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HIGROSCOPIC PROPERTIES OF CASTOR SEEDS (*Ricinus Comunis L.*)

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Abstract - Sorption isotherms of castor seeds were evaluated at 30, 40, 50 and 60°C using the static gravimetric method. Sigmoid trends were observed for isotherms obtained showing a clear effect of temperature. Experimental values were adjusted using the modified isotherms of Henderson, Halsey, Oswin and Guggenheim-Anderson-de Boer (GAB). Models were compared using four statistics parameters. The results showed that Modified Henderson model adjusted adequately the experimental values in the range of temperature evaluated. The experimental values of the safe storage moisture content for castor seeds varied between 6.1 to 8.4 % (d.b.) between 20 and 40°C, showing lower values than those reported for other traditional oilseeds as sunflower or rapeseed. The sorption heats evaluated from the combination of Clapeyron equation and Modified Henderson equation varied between 3400 and 2373 kJ/kg for moisture contents between 1 and 28 % (d.b.). Through Othmer relationship the value of the ratio L_b/L_f varied between 1.01 and 1.34 (for 14.5 and 1% d.b. moisture content respectively). The values obtained showed an exponential relationship with moisture content, of the form $L_b/L_f=1+0.44\exp(-0.17M)$ with a determination coefficient R^2 of 0.97.

Keywords: Castor seeds; Isotherms; Equilibrium moisture content.

INTRODUCTION

Castor (*Ricinus comunis*) culture grows in warm regions of north Argentina and Brazil. The high content of ricinoleic acid in the oil (higher than 85%) indicates that it is not apt for human consumption. Due to its physical and chemical properties the oil is used as raw material for several industrial applications and for the production of biofuels. The resistance of the culture to dough conditions gives an additional opportunity to increase its exploitation in marginal regions, promoting also the developing of regional economies without competition with traditional oilseeds (Falasca et al., 2006).

There is a lack of information about the behavior of these oilseeds during post-harvest stages, mainly storage and drying processes. The current situation in Argentine is the culture of the seed in a manual way and storage in silos until oil extraction.

Equilibrium moisture content (M_e) and equilibrium relative humidity (ERH) relationships are essential factors in the design of the drying and storing processes. To determine safe moisture values where microbial growth can be prevented, is a useful tool. The equilibrium moisture content of the grain at different relative humidity and temperature is also helpful for calculating the heat of vaporization, which is an important thermodynamic grain property. This property, defined as the energy required to vaporize the water from the grain at different conditions, showed marked differences between grains (Brooker et al., 1992) and constitutes one of the key factors in the design of the drying equipment.

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Rao and Rizvi (1994) demonstrated that at equilibrium conditions, the relative humidity equals to water activity of the grain. Therefore an equation that could describe the relationship between water activity (a_w), equilibrium moisture content (M_e) and temperature (T) would be an useful tool for the simulation of agricultural product during post-harvest processes. Many theoretical, semi-theoretical and empirical isotherm equations have been developed for modeling the water sorption behavior of many grains (Chen and Jayas, 1998). However it is always desirable to find both, a justification using the physico-chemical phenomena for a sorption equation and a simple theoretical equation that describes accurately the experimental sorption data (Shatadal and Jayas, 1990). A sorption isotherm with temperature dependent parameters would be a helpful tool to predict the equilibrium moisture content for different drying process conditions.

Chirife and Iglesias (1978) found that each model has some success in the prediction of equilibrium moisture data for a product under determined moisture and temperature conditions. Therefore the selection of the most adequate moisture sorption isotherm equation for each grain in a range of relative humidity and temperature is relevant. On the other hand, the heat of sorption is an estimation of the minimum amount of heat required for removing a given amount of water and it also allows some deduction about the grain micro-structure and the physical changes occurring on the grain surface. One method widely used to calculate the heat of sorption (L_b) of many foods is based on the Clausius-Clapeyron equation, which assumes temperature-independent heat of sorption and allows a simple calculation of the isosteric heat from the sorption. An alternative method for calculating isosteric heats developed by Othmer (Perry and Chilton, 1991) assumes that the heats of both sorption and condensation have the same temperature dependence. This assumption is less restrictive than the Clapeyron method, in which both heats are considered to be constant (Aguerre et al., 1988).

The objectives of this work are to know the behavior of equilibrium moisture content of castor seeds in the temperature range that usually is applied in post-harvest process, to evaluate an isotherm model that could predict equilibrium values at different temperatures and to estimate the heat of sorption of water of castor seeds.

MATERIALS AND METHODS

Castor seeds IAC-Guaraní variety, harvested at Misiones, Argentina (WL 27° 19' SL 55° 53) during year 2005 were used. The seeds were stored at 5°C after harvest and before utilization.

The seeds were manually cleaned to eliminate strange, immature and crashed materials. Moisture content was determined according AOAC 14.003 method (AOAC, 1980), under vacuum, 100°C, 8 h or until constant weight. Oil content was determined by solvent extraction according to the American Oil Chemist's Society (AOCS, 1997), Ae 3-52 method. All determinations were carried out by triplicate.

Equilibrium moisture content of castor seeds was experimentally determined through static gravimetric method using saturated solutions at different concentrations in order to maintain constant relative humidity. Seven values for the relative humidity were used, varying between 11 and 80 % at 30, 40, 50 and 60°C. Castor seeds were wetted over their equilibrium values in order to assure the desorption process. After wetting, samples were kept during three days to allow homogenization of moisture in the core of the grains. Approximately 10 g of seeds were kept in desiccators under saturated saline solutions of known relative humidity. Phenol was used in higher relative humidity containers, in order to avoid the fungi development during testing. Samples into desiccators were kept under controlled atmosphere (± 1°C) allowing all samples to equilibrate until weight changes lower than ±0.001 g. The time to reach equilibrium varied between samples but it was approximately three weeks. Finally, equilibrium moisture content was determined according AOAC 14.003 method. The samples that deviated more than 0.6% from the mean of triplicates were eliminated.

According to recommendations of ASAE standard (ASAE, 1999), four equations were selected for the adjusting of experimental data of M_e/a_w (Chen and Morey, 1989). The equations used were Modified Henderson (Eq. 1), Modified Halsey (Eq. 2), Modified Oswin (Eq. 3) and Guggenheim-Anderson-de Boer (GAB) equation (Eq. 4). Equations (1), (2) and (3) are temperature-dependent while the GAB isotherm (Eq. 4), one the most satisfactory theoretical equations, has its parameters dependent with temperature (Shatadal and Jayas, 1990) which can be explicitly resolved for a_w and M_e. Sun (1999) has reported that equations with three parameters (A, B and C) will give better adjustments of equilibrium data than equations with more parameters.

$$M_e = \left(\frac{\ln(1-a_w)}{\left(-A(T+C)\right)} \right)^{(1/B)} \quad (1)$$

$$M_e = \left(\frac{\ln(a_w)}{-\exp(A + BT)} \right)^C \tag{2}$$

$$M_e = (A + BT) \left(\frac{a_w}{1 - a_w} \right)^C \tag{3}$$

$$M_e = \frac{ABCa_w}{(1 - Ba_w)(1 - Ba_w + BCa_w)} \tag{4}$$

Systat Statistical Software (Wilkinson, 1990) was used for the adjustment of experimental data. Residue analysis and the following four standard quantitative parameters were applied to compare the accuracy of the adjustments: coefficient of determination (R^2), standard error of the parameter (ASE), standard error of the estimated value (SE) and the mean relative percentage of deviation (P).

The heat of sorption of water in castor seeds (L_b) was calculated by combining the best isotherm model with Clapeyron equation (Gely, 2003; Rohvein et al., 2004) obtaining the following expression:

$$L_b = L_f + \frac{RT^2}{M_v} \frac{\partial \ln a_w}{\partial T} \tag{5}$$

In addition L_b/L_f was found by using Othmer method. From Clapeyron equation (Eq (5)):

$$\frac{\partial P_s}{\partial T} = \frac{L_f p_s}{RT^2} \quad \frac{\partial P_v}{\partial T} = \frac{L_b p_v}{RT^2} \tag{6}$$

by assuming L_b/L_f independent of temperature (Hunter, 1987), the integration of the equation obtained from the mathematical relation of equation 6, gives:

$$\ln(p_v) = \frac{L_b}{L_f} \ln(p_s) + D \tag{7}$$

Othmer (1940) showed that the ratio of L_b/L_f is the slope of the straight-line obtained by plotting (for a range of temperature) the log of the partial pressure of water vapor generated within a seed at a single moisture content against the equivalent saturated vapor pressure of water (Eq. (7)). The variation of the partial vapor pressure in the grain with the temperature can be calculated from the relationship between RH and M_e given by equations of sorption isotherms (Nellist and Bruce, 1995).

Gallaher (1951) expressed the dependence of L_b/L_f with moisture content through the following equation:

$$L_b = L_f \left(1 + \alpha \exp(\beta M) \right) \tag{8}$$

RESULTS AND DISCUSSION

Initial moisture content of original castor seeds was 7.5% d.b. Oil contents of whole seeds and kernels resulted 55.5 and 72.3 % (d.b.) respectively. Experimental data of sorption moisture for castor seeds are showed in Figure 1 (symbols). The isotherms show an increase of the equilibrium moisture content with water activity at constant temperature. At constant relative humidity, a decreasing of equilibrium moisture content with temperature was observed.

Table 1 shows the adjustment of the sorption isotherms evaluated through equations (1), (2) and (3). The statistics parameters obtained showed a reasonable adjustment for all models studied with similar values for the parameters R^2 and SE, although P parameter of modified Henderson equations resulted 11.4% lower than the corresponding parameter of modified Oswin equation and 47.67% lower than the same parameter of modified Halsey equation.

Table 2 shows the results of the adjustment of GAB equation (Eq. 4) for each temperature. The statistical parameters R^2, SE and P suggest a good adjustment for temperature.

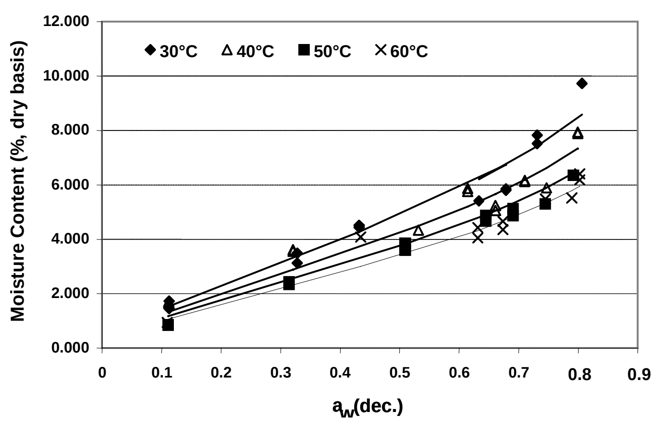

Figure 1: Desorption isotherms for castor seeds at 30, 40 50 and 60°C. Symbols represent experimental data and lines represent the modified Henderson equation.

Table 1: Adjustment of modified Halsey, Oswin and Henderson models for castor seeds

Model	A (ASE)*	B (ASE)*	C (ASE)*	R^2	SE	P
Modified Henderson	1.5E-3 (4E-21)	1.52 (0.06)	11.31 (5.36)	0.94	1.86	9.46
Modified Halsey	2.68 (0.18)	-2.03E-2 (2.3E-3)	-0.62 (2.86E-2)	0.94	1.95	13.97
Modified Oswin	6.02 (0.23)	-4.7E-2 (4.7E-3)	4.54E-1 (2.1E-2)	0.95	1.79	10.54

*Values into parenthesis indicate the standard error in the estimation of the corresponding parameter.

Table 2: Adjustment for temperature of GAB isotherm for castor seeds

Temperature (°C)	A (ASE)*	B (ASE)*	C (ASE)*	R^2	SE	P
30	2.56 (0.32)	0.91 (0.05)	15.18 (9.66)	0.99	0.86	8.84
40	2.90 (0.46)	0.79 (0.08)	14.55 (8.43)	0.99	0.94	8.21
50	3.94 (1.12)	0.62 (0.11)	3.82 (1.09)	0.99	0.32	4.10
60	2.82 (0.86)	0.71 (0.13)	8.24 (6.10)	0.99	0.71	9.34

*Values into parenthesis indicate the standard error in the estimation of the corresponding parameter.

The analysis of the relationship between Gab's parameters and temperature shows that an increase in temperature from 30°C to 60°C causes an increase of 10% for A parameter, with an average value of 3.05±0.6. For B, the same change in temperature causes a decrease of 22.2% with an average value of 0.76 ±0.12. This behavior shows a lower influence of the temperature on these two parameters when compared to the variation of C parameter that shows a decreasing of 45.7% with the increase of temperature. From these results, a modification of GAB equation including the C parameter temperature-dependent was proposed and showed in Equation (9). Table 3 shows the statistical results of this adjustment.

$$M_e = \frac{AB\frac{C}{T}a_w}{\left(1-Ba_w\right)\left(1-Ba_w+B\frac{C}{T}a_w\right)} \quad (9)$$

Despite the coefficient of determination being higher than the values obtained from the adjustments of equations (1), (2) and (3) from Table 1, the values of SE and P resulted 15% and 7.2% higher than the previous values obtained from the adjustment of Henderson modified equation.

The analysis of the residues of M_e, calculated as the difference between experimental equilibrium moisture values and the predicted ones, showed an horizontal band rounding zero with no identification of a trend for any of the functionalities analyzed (Fig. 2). Normally the residues would show a horizontal band centered in zero with any behavior pattern (Chen and Morey, 1989).

Although the Eq. (1), (2) and (3) and (9) predicted reasonably the experimental values, modified Henderson equation showed in Fig. 1 indicated a lower valor of the mean relative percentage deviation (P).

From the modified Henderson equation, the safe storage moisture content (M_s) was evaluated for a water activity a_w of 0.7 in a temperature range between 20 and 40°C (Fig 3). According to Barbosa-Cánovas et al. (2003) the value of 0.7 represents the moisture level at which the rate of fungi growth is minimum. The values obtained varied between 6.1 (for 40°C) and 8.4 % d.b. (for 20°C). As can be observed, a temperature decrease of 20°C caused an increase of the safe storage moisture content of 38.22 %.

The experimental values of the safe storage moisture content for castor seeds in the range of temperature evaluated showed lower values than those reported for other traditional oilseeds in the commercialization standard norms as e.g. sunflower 12.36% d.b. and rapeseed 9.3% d.b.

Table 3: Adjustment of GAB model modified in this work (Eq. 9) for castor seeds

Parameter		R^2	SE	P
A	7.75 (1.52)	0.98	2.19	10.19
B	0.44 (0.07)			
C	108.14 (22.11)			

*Values into parenthesis indicate the standard error in the estimation of the corresponding parameter.

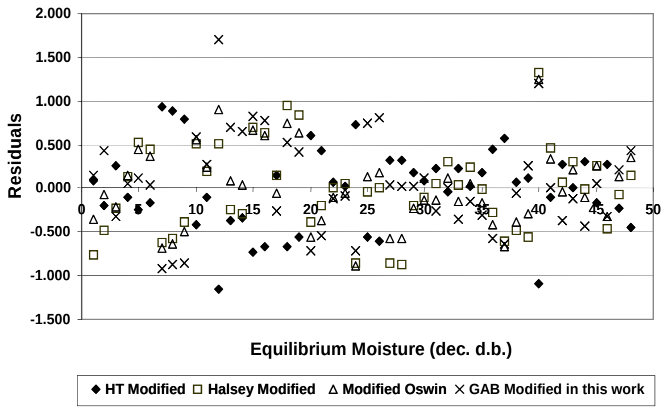

Figure 2: Analysis of the residues of M_e by using modified Henderson, Halsey, Oswin and GAB models.

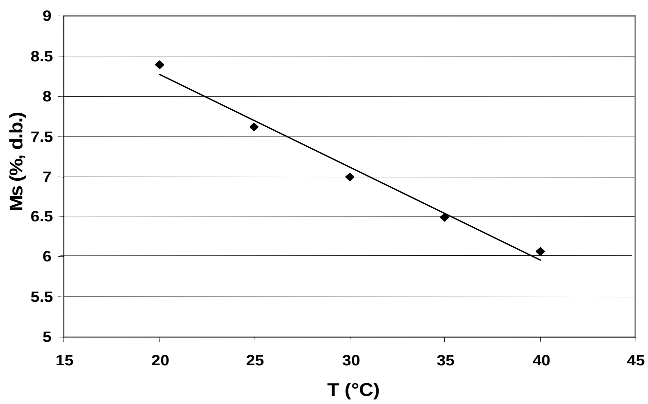

Figure 3: Variation of the safe storage moisture content (M_s) with temperature. Experimental (symbols) and predicted by equation 10 (line)

The variation of the safe storage moisture content with temperature showed a lineal trend (Eq. 10) with a determination coefficient R^2 of 0.99

$$M_s = -0.1155T + 10.58 \tag{10}$$

Heat of Vaporization

The heat of vaporization for castor seeds was evaluated at four temperatures in a range of moisture between 1 and 30% d.b. The behavior of L_b resulted similar for all analyzed conditions decreasing with the increase of moisture and temperature and trending to the water heat of vaporization value at each corresponding temperature (Fig. 4). At 30°C a decrease of moisture content from higher values to 15% (d.b.) caused a light increase of L_b from 2431.7 (coincident with L_f at 30°C) to 2531.6 kJ/kg and represents an increment of 4.1%. A decrease of moisture from 14.5% to 1% caused a deep change in L_b to a final value of 3427.8 kJ/kg, which represents an increment of 35.4%.

The vapor pressure of water in castor seeds against the vapor pressure of pure water in log-log graphic according the concept of Othmer (1940) was represented through equations (7) and (8) for a temperature range between 30 and 60°C. Figure 5 represents the vapor pressure of castor seeds for moisture content of 1 and 8.5%. From the slopes of the parallel lines obtained, the values of L_b/L_f (Equation (11)) resulted 1.338 (for 1 % m.c.) and 1.102 (for 8.5 % m.c.).

$$\begin{aligned} \ln(p_s) &= 1.338\ln(p_v) - 5.6289\Big|_{M=1\%} \\ \ln(p_s) &= 1.1019\ln(p_v) - 1.0621\Big|_{M=8.5\%} \end{aligned} \tag{11}$$

The relationship between moisture content and L_b/L_f (obtained from the Othmer relationship) represented in Fig. 6, showed values varying between 1.01 (for 14.5 % d.b.) and 1.34 (for 1 % d.b.). The adjusting of these values through Eq. (8) allowed obtaining the characteristic parameters for castor seeds, which are α= 0.44 (ASE= 0.022) and β= –0.17 (ASE=0.012) with a determination coefficient R^2 of 0.97. The form of Eq. (8) for castor seeds resulted:

$$Lb/Lf = 1 + 0.44 \times \exp(-0.17M) \tag{12}$$

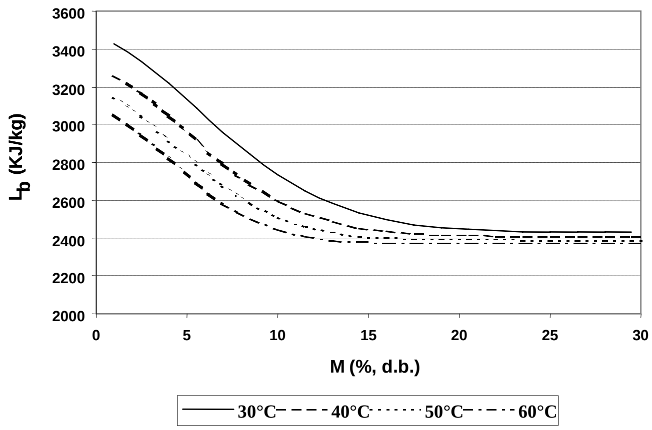

Figure 4: Variation of the heat of vaporization of water in castor seeds (L_b) with moisture content for temperatures between 30°C and 60°C.

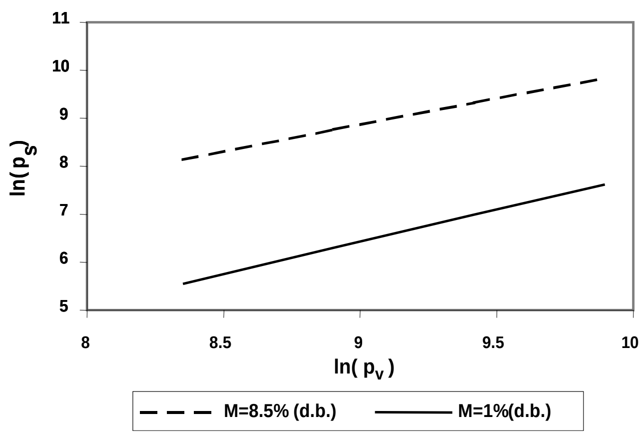

Figure 5: Othmer relationship for moisture content of 1 and 8.5% d.b.

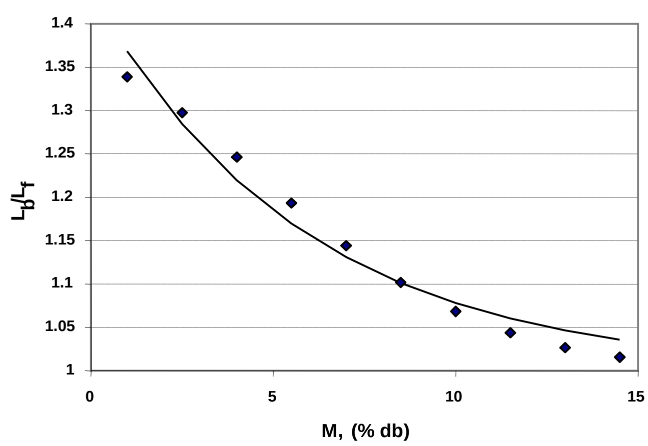

Figure 6: Relationship between the heat of vaporization of water in castor seeds and free water at different moisture contents. Values evaluated from Othmer (symbols) and from adjustment of Eq. 12 (lines).

CONCLUSIONS

Experimental values of M_e of castor seeds obtained from static gravimetric method were adjusted using modified Oswin, Halsey, Henderson and GAB equations. Modified Henderson resulted the best model to predict equilibrium moisture content for castor seeds with a determination coefficient higher than 0.94.

The experimental values of the safe storage moisture content for castor seeds evaluated in the range of temperature between 30 and 60°C varied between 6.1 (for 40°C) and 8.4 % d.b. (for 20°C), showing lower values than those reported for other traditional oilseeds.

The sorption heats evaluated from the combination of Clapeyron and modified Henderson equations varied between 3400 and 2373 kJ/k for moisture contents between 1 and 28 % (d.b.) respectively. Using Othmer relationship the ratio L_b/L_f varied between 1.01 and 1.34 in the range of moisture content between 1 and 14.5 % d.b. explained through an exponential relationship.

NOMENCLATURE

a_w	Water activity
A, B, C	Parameters of Equations 1, 2, 3 and 4
d.b.	dry basis
D	constant of integration
ERH	Equilibrium Relative Humidity
L_b	Heat of sorption of water in the castor seeds
L_f	Heat of sorption of water
M	Moisture content (m.c.)
M_e	Equilibrium moisture content
M_s	Safe moisture
M_v	Molecular weight of water
p_s	Saturation pressure of water
p_v	Partial pressure of water vapor
R	constant universal of gases
RH	Relative humidity
T	Temperature
α, β	Parameters of the Equation 8

Statistical Parameters

ASE	Standard error of the parameter
P	Mean relative percentage of deviation
R^2	Coefficient of determination
SE	Standard error of the estimated value

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