MOISTURE ADSORPTION ISOTHERMS OF CASTOR BEANS

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ABSTRACT The knowledge of equilibrium moisture content of agricultural products is of fundamental importance in the determination of water loss or gain at a given condition of temperature and relative humidity, relating directly with drying and storage processes. The relationship among moisture content and relative humidity of a certain product at a specific temperature can be expressed by mathematical equations, denominated sorption isotherms. They are important to define dehydration limits of the products, as well as to estimate alterations of moisture content due to variations of environment conditions. Also, they provide information that can be used to define adequate moisture content range during storage in order to prevent processes that deteriorate the products quality. That being stated, the aim of the present work was to obtain the adsorption isotherms of castor beans at several temperature and relative humidity conditions of air. The dynamic method was employed to obtain the equilibrium moisture content of castor beans. The air conditions were provided by a temperature controlled chamber, in which removable perforated trays were placed inside the equipment to allow air to pass through the samples. Mathematical models to represent the hygroscopic properties of agricultural products were fitted to the experimental data. It was concluded that the equilibrium moisture content of castor beans, obtained through adsorption, decreases with temperature increase at a certain relative humidity, as observed by most agricultural products. Based on statistical parameters, the Modified Halsey model is the best model to represent the hygroscopic properties of castor beans to describe this phenomenon.

Keywords: Mathematical modeling, Adsorption, Equilibrium moisture content.

INTRODUCTION: The knowledge of the existent relationship among temperature and relative humidity of air is required to the correct use of drying and storage operations to preserve the product. In order to guarantee the quality of the final product, it is important that the castor beans are stored under dry environments and especially with low levels of moisture content. Otherwise, the development of microorganisms can cause...
fermentations and toxin contaminations that depreciate the product, difficulting its commercialization. Like several agricultural products, castor beans possess the capacity to concede and absorb water from the environment. If the moisture content increases, the risk of fungi growth is higher, compromising the germinative and vigor capability of seeds. From another point of view, the moisture content reduction can promote economic losses due to the weight loss of the product (Yazdani et al., 2006). These moisture content changes continue until the product reaches the equilibrium with the environmental air that surrounds it. When this trend occurs, the moisture content of the product is usually named equilibrium moisture content or hygroscopic equilibrium. The equilibrium moisture content is useful on the determination of water loss or gain under determined conditions of temperature and relative humidity, interfering directly on the drying and storage processes of agricultural products (Ghodake et al., 2007). The equilibrium moisture content happens when the partial pressure of water vapor of the product is equal to the partial pressure of water vapor of the air that surrounds the product.

The equilibrium moisture content of a hygroscopic product, in a given condition of temperature and relative humidity, depends on the path used to achieve this equilibrium. That way, to the same relative humidity, two different isotherms can be obtained, denominated adsorption and desorption isotherms, acquired in function of the initial experimental conditions. The difference between desorption and adsorption is known as hysteresis (Wolf et al., 1972).

Relationship between the moisture content of a determined product and the relative humidity of equilibrium for a specific temperature can be expressed by mathematical equations, which are known as isotherms or hygroscopic equilibrium curves (Kaymak-Ertekin & Gedik, 2004). Currently, more than 200 proposed equations exist in literature for representation of the hygroscopic equilibrium phenomenon for agricultural products. These models differ in their theoretical or empirical basis and in the quality of involved parameters (Mulet et al., 2002).

According to Ayranci and Duman (2005), isotherms are important for definition of the dehydration limits of the products, estimates of changes in the moisture content at determined temperature and relative humidity conditions, and definition of the levels of adequate moisture for initiation of microorganism activity, which can promote deterioration of the product.

Due to the importance of understanding the hygroscopicity of agricultural products, the objective of the present work was to determine adsorption isotherms for castor beans at diverse temperature and relative humidity conditions of the air and adjust different mathematical models to the experimental data, selecting that which best represents this phenomenon.

**MATERIAL AND METHODS:** The present work was carried out in the Laboratory for the Physical Properties and Quality Evaluation of Agricultural Products of National Grain Storage Training Center – CENTREINAR, Federal University of Viçosa, Viçosa, MG, Brazil.
The initial moisture content of castor beans was found to 2.5 % dry basis. The castor beans moisture content was determined by applying the oven method at 105 ± 1 °C, for a 24 h period, in triplicate according to the of Seeds Analysis Standard of Brazil (Brazil, 1992).

The adsorption method used was the dynamic technique or gravimetric method, in which the material is brought into equilibrium with air of fixed temperature and relative humidity and the equilibrium moisture content (EMC) of the material is measured. Different controlled temperature (25, 35, 45 and 55°C) and air relative humidity (between 0.37 and 0.87) were used until the product reached equilibrium moisture content at the specified air condition.

The environmental conditions for the performance of the tests consisted of a temperature controlled chamber, manufactured by Aminco, model Aminco-Aire 150/300 CFM. Removable perforated trays were placed inside the equipment so as to allow air to pass through the samples, each containing 50 g of product. Airflow was monitored with an anemometer with rotating blades and kept around 10 m³ min⁻¹ m⁻². Temperature and air relative humidity were monitored with a psychrometer installed next to the trays containing the samples.

The mathematical models presented in table 1 were adjusted to the experimental data for the equilibrium moisture content (EMC) of castor beans.

Table 2. EMC Mathematical models used for the castor beans.

<table>
<thead>
<tr>
<th>Model designation</th>
<th>Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chung-Pfost</td>
<td>[ M_e = a - b \ln \left[ - (T + c) \ln (RH) \right] ] (1)</td>
</tr>
<tr>
<td>Copace</td>
<td>[ M_e = \exp \left( a - bT + cRH \right) ] (2)</td>
</tr>
<tr>
<td>Modified GAB</td>
<td>[ M_e = \frac{ab \left( \frac{c}{T} \right)RH}{(1-bRH) \left( 1-bRH + \frac{bcRH}{T} \right)} ] (3)</td>
</tr>
<tr>
<td>Modified Halsey</td>
<td>[ M_e = \left[ \exp(a-bT)/\ln(RH) \right]^{1/c} ] (4)</td>
</tr>
<tr>
<td>Modified Henderson</td>
<td>[ M_e = \left[ \ln(1-RH)/a(T+b) \right]^{1/c} ] (5)</td>
</tr>
<tr>
<td>Modified Oswin</td>
<td>[ M_e = (a+bT)/\left[ (1-RH)/RH \right]^{1/c} ] (6)</td>
</tr>
</tbody>
</table>

where,
**M**: moisture equilibrium level, % d.b.;

**RH**: relative humidity, decimal;

**T**: temperature, °C; and

a, b, c: coefficients dependent on the product.

For selection of the model which best represents hygroscopicity of the castor beans, consideration of the magnitude of the determination coefficient ($R^2$), the relative mean error (MRE) and the standard error of estimation (SEE), and verification of the behavior of residual distribution, were all taken into account. A relative mean error value less than 10% was one of the criteria used for selection of the models, according to Mohapatra and Rao (2005). The relative mean error and standard error of estimation, for each of the models, were calculated in accordance with the following expressions:

\[
SEE = \sqrt{\frac{\sum_{i=1}^{n} (Y - \hat{Y})^2}{DF}}
\]  

\[
MRE = \frac{100}{n} \sum_{i=1}^{n} \left( \frac{|Y - \hat{Y}|}{Y} \right)
\]

in which

- \( n \): number of experimental observations;
- \( Y \): experimentally observed value;
- \( \hat{Y} \): value calculated by the model; and
- \( DF \): degree of freedom of the model.

The residual values, which are the differences between the experimentally observed values from the estimated values from the models, were plotted in function of the estimated levels of moisture equilibrium. A model is considered acceptable if the residual values are found in a horizontal zone near zero, not including biased results. If biased distributions are presented for the residual values, the model is considered inadequate to represent the phenomenon in question.

**RESULTS AND DISCUSSION**: Table 2 lists parameters of the models adjusted to the equilibrium moisture content (EMC) data of castor beans, obtained by adsorption, as well their respective coefficients of determination ($R^2$), standard errors of estimation (SEE) and relative mean errors (MRE).
Table 2. Parameters of the EMC models for castor beans, with their respective determination coefficients ($R^2$), standard errors of estimation (SEE) and relative mean errors (MRE).

<table>
<thead>
<tr>
<th>Models</th>
<th>Parameters</th>
<th>$R^2$ (%)</th>
<th>SEE (% d.b.)</th>
<th>MRE (%)</th>
<th>Residual Plot</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chung-Pfost</td>
<td>a = 18.1100</td>
<td>96.87</td>
<td>0.4114</td>
<td>4.7921</td>
<td>Patterned</td>
</tr>
<tr>
<td></td>
<td>b = 3.2058</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>c = 37.4229</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Copace</td>
<td>a = 1.0507</td>
<td>97.44</td>
<td>0.3722</td>
<td>4.1002</td>
<td>Patterned</td>
</tr>
<tr>
<td></td>
<td>b = 0.0069</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>c = 18.1100</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Modified GAB</td>
<td>a = 4.3971</td>
<td>95.94</td>
<td>0.4687</td>
<td>5.4516</td>
<td>Patterned</td>
</tr>
<tr>
<td></td>
<td>b = 0.7204</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>c = 228.5399</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Modified Henderson</td>
<td>a = 4.78 x 10$^{-4}$</td>
<td>97.42</td>
<td>0.3734</td>
<td>4.2635</td>
<td>Patterned</td>
</tr>
<tr>
<td></td>
<td>b = 56.1358</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>c = 1.6276</td>
<td></td>
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</tr>
<tr>
<td>Modified Halsey</td>
<td>a = 4.0932</td>
<td>97.88</td>
<td>0.3387</td>
<td>3.4379</td>
<td>Random</td>
</tr>
<tr>
<td></td>
<td>b = 0.0140</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>c = 2.3129</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Modified Oswin</td>
<td>a = 6.7476</td>
<td>98.14</td>
<td>0.3169</td>
<td>3.4472</td>
<td>Random</td>
</tr>
<tr>
<td></td>
<td>b = -0.0341</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>c = 2.7782</td>
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</table>

According to the results presented in table 2, for the temperature range varying from 25 to 55 °C and relative humidity of air from 0.37 to 0.87, it can be observed that the modified Halsey and modified Oswin models presented the smallest values of standard error of estimation and relative mean error, as well as the greatest determination coefficient. The rest of the models, Copace, modified Henderson, modified GAB and Chung Pfost, presented inferior adjustments when compared to the modified Halsey and modified Oswin models. All models presented relative mean errors inferior than 10 % which, according to Mohapatra and Rao (2005), is a good parameter to evaluate the adequacy of a statistical model to satisfactorily represent a biological phenomenon.

According to Aviara et al. (2004), the determination coefficient ($R^2$) and standard error of estimation (SEE) are not sufficient to prove adjustment quality of a equilibrium moisture content model to the experimental data of equilibrium moisture content, since with these statistical parameters, the distribution tendency of residual values is evaluated. Graphing of the resulting residual values from the tested models revealed that only the modified Halsey and modified Oswin models presented random distribution tendency of residual
values when compared to the other models, indication more suitable adjustment to the hygroscopicity phenomenon.

Therefore, according to the statistical parameters used in the present work, it can be observed that Modified Halsey and Modified Oswin models are the ones recommended to estimate the equilibrium moisture content of castor beans, obtained through adsorption. Among them, the Modified Halsey was the model that, in general, presented the best results, being the equation recommended to represent the equilibrium moisture content of castor beans, obtained through adsorption. These results are similar to the ones reported by Chen (2000), which recommended the Modified Halsey model to represent the equilibrium moisture content of peanut grain, through adsorption and desorption.

Giner and Gely (2005), studying the hygroscopicity of sunflower seeds, concluded that the Modified Halsey model with three parameters including the temperature effect, was the one that best represented the desorption isotherms of this product. According to these authors, the Modified Halsey model allows a better representation of the sorption isotherms of oil seeds, since it reproduces the abrupt increase of the moisture content in high relative humidity, a characteristic of oil seeds.

In figure 1, the experimental results are shown for equilibrium moisture content of the castor beans, obtained by adsorption, as well as their isotherms calculated with the modified Halsey model. The obtained adsorption isotherms showed a sigmoidal format, typical for many agricultural products (Aviara et al., 2004; Furmaniak et al., 2007; Iguaz & Vírseda, 2007). The existence of a high concordance between experimental data and the data estimated by the modified Halsey model was observed. Therefore, from these isotherms, the product can be adequately managed with the aim of maintaining its moisture content at recommended safe storage levels for castor beans.

Analyzing Figure 1, it can also be observed the temperature effect upon the adsorption isotherms of castor beans, once that, with temperature increase at a constant relative humidity value, a reduction of the equilibrium moisture content of the grains occurs. This is an indicative of the low hygroscopicity of castor beans at elevated temperatures. This tendency is probably due to the reduction of the number of active sorption sites for water to bond, as a result of physical and chemical alterations in the product induced by temperature (Mazza & LeMaguer, 1980). In addition, the temperature increase can also lead to alterations on isotherms, promoting an increase in the values of relative humidity at constant equilibrium moisture content. This trend can make the product more susceptible to microorganisms attack (Rockland, 1969).
CONCLUSIONS: From the data observed in this work, it can be concluded that the adsorption isotherms obtained for castor beans within the temperature range of 25 to 55°C presented a sigmoidal format, typical of many agricultural products. It was also observed that the equilibrium moisture content of castor beans is directly proportional to the relative humidity of the air and decreases with increases in temperature, at the same relative humidity. The modified Halsey best represented the hygroscopicity of the castor beans at the conditions under which this experiment was performed.

REFERENCES


