MOISTURE DESORPTION ISOTHERMS AND ISOSTERIC HEAT OF SORPTION CHARACTERISTICS OF MALTING BARLEY (HORDEUM DISTICHUM L.)

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Abstract — **The equilibrium moisture content of malting barley grains (cv. *Scarlett*) was determined by gravimetric-static method in the range 20-50°C using saturated salt solutions (LiCl, $MgCl_2.6H_2O$, K_2CO_3, NaBr, $NaNO_2$, KI, $NaNO_3$, NaCl, $(NH_4)_2SO_4$) to provide water activities for each temperature between 0.11 and 0.813. Desorption isotherms were obtained at 20, 30, 40, and 50°C. All the sorption curves were found to be Type II, increasing moisture content with the increase of water activity from approximately 5.5–7.45% d.b. (dry basis) for different temperatures when the water activity was 0.111. Different models (Modified Henderson, Modified Chung-Pfost, Modified Halsey, Modified Oswin and GAB) were fit to the data and it was found that the best results corresponded to the Modified Henderson equation. The isosteric sorption heat varied from 3479 kJ/kg (20ºC) to 2393 kJ/kg (50ºC) decreasing with increasing moisture content, thus indicating that reducing the moisture content increases the energy required to remove water.**

Keywords — **Equilibrium, isotherms, heat of sorption, malting barley, modeling.**

I. INTRODUCTION

World production of malting barley (*Hordeum distichum* L.) amounts to 155 million tons of which Argentina contributes about 1.68 mill. tons of barley (SAGPyA, 2010). Most of the deterioration mechanisms of plant products are associated with water activity and moisture content, so the drying process is essential to maintain their quality. Full knowledge of the hygroscopic and thermal properties of the grains is crucial for the mathematical description of drying and rewetting of the grain and to find the optimum operating conditions for drying and storage. Sorption isotherms of products are highly relevant to model moisture uptake during storage and distribution. The net isosteric heat of sorption is a thermodynamic parameter obtained from equilibrium data for sorption isotherms it represents the difference between the latent heat of adsorption and the latent heat of condensation of pure water (Mulet *et al*., 1999). Heat of sorption varies throughout the drying process, depending on both temperature and moisture-content of the grain to be different in the heat of vaporization of pure water (Rucklod *et al*., 2003). A mathematical model that includes these factors in calculating the latent heat of vaporization is an appropriate tool for designing efficient and economical drying. Isosteric heat of sorption with sorption isotherms are essential tools for the proper design of storage systems. Very little work is available on the equilibrium moisture content of barley. Vermuganti *et al.* (1980) published experimental equilibrium data of barley in the ranges 5-40°C and 30-90% relative humidity; the researchers adjusted these values by the Chung-Pfost equation. Chen and Morey (1989) adjusted different models to experimental data at low temperatures (5-25°C). Brooker *et al.* (1992) reported equilibrium moisture content data of barley at 25°C. Sun and Woods (1994) studied the dynamic equilibrium moisture content for desorption in the range restricted to low temperatures from 3.9 to 19.6°C. ASAE (2003) reported only sorption equilibrium data in tabular form at temperatures between 25-28ºC and the parameters of the Chung-Pfost equation valid in the ranges 5-25ºC of temperature and 18-95% of relative humidity. Basunia and Abe (2005) determined the dynamic equilibrium moisture for adsorption at temperatures between 5.7 and 46.3°C. Also, Neagu *et al.* (2009) studied the adsorption moisture isotherms of barley at ambient temperatures (16-25ºC). No studies were found about desorption equilibrium moisture content for a more wide range of temperatures applicable to the drying of barley. Therefore, further information on the sorption equilibrium between the grains of barley and the environment is requested in order to properly interpret the mechanisms contributing to the kinetics of wetting and drying operations, as well as for the selection of appropriate storage conditions of dehydrated products. On the other hand, Chen and Morey (1989) noted, after studying four isotherms equations for a set of 36 data of sorption, that there is not a "universal" isotherm capable of adequately describing the equilibrium in the behavior of all types of biological materials. These authors found that the Modified Halsey equation and the Modified Oswin equation were appropriate for the adjustment of commodities with high contents of oil and protein. The GAB isotherm, which was adequate to represent mathematically the sorption equilibrium data of different cereals, oilseeds and sub-products (Chen and Jayas, 1998; Pagano and Mascheroni, 2003; 2005; Cassini *et al.*, 2009), is difficult to use because of the complexity of the expression of water activity as a function of humidity and

its lack of dependence on their parameters with respect to temperature.

In view of the above exposed, the objectives of this work were:

1. to quantify the equilibrium moisture content of water desorption of malting barley grains (cv. *Scarlett*) using the static gravimetric method in the temperature range 20 to 50ºC,

2. to verify the capability of different EMC/ERH models to fit the experimental data, and

3. to determine the isosteric heat of sorption in relation with the moisture content and temperature.

II. MATERIALS AND METHODS

A. Materials

The material used for the experiments was malting barley cv. *Scarlett* harvested mechanically in 2009 in the central region of the Buenos Aires Province (Argentina) with initial moisture content (M_i) of 13.6% d.b. (dry basis) without any previous drying treatment.

Moisture content of grains was determined by the method of oven drying, using a small sample of about 10 g at 130ºC during 20 hours (ASAE, 1986). All determinations were made in duplicate.

In studying the hygroscopic equilibrium of the grains, seeds are usually moistened for obtaining the desorption isotherms (Sun and Woods, 1994), or apply moderate drying to reduce the initial moisture content and get the isotherms adsorption (Basunia and Abe, 2005). To ensure the construction of experimental isotherms of desorption for a wide range of temperature and relative humidity, the methodology of rewetting of samples gives barley reported by Sun and Woods (1994) was followed. According to this methodology, the original sample was moistened up to 30% d.b. in order to ensure the elaboration of the desorption isotherms. For this purpose, the employed procedure consisted in adding the exactly amount of water (W) (Eq. 1) to a sample in a hermetic container where the material was periodically mixed for 48 hours.

The moist samples were stored in air-tight plastic bags in a refrigerator for one week before use, in order to obtain a uniform distribution of moisture content in seeds (Sun and Woods, 1994).

$$W = m_{ss} \times \left(M_f - M_i \right) \qquad (1)$$

In all cases, the required amount of each test sample was removed from the refrigerator a day before the experiment was to be carried out, in order to allow the sample to reach thermal equilibrium with the environment (Basunia and Abe, 2005).

B. Experimental determination of desorption isotherms

In order to obtain the equilibrium moisture content atconstant temperature the static gravimetric method was used. Saturated salt solutions were employed to warrant constant vapor pressure into the containers with samples (Greenspan, 1977).

Glass desiccators containing saturated salt solutions were placed in an oven at controlled temperature of 20,

30, 40 and 50°C. For each temperature, five to eight different salt solutions were used (Table 1). This allowed a range of relative humidity between 11 and 81.3%. Barley samples were placed in perforated baskets suspended on salty solutions in glass desiccators. All experiments were performed in duplicate. Samples were periodically weighed until the difference between two consecutive measurements was less than 0.01 g (Mazza and Jayas, 1991). At this point, the equilibrium moisture content was determined by ASAE method (ASAE, 1986).

Each set of experiment was repeated twice and average values and corresponding standard deviation were recorded.

C. Desorption mathematical equations

In order to adjust the experimental data to mathematical equations, it was decided to analyze the behavior of the five isotherm equations recommended in D245.5 of ASAE Standard (ASAE, 2003). These are: Modified Henderson equation (MHE) (Eq. 2), Modified Chung-Pfost equation (MCPE) (Eq. 3), Modified Halsey Equation (MHaE) (Eq. 4), Modified Oswin equation (MOE) (Eq. 5) and Guggenheim-Anderson-de Boer equation (GAB) (Eq. 6).

The first four temperature-dependent equations (MHE, MCPE, MHaE and MOE) have been recommended by Chen and Morey (1989) due to their simple expression of three parameters and because they can be explicitly solved for both moisture equilibrium content (M_e) and moisture relative equilibrium (ERH) (variable equivalent to water activity of the material, a_w).

Table 1. Experimental conditions (Greenspan, 1977).

T (°C)	RH (dec.)	Saturated salt solutions
20	0.1131	LiCl
	0.3360	$MgCl_2.6H_2O$
	0.4316	K_2CO_3
	0.6990	NaBr
	0.7547	NaCl
	0.8134	$(NH_4)_2SO_4$
30	0.1128	LiCl
	0.3280	$MgCl_2.6H_2O$
	0.4317	K_2CO_3
	0.6330	$NaNO_2$
	0.6789	KI
	0.7314	$Na\ NO_3$
	0.7509	NaCl
	0.8063	$(NH_4)_2SO_4$
40	0.1121	LiCl
	0.3210	$MgCl_2.6H_2O$
	0.5317	NaBr
	0.6141	$NaNO_2$
	0.6609	KI
	0.7100	$Na\ NO_3$
	0.7468	NaCl
	0.7991	$(NH_4)_2SO_4$
50	0.1110	LiCl
	0.3140	$MgCl_2.6H_2O$
	0.5093	NaBr
	0.6449	KI
	0.6904	$Na\ NO_3$

Similarly, the GAB equation (Eq. 6) has been recommended by Van Den Berg (1984) because it accurately describes the equilibrium isotherms of food for a wide range of aw. Additionally, their parameters can be correlated with temperature and provide information about the values of monolayer and the activation energy for sorption systems.

$$M_e = \left[\frac{\ln(1-aw)}{-A(T+B)} \right]^{1/C} \qquad (2)$$

$$M_e = \frac{\ln(A)}{C} - \frac{1}{C} \ln\left[-(T+B)\ln(aw)\right] \qquad (3)$$

$$M_e = \left[\frac{-\exp(A + B\,T)}{\ln(aw)} \right]^{1/C} \qquad (4)$$

$$M_e = (A+BT)\left[\frac{1-aw}{aw} \right]^{-1/C} \qquad (5)$$

$$M_e = \frac{(A\,B\,C\,aw)}{(1-C\,aw)(1-C\,aw+B\,C\,aw)} \qquad (6)$$

where A, B and C are constants.

For the whole pool of data, parameters (A, B and C) of the different models were obtained using the minimum square regression. The best adjustment of experimental data to different models and the determination coefficients were obtained using the statistical software Systat (Wilkinson, 1990).

The statistical criteria for determining the goodness of fit were coefficient of determination (R^2), standard error of the estimation (SE), mean relative percent error (P), chi-square (χ^2) and residual plots.

The standard error of the estimation (SE) was defined by Eq. (7) (Chen and Morey, 1989):

$$SE = \sqrt{\sum \frac{(Y-Y^`)^2}{df}} \qquad (7)$$

where Y: measured value; $Y^´$: value predicted by the model; df: degree of freedom of the regression model.

The mean relative percent error (%) was (Eq. 8):

$$P = \frac{100}{N} \sum \frac{|Y-Y^`|}{Y} \qquad (8)$$

where N: number of data points.

This criterion was used by Tolaba et al. (2004). According to Lomauro et al. (1985) a good fit is obtained when $P<5\%$. Chi-Square was (Eq. 9):

$$\chi^2 = \sum_{i=1}^{k} \frac{(Y-Y^`)^2}{Y^`} \qquad (9)$$

where k: number of class intervals in the distribution of frequencies used.

The confidence level of 95% was used for the calculation of χ^2. The lowest values SE, P and χ^2, together with the highest R^2 or tending to one, are considered optimal and help choose the best model.

Also, in order to quantify the goodness of fitting of the models, the residual values obtained by difference between the measured values (Y) and the predicted values ($Y^´$) were considered. Random values falling near zero would indicate an adequate fit of the model (Chen and Morey, 1989). High values of SE and P and clear patterns in the residual plots indicate that the model fails

to explain the variation in the data (Chen and Jayas, 1998).

D. Calculation of the isosteric heat of desorption based on the combination of the Clausius-Clapeyron equation and the model of water activity

The isosteric heat of desorption (L_b) can be estimated by combining the Clausius-Clapeyron equation with a model of equilibrium sorption capable of describing precisely the EMC-ERH relation (Rucklod et al., 2003; Giner and Gely, 2005; Chen, 2006; Resende et al., 2006; Samapundo et al., 2007).

The method developed by Giner and Gely (2005) for sunflower grains generates an equation that evaluates the heat of desorption of water from the grain as the addition of the heat of vaporization of pure water (L_f) and an additional term associated to the water bound to the dry mass of the grain (Gely and Giner, 2000).

$$L_b = L_f + \frac{R(T+273.06)^2}{M_w} \frac{\partial \ln(aw)}{\partial T} \qquad (10)$$

where R: constant of ideal gases; T: Celsius temperature; M_w: molecular weight of water.

The isosteric heat of desorption is a variable that changes during drying, depending on both grain moisture content and temperature. In view of this, the second term of the Eq. (10) was evaluated by means of the four temperature-dependent EMC-ERH models previously mentioned MHE, MCPE, MHaE and MOE.

The corresponding equations generated for L_b by each equilibrium model were:

From MHE model:

$$L_b = L_f + \frac{R(T+273.16)^2}{M_w} \frac{AM_e^C \exp\left[-A(T+B)M_e^C\right]}{\left\{1-\exp\left[-A(T+B)M_e^C\right]\right\}} \qquad (11)$$

From MCPE model:

$$L_b = L_f + \frac{R(T+273.16)^2}{M_w} \left[\frac{A}{(T+B)^2} \exp(-CM_e) \right] \qquad (12)$$

From MHaE model:

$$L_b = L_f + \frac{R(T+273.16)^2}{M_w} \left[-\frac{B}{M_e^C} \exp(A+BT) \right] \qquad (13)$$

From MOE model:

$$L_b = L_f + \frac{-R(T+273.16)^2}{M_w} \frac{BC(A+BT)^{C-1}}{\left[M_e^C + (A+BT)^C\right]} \qquad (14)$$

III. RESULTS AND DISCUSSION

A. Analysis of the EMC-ERH data

Figure 1 presents the experimental EMC-ERH values for the water desorption isotherms from barley grains. For each value of water activity, the equilibrium moisture content is pointed as the average of the duplicates, and the corresponding error bars indicate the standard deviation between duplicates that were bellow 0.00279 in all the cases.

Each of the isotherms shown in Fig. 1 denoted that the equilibrium moisture content increases when relative humidity (or aw) increases, starting from moisture content between approximately 5.5–7.45% d.b. for different temperatures when the water activity was 0.111 and following a Type II sigmoid shape in the Brunauer classification (Brunauer et al., 1940).

Table 2. Estimated parameters and statistical criteria for MHE, MCPE, MHaE and MOE models.

Model Parameters[a]			R^2	SE	P	χ^2
A	B	C				
MHE						
3.9×10^{-5} (3×10^{-21})	18.588 (2.295)	2.295 (0.017)	0.99	0.38	2.8	0.09
MCPE						
338.032 (16.28)	16.581 (2.302)	0.182 (0.002)	0.99	2.42	18.16	0.48
MHaE						
6.057 (0.19)	-0.0176 (0.0017)	2.351 (0.059)	0.98	0.66	4.95	0.09
MOE						
15.753 (0.16)	-0.0998 (0.0044)	3.263 (0.046)	0.99	4.13	29.46	0.48

[a]Values between parentheses indicate the standard error of the parameter.

Table 3. Estimated parameters and statistical criteria for GAB model at temperatures in the range 20-50°C.

Model Parameters[a]			R^2	SE	P	χ^2
A	B	C				
20°C						
10.177 (0.251)	26.121 (2.615)	0.654 (0.014)	0.99	0.22	1.01	0.17
30°C						
9.286 (0.279)	22.858 (2.772)	0.674 (0.017)	0.99	0.26	1.26	0.33
40°C						
8.511 (0.300)	16.995 (1.950)	0.680 (0.019)	0.99	0.26	1.31	0.01
50°C						
8.126 (0.314)	21.651 (2.126)	0.646 (0.027)	0.99	0.17	1.24	0.05

[a]Values between parentheses indicate the standard error of the parameter.
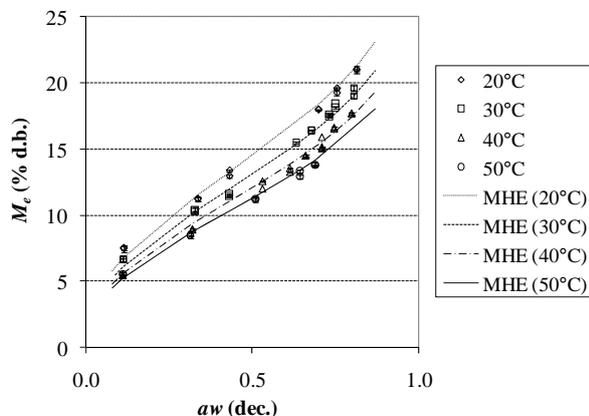

Figure 1. Experimental data (points) of the desorption isotherms for barley grains at temperatures in the range 20-50°C and curves predicted by MHE model equation (lines).

The results from statistical adjustments of the experimental EMC-ERH data by the different mathematical models are presented in Tables 2 and 3, together with the corresponding statistical criteria.

Table 2 shows the parameters of the temperature-dependent isotherm equations and their associated values of R^2 and SE; whereas Table 3 similarly displays the parameters of GAB equation which were determined at each temperature.

The analysis of Table 2 shows that all equations tested produced a good fit of the experimental results, emphasizing the suitability of MHE equation which ex-

hibited the highest coefficient of determination and the lowest SE, P and χ^2. The values obtained of χ^2 resulted lower than $\chi^2_{(0.05,1)}= 3.841$ (95% confidence level); this indicates that there was no strong evidence that the experimental values of the equilibrium moisture content do not fit properly for each of these isotherms. P values for the equation of HT and MHaE were below 5%, reflecting the good fit in these models.

On the other hand, when analyzing the fit of the GAB model shown in Table 3, can be noted that the parameters χ^2 were all lesser than $\chi^2_{(0.05,1)}= 3.841$ (95% confidence level), signifying that the experimental isotherms could be modeled by GAB model at each temperature; meanwhile, the values of R^2, SE and P indicated a good agreement of this equation.

Additionally, the residual plots for each assayed equation as a function of the dependent variable M_e resulted as drawn in Fig. 2, where clear trends for MCPE, MOE and MHaE models can be noted, while MHE and GAB equations have random distribution of the points.

The GAB model provided values between 8.126 % d.b. (50°C) and 10.177 % d.b. (20°C) for the monolayer moisture content, represent by the A parameter (Table 3). In addition, Neagu et al. (2009) used the GAB model to describe the experimental isotherms of adsorption of barley in the narrow range 16 to 25°C, reporting values for the monolayer moisture content (8.65-10.43% d.b.) in close agreement with this work.

With the purpose of generalizing the GAB model including the variable temperature (T) on their equation, an analysis of the variance was performed to quantify the effect of T on the parameters A, B and C. The results evidenced that temperature has significant influence only on the parameter B for a confidence level of 99%, proving F values of 16.35, 22.15 and 1.42 for A, B and C, respectively, compared with a critical value of $F_{(0.01;3;4)}= 16.7$. Although this result indicates that temperature affects only the parameter B, the results obtained could not be expressed using a function typically applied type Arrhenius (Chen and Jayas, 1998) in the range of T explored in this study.

Comparison between the values of M_e evaluated by the MHE isotherm in the whole range of the present work with other reported data available in literature (Vermuganti et al., 1980; Brooker et al., 1992; ASAE, 2003; Neagu et al., 2009) it can be noted that the bold lines at 20°C and 50°C of this work cover most of the data published for barley (Fig. 3). Small differences at each temperature can be attributed to the different grain varieties and methods of determination of the equilibrium moisture content.

In relation of this, as example, Fig. 4 shows the effect of the method of determination on sorption equilibrium data. In this graph at temperature of 20°C, experimental desorption data of the present work and the prediction of MCPE reported by Sun and Woods (1994) and Basunia and Abe (2005) were compared. Is clear that different equilibrium moisture contents are reached when the moisture equilibrium is obtained by desorption
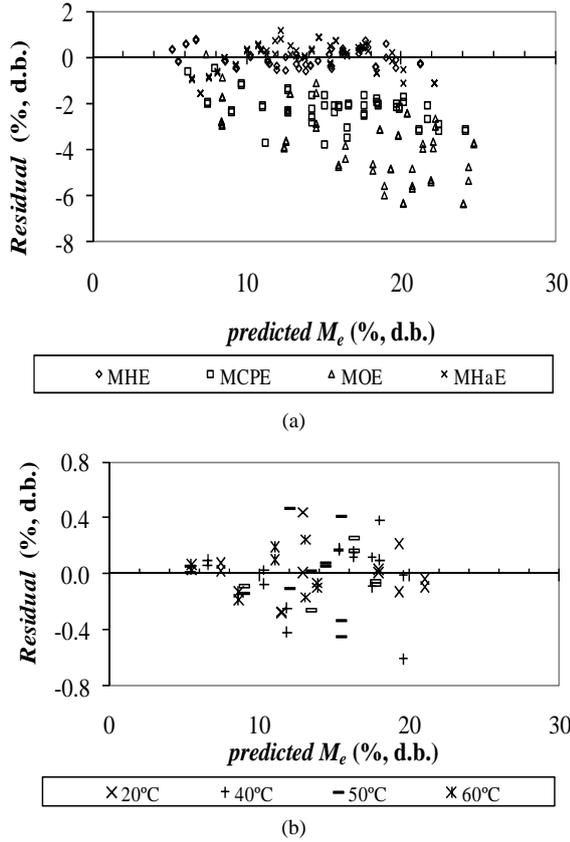
Figure 2. Residual plots as a function of the predicted variable M_e for different EMC-ERH models. (a): MHE, MCPE, MOE, MHaE; (b) GAB.
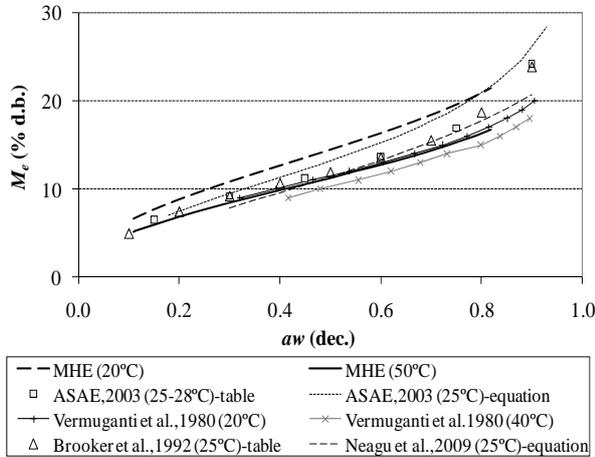

Figure 3. Comparison between M_e values predicted by MHE of this work for barley grains with reported data in literature.

or by adsorption, appearing the hysteresis phenomenon: for any given relative vapor pressure, the material shows a higher moisture content along desorption curve than it does along the adsorption curve.

Also, Fig. 4 shows that the use of the dynamic method (Sun and Woods, 1994) or the static gravimetric method (this work) to obtain the desorption isotherms causes small discrepancies between the M_e values of barley at 20°C; while, most important differences are found when hygroscopic equilibrium is reached by adsorption rather than desorption. That is, the mean rela-

tive differences between desorption M_e from dynamic method (Sun and Woods, 1994) and desorption M_e from static method (this work) were of about 4.3%. While, the mean relative differences between desorption M_e from static method (this work) and adsorption M_e from dynamic method (Basunia and Abe, 2005) were of about 7.8%.

Analysis of the effect of the EMC-ERH model on the calculation of the isosteric heat of desorption at 20°C
To evaluate the influence of the sorption equilibrium model on the isosteric heat of sorption, it was decided to realize the calculation of L_b at 20°C from the different equilibrium equation obtained by replacing the parameters of the nonlinear regression analysis presented in Table 2 in the Eqs. (11) to (14). The GAB isotherm was discarded due to the fact that its expression does not include the temperature variable. The resulting equations for each case are as follows:

From MHE model:

$$L_b = L_f + 1.55 \frac{M_e^{2.295} \exp\left(-0.0015 M_e^{2.295}\right)}{\left\{1 - \exp\left(-0.0015 M_e^{2.295}\right)\right\}} \qquad (15)$$

From MCPE model:

$$L_b = L_f + 10027\, exp\left(-0.182 M_e\right) \qquad (16)$$

From MHaE model:

$$L_b = L_f + 209930.6 M_e^{-2.351} \qquad (17)$$

From MOE model:

$$L_b = L_f + \left[\frac{4.88 \times 10^6}{M_e^{3.263} + 5.19 \times 10^3}\right] \qquad (18)$$

The relationships between the equilibrium moisture content and the isosteric heat of desorption evaluated by the different Eqs. (15) to (18) at 20°C are exposed in Fig. 5.

Due to the fact that the best fit of equilibrium data was provided by the MHE isotherm (Table 2), it was decided to establish heat data based on those obtained from the model MHE–Clausius-Clapeyron (Eq. 15) and perform comparisons of this prediction with the other
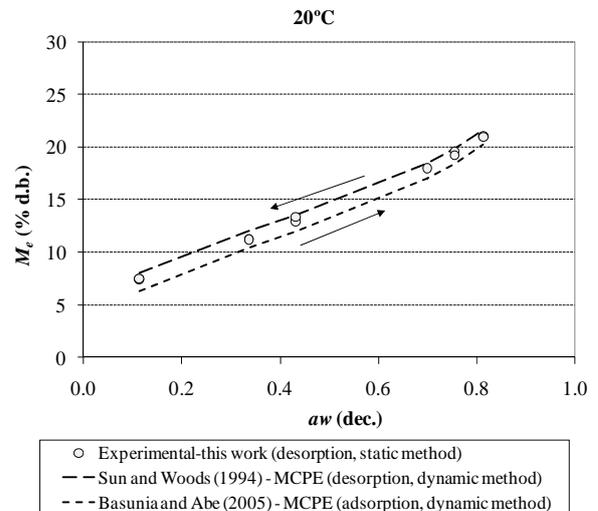

Figure 4. Comparison between M_e values for barley grains at 20°C obtained by different method (points: this work; curves: predicted by MCPE for desorption and adsorption).
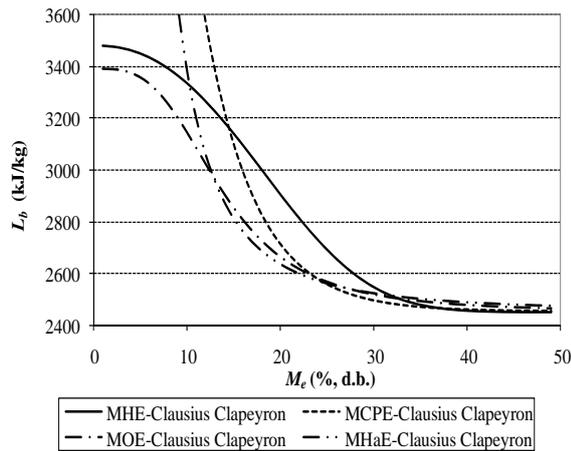
Figure 5. Isosteric heat of desorption for barley grains calculated by different equilibrium models.
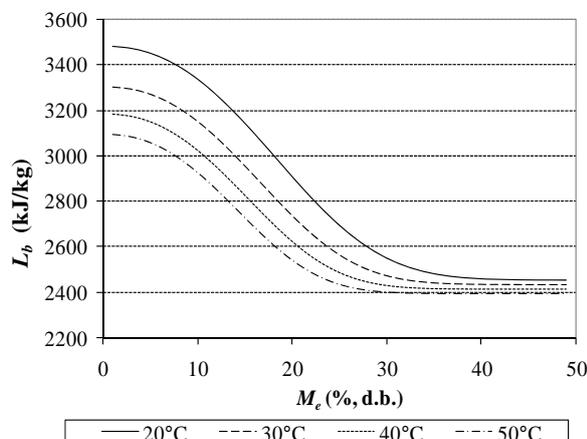

Figure 6. Isosteric heat of desorption for barley grains estimated by the model MHE –Clausius-Clapeyron at different temperatures.

isotherms (Eqs. 16-18). Figure 3 evidences that in face of an increase in equilibrium moisture content, the heat of desorption approximates to the value of the heat of vaporization of free water at 20°C, and the prediction of all the models resulting similar. But the behavior of these curves is dissimilar at lower moisture contents, where the isosteric heat of desorption calculated by models MHaE–Clausius-Clapeyron and MCPE–Clausius-Clapeyron is overestimated.

By contrast, the values calculated from the model MOE–Clausius-Clapeyron produces an underestimation of the sorption heat to low moisture content. These differences are due to the performance of the fit of the models used to estimate sorption isosteric heat of sorption. This highlights the importance of choosing the optimal equilibrium model to achieve a proper calculation of isosteric heat of sorption.

Considering the expression of modified Henderson isotherm (MHE) as the best equation to be applied to evaluate the heat of water desorption from barley grains in the explored temperature range, L_b values in function of M_e were calculated at temperature of 20, 30, 40 and 50°C as shown in Fig. 6.

Heat of desorption varied between 3479 kJ/kg (20°C) and 2393 kJ/kg (50°C), tending to the L_f value when the equilibrium moisture content decreases. For 10% d.b. of moisture content, the heat of sorption at 20°C was 14.4% higher than the corresponding at 50°C.

IV. CONCLUSIONS

Desorption isotherms for barley grains (cv. *Scarlett*) at temperatures of 20, 30, 40 and 50°C were experimentally determined using the static gravimetric method.

The results indicate a Type II sigmoid shape for the EMC-ERH curves, showing a decrease of the equilibrium moisture content with the increase of temperature.

The Modified Henderson isotherm (MHE) described precisely the experimental data of water desorption from barley grains.

An equilibrium model based on the combination between the EMC-ERH isotherm equation and the Clausius-Clapeyron equation was developed to predict the heat of water desorption from barley grains as a function of the moisture content and temperature.

NOMENCLATURE

χ^2	chi-square coefficient
ASE	standard error of the parameter
aw	Water activity, dec
d.b.	dry basis
df	degree of freedom
EMC	equilibrium moisture content
ERH	equilibrium relative humidity
k	number of class intervals
L_b	isosteric heat of sorption, kJ/kg
L_f	heat of vaporization of pure water, kJ/kg
M_e	equilibrium moisture content, % d.b.
M_f	final moisture content, % d.b.
M_i	initial moisture content, % d.b.
m_{ss}	dry mass, g
M_w	water molecular weight, kg/kmol
N	number of data points.
P	mean relative deviation, %
R	8.314 kJ/kmol K
R^2	coefficient of determination
RH	relative humidity, dec
SE	standard error of the estimated value
T	Celsius temperature, °C
T_a	absolute temperature, K
W	mass of water, g
Y	measured value
Y´	value predicted by the model

REFERENCES
ASAE, *"ASAE Standards,"* ASAE 352.1: Moisture Measurement-Grains and Seeds, American Society of Agricultural Engineers, St. Joseph, MI (1986).

ASAE, *"ASAE Standards,"* ASAE D245.5: Moisture relationships of plant-based agricultural products, American Society of Agricultural and Biological Engineers, St. Joseph, MI (2003).

Basunia, M.A. and T. Abe, "Adsorption isotherms of barley at low and high temperatures," *Journal of Food Engineering,* **66**, 129–136 (2005).

Brooker, D.B., F. Bakker-Arkema and C.W. Hall, *Drying and Storage of Grains and Oilseeds,* 1st Ed., Van Nostrand Reinold, NY, (1992).

Brunauer, S., L.S. Deming, W.E. Deming and E. Troller, "On the theory of Van der Waals adsorption of gases," *Journal of the American Chemical Society,* **62**, 1723–1732 (1940).

Cassini, A.S., L.D.F. Marczak and C.P.Z. Noreña, "Comparison between the isotherms of two commercial types of textured soy protein," *Latin American Applied Research*, **39**, 91–97 (2009).

Chen, C. and D.S. Jayas, "Evaluation of the GAB equation for the isotherms of agricultural products," *Transactions of the ASAE,* **41**, 1755–1760 (1998).

Chen, C.C., "Obtaining the isosteric sorption heat directly by sorption isotherm equations," *Journal of Food Engineering,* **74**, 178–185 (2006).

Chen, C.C. and R.V. Morey, "Comparison of four EMC/ERH equations," *Transactions of the ASAE,* **32**, 983–990 (1989).

Gely, M.C. and S.A. Giner, "Water–corn equilibrium: temperature dependency of the GAB model parameters and calculation of the heat of sorption," *Drying Technology,* **18**, 1449–1464 (2000).

Giner, S.A. and M.C. Gely, "Sorptional parameters of sunflower seeds of use in drying and storage stability studies," *Biosystems Engineering,* **92**, 217–227 (2005).

Greenspan, L., "Humidity fixed points of binary saturated aqueous solutions," *Journal of Research of the National Bureau of Standards – A Physics and Chemistry,* **81A**, 89–96 (1977).

Lomauro, C.J., A.S. Bakshi and T.P. Labuza, "Evaluation of food sorption isotherms equations. I: Fruit, vegetable and meat productos," *Lebensmittel-Wissenschaft Und Technologie*, **18**, 111–117 (1985).

Mazza, G. and D.S. Jayas, "Equilibrium moisture characteristics of sunflower seeds, hulls and kernels," *Transactions of the ASAE,* **34**, 534–538 (1991).

Mulet, A., J. García-Reverter, R. Sanjuán and J. Bon, "Sorption isosteric heat determination by thermal analysis and sorption isotherms," *Journal of Food Science,* **64**, 64–68 (1999).

Neagu C., C. Tofan and D. Borda, "Mathematical models for moisture sorption isotherms of barley and wheat," *The Annals of the University Dunarea de Jos of Galati* Fascicle VI – Food Technology, New Series Year III (XXXIII), International Symposium Euro-Aliment 2009, Galati–Romania (2009).

Pagano, A.M. and R.H. Mascheroni, "Sorption isotherms for amaranth grains," *Journal of Food Engineering,* **67**, 441–450 (2005).

Pagano, A.M. and R.H. Mascheroni, "Water sorption of Amaranthus cruentus L. seeds modelled by GAB equation," *International Journal of Food Properties,* **6**, 369–391, (2003).

Resende, O., P.C. Corrêa, A.L.D. Goneli and D.M. Ribeiro, "Isotermas e calor isostéricico de sorção do Feijoo," *Ciência e Tecnologia de Alimentos,* **26**, 626–631 (2006).

Rucklod, S., H.D. Isengard, J. Hanss and K.H. Grobecker, "The energy of interaction between water and surfaces of biological reference materials," *Food Chemistry,* **82**, 51–59 (2003).

SAGPyA, Ministerio de Agricultura, Ganadería y Pesca, Presidencia de la Nación Argentina, http:// www. minagri.gob.ar/SAGPyA/agricultura Last accessed: 05/14/2010 (2010).

Samapundo, S., F. Devlieghere, B. De Meulenaer, A. Atukwase, Y. Lamboni and J.M. Debevere, "Sorption isotherms and isosteric heats of sorption of whole yellow dent corn," *Journal of Food Engineering,* **79**, 168–175 (2007).

Sun, D.W. and J.L. Woods, "Low temperature moisture transfer characteristics of barley: Thin-layer models and equilibrium isotherms," *Journal of Agricultural Engineering Research,* **59**, 273–283 (1994).

Tolaba, M.P., M. Peltzer, N. Enriquez and M.L. Pollio, "Grain Sorption equilibria of Quinoa grains," *Journal of Food Engineering,* **61,** 365-371(2004).

Van Den Berg, C., "Description of water activity of foods for engineering purposes by means of the GAB model of sorption," *Engineering and Foods,* Vol. 1, McKenna B.M. (ed.), Elsevier Applied Science Publishers, NY (1984).

Vermuganti, G.R., H.B. Pfost, D.S. Chung and R. Burroughs, "Some properties of cereal grains, food legumes and oilseeds (hygroscopic, thermal, physical) affecting storage and drying", *Grain Storage, Processing and Marketing,* Kansas State University, Research Report N°18, 39 pp. (1980).

Wilkinson, L., *SYSTAT: The System for Statistics,* SYSTAT, Inc., Evanston, IL (1990).