining the properties of the traditional sun-dried pear. Therefore, the small production of this dried variety of pear is expected to increase its economical importance in the near future. In addition, some other varieties of pears are gaining importance on the dried fruits market.
The aim of this paper is to investigate the sorption isotherms of four portuguese varieties of pears, including, *S. Bartolomeu* in order to compare their behaviour.

2. Material and methods

The pears used in this study are of four different varieties original from Portugal, namely: *Amêndoa*, *Amorim*, *Carapinheira Branca* and *S. Bartolomeu*. The pears of these varieties are very sweet and quite small (about 4 to 5 cm diameter maximum) and exhibit good drying features. Their initial water content ranged between 71.6 and 79.1 % and the dry basis sugar content between 57.5 and 70.7 %.
The sorption behaviour of pears has been investigated using circular slices of pears (30 mm diameter and 3 mm thick) dried in a ventilated chamber for constant drying temperature of 30 ºC. The sorptions isotherms were obtained from the measurements of the equilibrium moisture content of the pears (Mettler Toledo, HG53 Halogen moisture analyser) and the corresponding water activity (Rotronic hygrometer).

3. Results and discussion

Due to the complex food composition, theoretical prediction of water sorption isotherms is not possible and sorption data has to be determined experimentally. Many attempts have been proposed to describe mathematically the sorption isotherms of foods products. Some of these equations are based on theories on the mechanisms of sorption, others are semi-empirical or purely empirical (Adam *et al.*, 2000; Viswanathan, 2003). Out of the various types of the isotherm models some of the more widely used equations have been selected to examine whether they can be used to describe the sorption data of pears (Table 1). Halsey and Henderson models exhibit explicit temperature dependency, other include temperature dependent parameters (GAB) and in the Oswin model the temperature dependency has not been considered.
To the different models W_e is the equilibrium moisture content (dry basis), W_m is the monolayer moisture content (dry basis), a_w is the water activity, R is the gas constant (8,31451 $J.mol^{-1}.K^{-1}$) and T is the absolute temperature.

Table 1 – Common models found in literature to describe food sorption isotherms.

Model	Equation	Parameter
GAB	$W_e = \dfrac{W_m\ C\ K\ a_w}{(1 - K\ a_w)\ (1 - K\ a_w\ + C\ K\ a_w)}$	W_m , C(T) , K(T)
Halsey	$a_w = \exp\left(-\ \dfrac{A}{R\ T\ (W_e/W_m)^b}\right)$	W_m , A , b
Henderson	$1 - a_w = \exp\ (-\ C\ T\ W_e^{\ b})$	C , b
Oswin	$W_e = C\left(\dfrac{a_w}{1 - a_w}\right)^b$	C , b

Based on experimental results obtained for the different varieties of pears, the values of the parameters for the GAB, Halsey, Henderson and Oswin equations are given in Table 2. In addition to the various coefficients of the models, standard deviations of the parameters, and the coefficient of correlation (R) were also included to judge the fit. The fit of the experimental data was done using the software Sigma Plot, v. 8.0 (SPSS, Inc.).

Table 2 – Parameters for the isotherm equations for Portuguese varieties of pears.

S. Bartolomeu							
GAB		**Halsey**		**Henderson**		**Oswin**	
W_m	0.1656 (± 0.0578)	W_m	1.2601 (± 0.0653)	**C**	0.0076 (± 0.0003)	**C**	0.1940 (± 0.0304)
C	0.4112 (± 0.0330)	**A**	264.1035 (± 14.1339)	**b**	0.3628 (± 0.0259)	**b**	0.6651 (± 0.0458)
K	0.9609 (± 0.0136)	**b**	0,5455 (± 0.0265)				
R	0.9960	**R**	0.9524	**R**	0.9835	**R**	0.9864
Amêndoa							
GAB		**Halsey**		**Henderson**		**Oswin**	
W_m	0.3384 (± 0.0532)	W_m	0.1896 (± 0.0184)	**C**	0.0073 (± 0.0002)	**C**	0.1836 (± 0.0553)
C	0.1211 (± 0.0342)	**A**	731.1680 (± 57.1560)	**b**	0.3363 (± 0.0106)	**b**	0.8306 (± 0.0904)
K	0.9640 (± 0.0454)	**b**	0.5106 (± 0.0137)				
R	0.9830	**R**	0.9792	**R**	0.9965	**R**	0.9712
Amorim							
GAB		**Halsey**		**Henderson**		**Oswin**	
W_m	0.3054 (± 0.0245)	W_m	1.3653 (± 0.1693)	**C**	0.0077 (± 0.0004)	**C**	0.1254 (± 0.0272)
C	0.0885 (± 0.0046)	**A**	278.1028 (± 13.6434)	**b**	0.3491 (± 0.0231)	**b**	0.8473 (± 0.0626)
K	0.9624 (± 0.0509)	**b**	0.4870 (± 0.0215)				
R	0.9932	**R**	0.9664	**R**	0.9877	**R**	0.9861
Carapinheira Branca							
GAB		**Halsey**		**Henderson**		**Oswin**	
W_m	0.2936 (± 0.0432)	W_m	1.0465 (± 0.1698)	**C**	0.0073 (± 0.0002)	**C**	0.1513 (± 0.0370)
C	0.1547 (± 0.0317)	**A**	313.7070 (± 16.2987)	**b**	0.3410 (± 0.0119)	**b**	0.8720 (± 0.0750)
K	0.9631 (± 0.0441)	**b**	0.5075 (± 0.1228)				
R	0.9894	**R**	0.9871	**R**	0.9960	**R**	0.9835

Using a temperature of 30 ºC for the four varieties of pears the equilibrium moisture content ranged from 3.77 to 0.02 % (dry basis) and the water activity ranged between 0.981 and 0.461.

For all the varieties and in all the equations fitted, the coefficient of fit (R) ranged from 0.9524 and 0.9960 with the highest values being observed in the GAB and Henderson models. The isotherm data of *S. Bartolomeu, Amêndoa*, *Amorim* and *Carapinheira Branca* varieties fitted with the GAB, Halsey, Henderson and Oswin models are illustrated in Figures 1 to Figure 4, respectively.

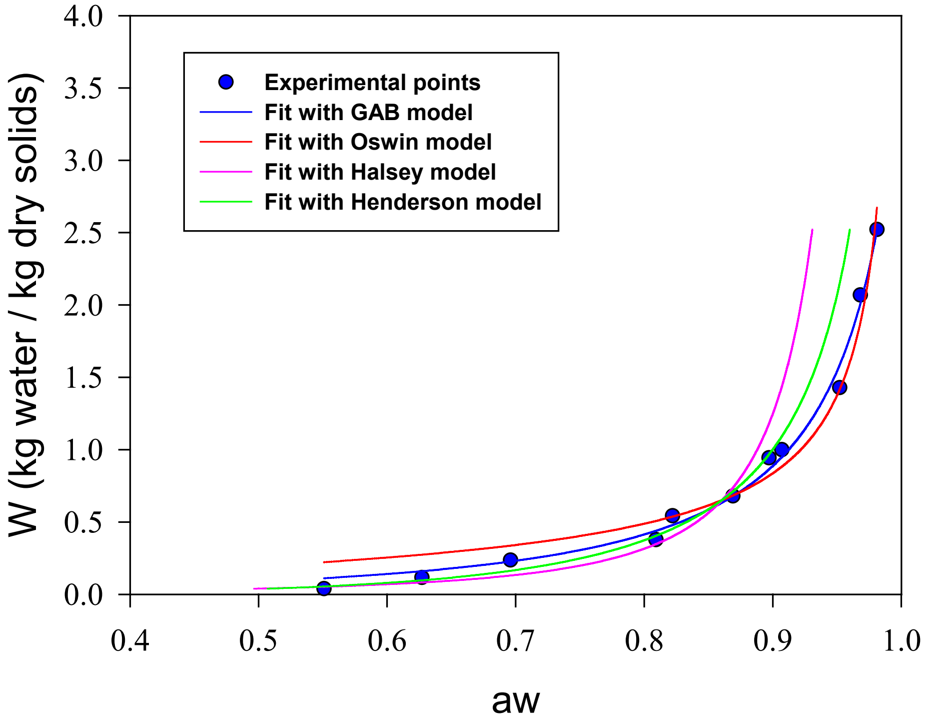

Figure 1 – Equilibrium moisture content – water activity relationship of *S. Bartolomeu* pear variety at 30 ºC: experimental data and prediction given by GAB, Halsey, Henderson and Oswin isotherm equations.

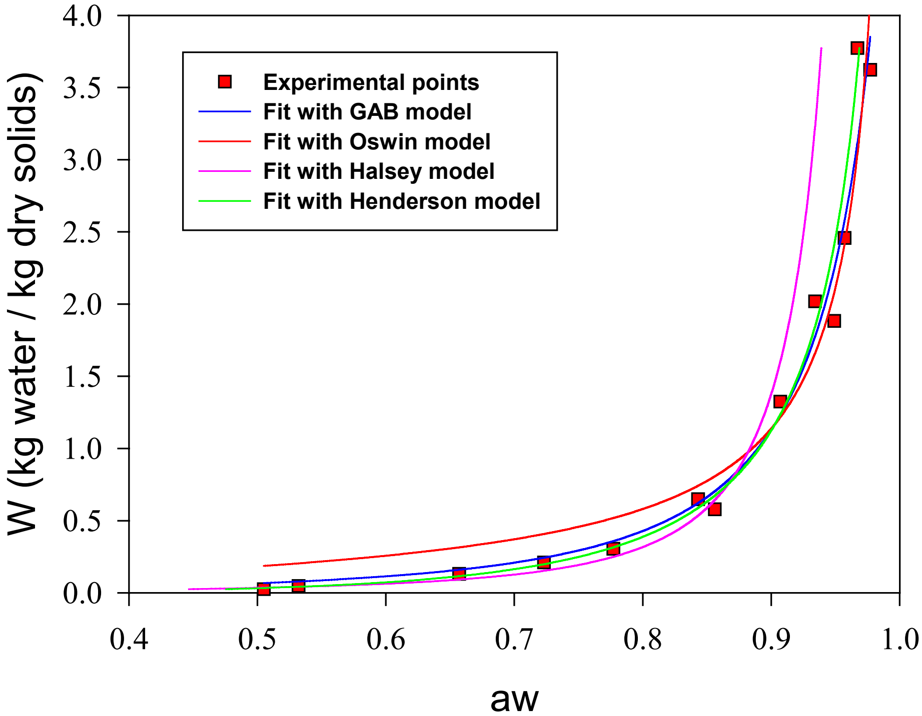

Figure 2 – Equilibrium moisture content – water activity relationship of *Amêndoa* pear variety at 30 ºC: experimental data and prediction given by GAB, Halsey, Henderson and Oswin isotherm equations.

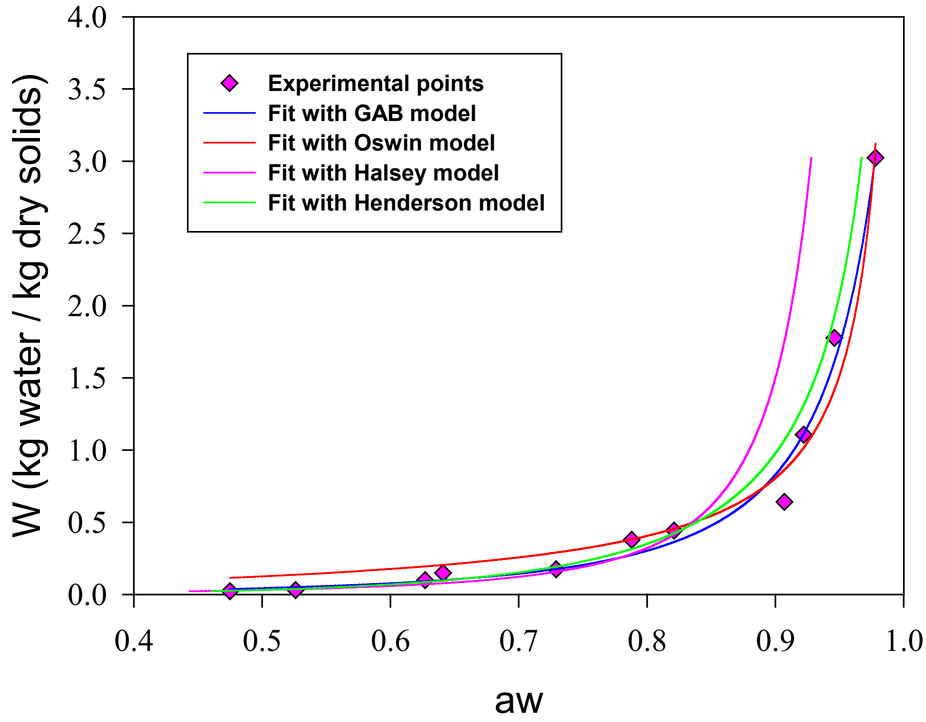

Figure 3 – Equilibrium moisture content – water activity relationship of *Amorim* pear variety at 30 ºC: experimental data and prediction given by GAB, Halsey, Henderson and Oswin isotherm equations.

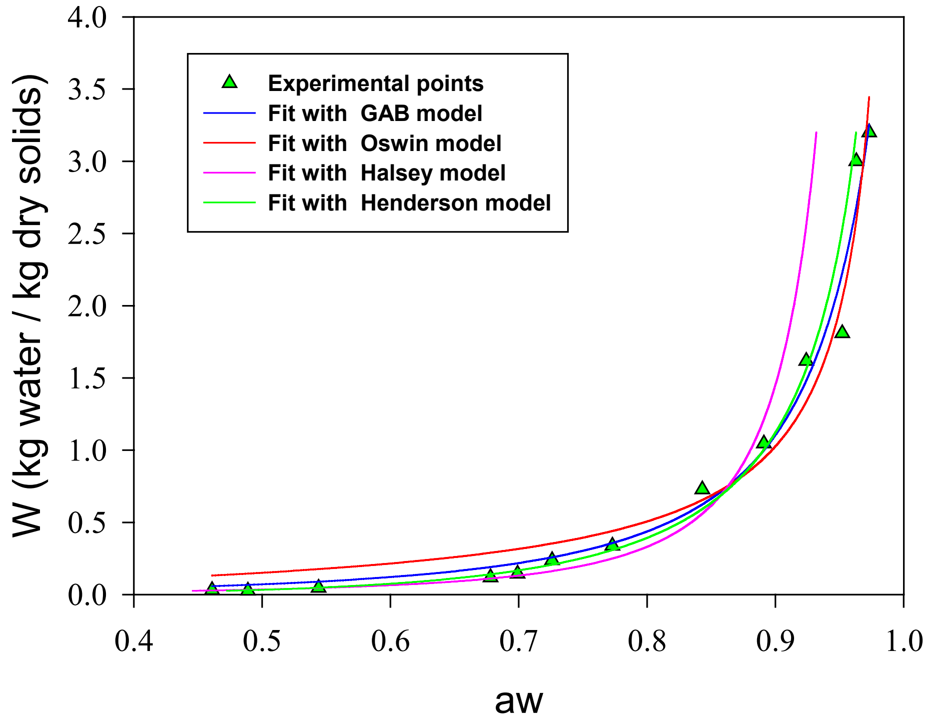

Figure 4 – Equilibrium moisture content – water activity relationship of *Carapinheira Branca* pear variety at 30 ºC: experimental data and prediction given by GAB, Halsey, Henderson and Oswin isotherm equations.

From the results obtained it was possible to verify that the behaviour of the sorption isotherms is very similar for the four varieties of pears and presents a typical increasing exponential behaviour characteristic of products rich in carbohydrates (Vásquez-Uña, 2001; Rizvi, 1986).
Based on the highest R and residual analysis, the GAB equation, among the equations tested, exhibited the best fit over the entire water activity for the four pear varieties. This is a good indication of the GAB model ability to predict the moisture sorption isotherms of pears. Generally, the Halsey and Henderson models are adequate to predict the experimental data to values of a_w up to 0.85, yet both models are less accurate for higher values of water activity. The Oswin equation, however, highlights an inverse behaviour, i.e., it is not suitable for low levels of a_w, but it fits well for higher values of water activities.
Figure 5 illustrates, for comparison, the predicted isotherm curves of the four pear varieties. Each curve was predicted using the GAB model since it was the equation with the best performance to fit the experimental values.

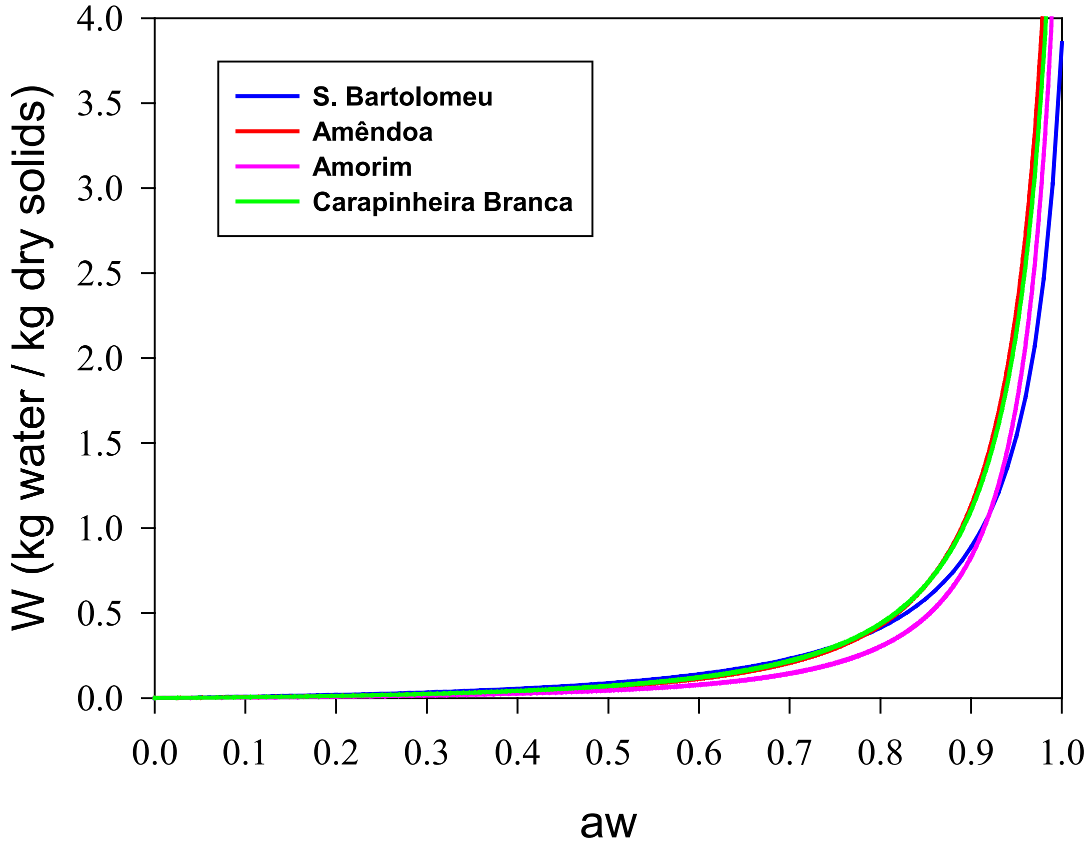

Figure 5 – Sorption isotherms for the four varieties of pears, at 30 ºC, predicted by GAB isotherm equations.

The results show a similar relationship between the a_w and the equilibrium moisture content for the four varieties of pears studied. At low moisture content, corresponding to water activities values between 0.02 and 0.5, the sorption isotherms are almost coincident for four varieties. As the moisture content rises beyond 0.45 (dry basis) the differences between the sorption isotherms for the four varieties of pears become more evident.

However, the varieties *Amêndoa* and *Carapinheira Branca* seem to exhibit an analogous behaviour over the entire water activity range. This could be due to their greater similarity, when compared to the other two varieties, and in particular their initial sugar content, 57.7 % and 61.2 % (dry basis), since it is well known that this variable greatly influences the water activity of foods (Vázquez-Uña, 2001).

4. Conclusions

At the temperature of 30 ºC and water activities range of 0.981 and 0.461, the equilibrium moisture content of four varieties of pears ranged from 3.77 to 0.02 % (dry basis).
Among the various isotherm models under test, the GAB equation adequately fitted the isotherm data of the four Portuguese varieties of pears: *Amêndoa*, *Amorim*, *Carapinheira Branca* and *S. Bartolomeu.*

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