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Moisture sorption isotherms of castor beans. Part 1: Mathematical modeling and hysteresis

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ABSTRACT

Sorption isotherms are of great importance in post-harvest procedures, especially for predicting drying and storage, which help to establish the final moisture content of the product under certain environmental condition. Hysteresis is a phenomenon that occurs due to the difference between adsorption and desorption curves, which aids the evaluation of chemical and microbiological deteriorations, indicating the stability of stored products. Moisture sorption isotherms of castor beans were determined and hysteresis was analyzed. Static gravimetric technique at different temperatures (25, 35, 45 and 55 ± 1 °C) was used. Saturated salt solutions in the range of 37-87% ± 2% were utilized to create the required controlled relative humidity environment. Equilibrium moisture content data were correlated by different mathematical models and the Modified Halsey model presented good adjustment for the data, according to statistical procedures. Hysteresis between adsorption and desorption isotherms is present over the range of 0.2-0.9 of water activity, regardless of the temperature. This phenomenon decreases with temperature increase.

Palavras-chave:
Ricinus communis L.
teor de água de equilíbrio
modelagem matemática

Isotermas de sorção de grãos de mamona. Parte 1: Modelagem matemática e histerese

RESUMO

As isotermas de sorção são de grande importância em procedimentos pós-colheita de produtos agrícolas, em especial para predizer os processos de secagem e armazenamento os quais auxiliam a estabelecer o teor de água final no produto em determinada condição ambiental. A histerese é um fenômeno que ocorre em virtude da diferença entre as curvas de adsorção e dessorção que auxilia a avaliação de deteriorações químicas e microbiológicas indicando a estabilidade de produtos armazenados. Isotermas de sorção de grãos de mamona foram determinadas e a histerese analisada. Utilizou-se a técnica de gravimetria estática em diferentes temperaturas (25, 35, 45 e 55 ± 1 °C). Soluções salinas saturadas na faixa de 37-87% ± 2% foram utilizadas para criar o requerido ambiente controlado de umidade relativa. Os dados de teor de água de equilíbrio foram correlacionados com diferentes modelos matemáticos e o modelo de Halsey Modificado apresentou bom ajuste aos dados, de acordo com procedimentos estatísticos. Histerese entre as isotermas de adsorção e dessorção está presente na faixa de 0,2-0,9 de atividade de água independentemente da temperatura; este fenômeno decresce com o aumento da temperatura.

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Introduction

Castor beans, like most agricultural products, have the capacity to gain or lose moisture from the environment. If the moisture content increases, the risk of fungi development is higher, compromising the product's quality. Reduction of moisture content may provide economic loss due to weight loss. These moisture content changes continue until the product enters in equilibrium with the air conditions. When this occurs, it is called equilibrium moisture content or hygroscopic equilibrium. This information is useful, relating directly with drying and storage (Hessini et al., 2015).

Moisture availability for microorganisms and chemical process in hygroscopic materials is well indicated by water activity (a_w). The relationship between X_{eq} and a_w for a certain product at a given temperature (sorption isotherms) can be expressed by mathematical models. The main criteria for model selection are the fitness degree to the experimental data and model simplicity (Yanniotis & Blahovec, 2009). Usually, the temperature (T) and relative humidity (RH) range between 25-55 °C and 30-90%, respectively, is used. Modeling will provide values of X_{eq} at any given T/RH condition within this range and these conditions are encountered worldwide during storage.

Chemical composition of the product directly affects the sorption process. According to Brooker et al. (1992), products with elevated oil content adsorbs lower amount of moisture from the environment in comparison to products with high carbohydrate content. In addition, cultivar, maturity stage, physical aspects along with the form of equilibrium acquisition (adsorption or desorption) are key factors for X_{eq} of hygroscopic products. Difference between X_{eq} obtained by desorption and adsorption is denominated hysteresis (Wolf et al., 1972). Knowledge on hysteresis aids the evaluation of chemical and microbiological deteriorations, indicating the stability of stored products.

With that being stated, this work had the objective to determine sorption isotherms of castor beans. Furthermore, different mathematical models were adjusted to experimental data, in order to analyze hysteresis.

Material and Methods

Castor beans (cv. Guarani) were used. They were acquired at commercial farms from Divino city (MG, Brazil). Plantation was monitored during its growing cycle in order to obtain high quality products.

Two lots were used: the first one with initial moisture content of 82% (d.b.) for desorption process, and the second lot with moisture content of approximately 7% (d.b.) in order to perform adsorption procedure. In both lots, fruits were collected from medium part from the first plant bunch. Fruits were then homogenized and stored in low-density polypropylene bags and immediately transported to municipality of Viçosa (MG, Brazil). Beans were manually removed from fruits.

Beans from the first lot were used for desorption process. For adsorption process, the second lot was dried in an oven with forced air circulation, at 80 °C, until a final moisture content of 2.5% (d.b.). This procedure had the goal to increase data points regarding adsorption process.

Different conditions of temperature (25, 35, 45 and 55 ± 1 °C) and relative humidity (between 37 and 87 ± 2%) were used for sorption processes. These conditions were provided by an atmosphere control unit (Aminco-Aire 150/300). Removable perforated trays were placed inside the apparatus to allow air to pass through the samples, each containing 50 g of product. Airflow was monitored with rotating blades and kept around 4 m^3 min^{-1} m^{-2}. Temperature and air relative humidity were monitored using a psychrometer installed next to the trays containing the samples.

The trays containing the product were periodically weighed during drying by removing the trays from the atmosphere control unit. Hygroscopic equilibrium was reached when the mass variation of the trays remained constant during three consecutive readings. Equilibrium moisture content of castor beans for desorption and adsorption processes were determined by the gravimetric method in an oven at 105 ± 1 °C, for a 24 h period, in triplicate, according to the seed analysis standard of Brazil (Brasil, 2009).

The drying data were used to fit different mathematical models frequently used to represent the hygroscopicity of agricultural products (Eqs. 1 to 6).

- Chung Pfost (Pfost et al., 1976):

$$X_{eq} = a - b\ln\left[-\left(T + c\right)\ln\left(RH\right)\right] \tag{1}$$

- Copace (Corrêa et al., 1995):

$$X_{eq} = \exp\left(a - bT + cRH\right) \tag{2}$$

- Modified Halsey (Iglesias & Chirife, 1976):

$$X_{eq} = \left[\frac{\exp\left(a - bT\right)}{-\ln\left(RH\right)}\right]^{1/c} \tag{3}$$

- Modified Henderson (Thompson et al., 1968):

$$X_{eq} = \left[\frac{\ln\left(1 - RH\right)}{-a\left(T + b\right)}\right]^{1/c} \tag{4}$$

- Modified Oswin (Chen & Morey, 1989):

$$X_{eq} = \frac{\left(a + bT\right)}{\left[\frac{\left(1 - RH\right)}{RH}\right]^{1/c}} \tag{5}$$

- Modified GAB (Jayas & Mazza, 1993):

$$X_{eq} = \frac{a\left(\frac{b}{T}\right)cRH}{\left(1 - cRH\right)\left(1 - cRH + \frac{bcRH}{T}\right)} \tag{6}$$

where:

X_{eq} - equilibrium moisture content, % d.b.;

RH - relative humidity, decimal;
T - temperature, °C; and,
a, b, c - coefficients dependent on the product, dimensionless.

The models were estimated using a nonlinear regression by the Gauss-Newton approximation method, which minimizes the sum of square errors in a series of interactive stages. The Statistica® package version 8.0 for windows was used to fit the equations to the experimental data of castor beans.

For the selection of the model that best represents the hygroscopicity of castor beans, the significance of its parameters was evaluated by t-test, adopting a probability level of 0.01. In addition, the coefficient of determination (R^2), the mean relative error (MRE), the standard deviation of the estimate (SDE), and verification of the behavior of the residual distribution were all taken into account for the model selection. MRE of less than 10% was one of the criteria used for the selection of the model, according to Mohapatra & Rao (2005). MRE and SDE were calculated for each model using the following equations:

$$\mathrm{SDE} = \sqrt{\frac{\sum_{i=1}^{n}\left[Y - \hat{Y}\right]}{\mathrm{DF}}} \qquad (7)$$

$$\mathrm{MRE} = \frac{100}{n}\sum_{i=1}^{n}\left(\frac{\left|Y - \hat{Y}\right|}{Y}\right) \qquad (8)$$

in which:
MRE - mean relative error, %;
SDE - standard deviation of the estimate, % d.b.;
n - number of experimental observations;
Y - experimentally observed values of equilibrium moisture content;
$\hat{Y}$ - value of equilibrium moisture content calculated by the model; and,
DF - degree of freedom of the model.

The residual values, which are the differences between the experimentally observed values and the model-estimated values, were plotted as a function of the estimated levels of moisture equilibrium. A model was considered acceptable if the residual values were found in a horizontal zone near zero, not including biased results. If biased distributions were present for the residual values, the model was considered inadequate to represent the phenomenon of concern.

After model selection, an analysis of hysteresis was accomplished. It was obtained by the difference between equilibrium moisture content of desorption and adsorption.

Results and Discussion

Tables 1 and 2 list parameters of the models fitted to the hygroscopic equilibrium data of castor beans, respectively obtained by desorption and adsorption, as well their respective coefficients of determination (R^2), standard deviation of the estimate (SDE), mean relative errors (MRE), and the state of the residual plot.

From Tables 1 and 2, it is noticed that the mathematical models used to describe the hygroscopicity of castor beans presented significant parameters at 0.01 probability level by t-test, determination coefficients superior than 0.94 and low values of standard error of the estimate. According to Draper & Smith (1998), the capacity of the model to faithfully describe a certain physical process is inversely proportional to the SDE values. Thus, model selection was made by means of residual plots and lower values of SDE.

According to the results presented in Tables 1 and 2, among six models tested, Modified Halsey and Modified Oswin models presented lower values of MRE and SDE, higher values of R^2 and random residual plots. Thus, these two models are recommended to represent the equilibrium moisture content of castor beans. Furthermore, among these two models, Modified

Table 1. Parameters of the hygroscopic equilibrium models for castor beans desorption, with their respective determination coefficient (R^2), standard deviation of the estimate (SDE), mean relative error (MRE), and distribution tendency of the residual values

Model	Parameters			R^2	SDE	MRE	Residual
	a	b	c		(% d.b.)	(%)	plot
Chung Pfost	27.6764	5.5529	26.4855	0.9423	1.0021	7.9937	Biased
Copace	1.0716	0.0107	2.3624	0.9611	0.8231	6.6688	Biased
Modified Halsey	3.6311	0.0167	1.7796	0.9765	0.6373	4.5986	Random
Modified Henderson	8.78×10^{-4}	43.8799	1.2231	0.9650	0.7803	6.5432	Biased
Modified Oswin	9.0173	-0.0638	2.1239	0.9766	0.6394	4.4979	Random
Modified GAB	6.1590	0.7803	95.4824	0.9449	0.9791	8.5615	Biased

Table 2. Parameters of the hygroscopic equilibrium models for castor beans adsorption, with their respective determination coefficient (R^2), standard deviation of the estimate (SDE), mean relative error (MRE), and distribution tendency of the residual values

Model	Parameters			R^2	SDE	MRE	Residual
	a	b	c		(% d.b.)	(%)	plot
Chung Pfost	18.11	3.2058	37.4229	0.9687	0.4114	4.7921	Biased
Copace	1.0507	0.0069	1.7751	0.9744	0.3722	4.1002	Biased
Modified Halsey	4.0932	0.0140	2.3129	0.9788	0.3387	3.4379	Random
Modified Henderson	4.78×10^{-4}	56.1358	1.6276	0.9742	0.3734	4.2635	Biased
Modified Oswin	6.7476	-0.0341	2.7782	0.9814	0.3169	3.4472	Random
Modified GAB	4.3971	0.7204	228.5399	0.9594	0.4687	5.4516	Biased

Halsey presented, in general, better statistical results for the adsorption and desorption processes. Thus, the Modified Halsey model is the best mathematical model to represent sorption process of castor beans under the conditions used in the present work.

Giner & Gely (2005) studied the hygroscopicity of sunflower seeds and concluded that the Modified Halsey model was the best model to represent desorption isotherms of this product. According to these authors, the Modified Halsey model allows a better representation of sorption isotherms of oilseed crops due to the reproducibility of the abrupt increment of moisture content at elevated values of relative humidity.

Desorption and adsorption isotherms, calculated by the Modified Halsey model, are shown in Figures 1 and 2, respectively.

From Figures 1 and 2, it is noticed that hygroscopic equilibrium curves of desorption and adsorption presented sigmoidal shape-type, typical for several agricultural products (Thys et al., 2010; Oliveira et al., 2010; Cladera-Olivera et al., 2011; Noshad et al., 2012; Hessini et al., 2015). Also, it can be observed the high agreement between the experimental data and those estimated by the Modified Halsey model throughout the entire range of temperature and relative humidity utilized.

Furthermore, the temperature effect can be seen in both desorption and adsorption processes of castor beans. At a constant value of relative humidity, an increment of temperature leads to a reduction of moisture content, indicating a low hygroscopicity of castor beans at elevated temperatures. This trend is probably due to a reduction of active sorption sites available for water molecules to bond, as a result from the physical and chemical alterations promoted by the temperature (Mazza & LeMaguer, 1980). Besides, a temperature increase may also promote isotherm alteration, leading to an increase of relative humidity at the same equilibrium moisture content, allowing the product to be more susceptible to microorganism attack.

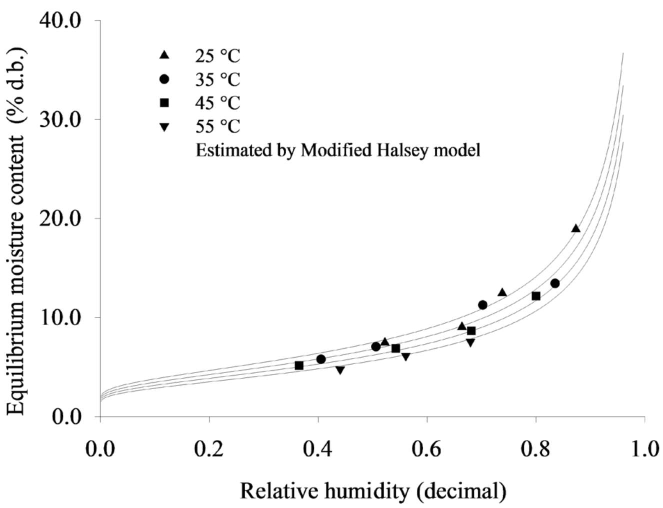

Figure 1. Desorption isotherms estimated by the Modified Halsey model

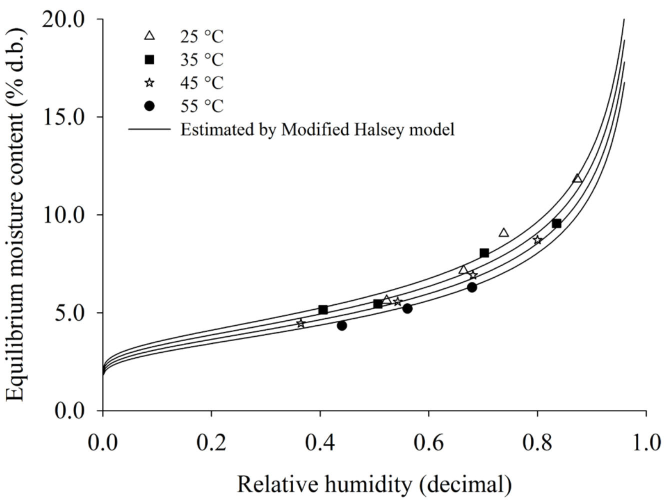

Figure 2. Adsorption isotherms estimated by the Modified Halsey model

According to Palipane & Driscoll (1992), with increase in temperature, water molecules reach higher energy levels, becoming thermodynamically less stable and, thus, permitting bonding break between water and sorption sites, reducing the moisture content of the product. As temperature varies, molecules excitation and attraction also varies. This trend makes sorbed water quantity changes as temperature varies at a given relative humidity (Mohsenin, 1986).

Figure 3 presents desorption and adsorption isotherms, estimated by the Modified Halsey model, at the different temperatures used. Through this figure, it can be observed that equilibrium moisture content values obtained by desorption are higher than those obtained by adsorption, denoting the hysteresis effect in the temperature range studied.

Different explanations for the hysteresis phenomenon are given. Al Hodali (1997) considered the structure rigidity of a connected pore, in its surroundings, by a small capillary. During adsorption, the capillary begins to swell up as a consequence of relative humidity increase, when the pore is empty. When the partial pressure of air water vapor becomes higher than capillary water vapor, water moves to the interior of the pore. On the other hand, during desorption, the pore is initially in a saturated state. Water diffusion, from periphery to the surface of the material occurs solely when the partial pressure of air water vapor is lower than water vapor from inside the capillary. Since the pore system generally shows a large variety of capillary diameter, differences between adsorption and desorption are observed (Lahsasni et al., 2004).

One of the theories most utilized to explain the hysteresis effect suggests that, in a condition of elevated water quantity, almost all sorption sites from the material's molecular structure are filled with adsorbed water. After drying, available sorption sites are reduced along with the product shrinkage. This trend leads to a reduction of water bonding capacity for a future adsorption (Mohsenin, 1986). Since a limit factor of mass transfer mechanism is water diffusion on the capillary of the products, there is a reduction of pore diameter during shrinkage. Smaller pores lead to a lower mass transfer rate, which leads to a lower velocity of water removal at final stages of desorption or initial stages of adsorption.

According to Figure 3, at constant values of relative humidity, the differences between equilibrium moisture content values of desorption and adsorption decrease with

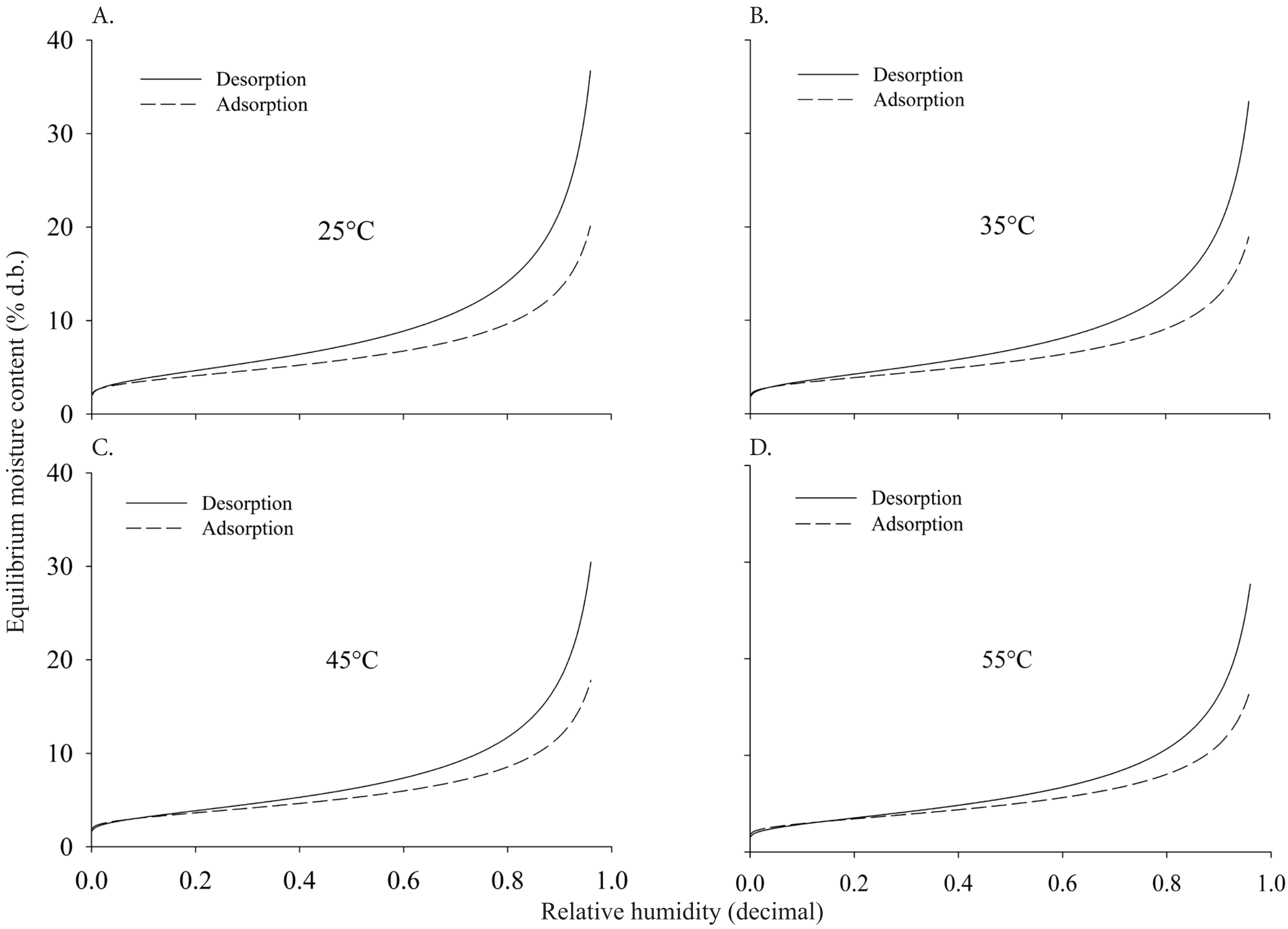

Figure 3. Desorption and adsorption isotherms, estimated by the Modified Halsey model, at different temperatures

temperature increase, indicating that hysteresis is temperature-dependent. These results are in agreement with those reported by Wolf et al. (1972), Oyelade et al. (2008), Yan et al. (2008) and Goneli et al. (2013).

Conclusions

1. Sorption process was well represented by the Modified Halsey model.

2. Hysteresis effect was noticed at all temperatures investigated.

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