The Annals of the University *Dunarea de Jos* of Galati
Fascicle VI – Food Technology, New Series Year III (XXXIII)
Paper presented at the International Symposium *Euro - aliment 2009*, 9th – 10th of October 2009, Galati – ROMANIA

# MATHEMATICAL MODELS FOR MOISTURE SORPTION ISOTHERMS OF BARLEY AND WHEAT

NEAGU CORINA, TOFAN CLEMANSA, BORDA DANIELA

*Dunarea de Jos University Galati, Faculty of Food Science and Engineering, 111 Domneasca Street*
*cneagu@ugal.ro*, *dborda@ugal.ro*

Received 2 June 2009
Revised 28 August 2009

Moisture sorption isotherms play an essential role in preservation and storage of dehydrated foods. To study the behavior of different cereals (wheat, barley), in a certain equilibrium static environment, gravimetric methods were applied for temperatures ranging between 16 and 25°C and water activities from 0.533 to 0.909. The moisture isotherms were sigmoid shaped and showed a clear temperature dependence of water activity ($a_w$). GAB and a second order polynomial equation were used to model the experimental data.

*Keywords*: sorption isotherms; equilibrium state, water activity, GAB, polynomial models

## 1. Introduction

Knowledge of the sorption characteristics is essential to: understand the stability in storage and acceptability of food products, model the drying process, design and optimization of the drying equipment, aeration, calculation of moisture content changes which may occur during storage, and for selecting appropriate packaging materials (Ngoddy et al., 1975, Samapundo et al., 2006). The static gravimetric technique was registered as the preferred method for determining the moisture sorption isotherms of food products. This method has several advantages over the manometric and hygrometric techniques, such as: ability to determine the exact dry weight of the sample, minimization of temperature fluctuation between samples and their surroundings or the source of water vapor, registering the weight change of the sample in equilibrium with the respective water vapor pressures, and achieving hygroscopic and thermal equilibrium between samples and the water vapor source. The differences in experimental techniques adopted influence the sorption properties of foods (Al-Muhtaseb et al., 2002). Saturated salt solutions are commonly used to create the necessary micro-climate for the sorption experiments. This implies production of template-like data to prepare the standard solutions referred to by several researchers (Chowdhury et al., 2005; Aviara et al., 2006). The main aim of this study was to determine the sorption isotherms of barley and wheat grains over a range of temperatures and humidity commonly experienced in the mild environment.

The specific objectives are to stress the influence of temperature on sorption isotherms, and model the adsorption moisture isotherms using two widely recommended isotherm models.

## 2. Materials and methods

### *2.1. Material preparation*

Wheat (Dropia) and barley (Andrei) from SCDA Company, BRAILA, were harvested in spring, 2008.

The wheat had an initial moisture content and $a_w$ of 8.72 ± 0.45 kg/100kg dry matter, and 0.578 ± 0.015, and the barley had an initial moisture content and $a_w$ of 6.74 ± 0.45 kg/100kg dry matter, and 0.533 ± 0.015, respectively.

The grains were kept at 7°C, in cold storage until being used. The initial moisture content (m.c.) of the grains was determined in duplicate according to the AOAC (1990) procedures.

### *2.2. Micro-climate*

The required micro-climate was prepared relying on previous experience using six saturated salt solutions (NaCl, KCl, $HN_4Cl$, $K_2SO_4$, $KNO_3$, $(NH_4)_2SO_4$) and a different range of relative humidity being selected to give different $a_w$ values in the wheat and barley. The relative humidity/$a_w$ values of the salt solutions at different temperatures are those indicated in other researches (Labuza T. P., 1984).

### *2.3. Determination of adsorption isotherms*

To determine adsorption isotherms the static gravimetric method was used. Three replicates of wheat and barley (15 and 10 g), sufficient to give a uniform single layer in the glass containers used as moisture pans, were placed in desiccators at each $a_w$ point and temperature level. The desiccators were placed in a Binder Incubator to maintain the required temperature. Samples were monitored for equilibration by weighing at intervals, until constant weights were attained. The moisture content of the equilibrated samples (the e.m.c.) was then found by calculation from the initial m.c. and the change in weight known (Igbeka, et al., 1975).

### *2.4. Isotherm equations and modeling*

Two widely recommended isotherm equations (GAB and Polynomial) that were investigated in relation with the experimental data are shown in Table 1 in the form M = f ($a_w$,T), where M is the moisture content. The SAS procedure for non-linear regression (Proc NLIN) was used.

**Table 1.** Models used to describe the sorption isotherms

| Model | Equation |
|---|---|
| GAB | $M = \frac{m_0 CKa_w}{[(1-Ka_w)(1-Ka_w+CKa_w)]}$ |
| Polynomial | $M = a + ba_w + ca_w^2$ |

*a*: constant, *k*: constant, $a_w$: water activity, *b*: constant, c: constant, *C*: GAB model parameter, *K*: GAB model parameter, $m_0$: monolayer moisture content (kg/100kg dry matter).

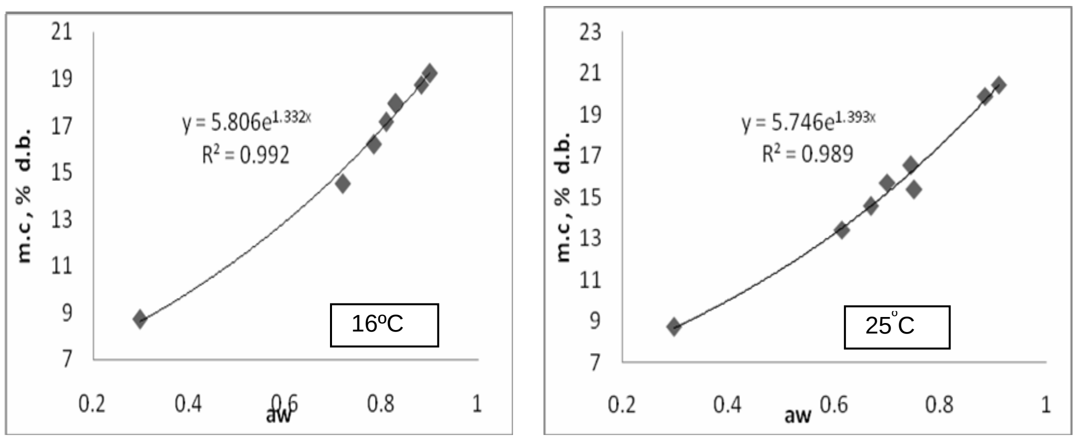
The goodness of fit of the models was evaluated by calculating the mean relative percentage of deviation modulus (P), defined as:

$$P(\%) = \frac{100}{N}\sum_{i=1}^{N}\frac{|M_{ei} - M_{ci}|}{M_{ei}} \quad (1)$$

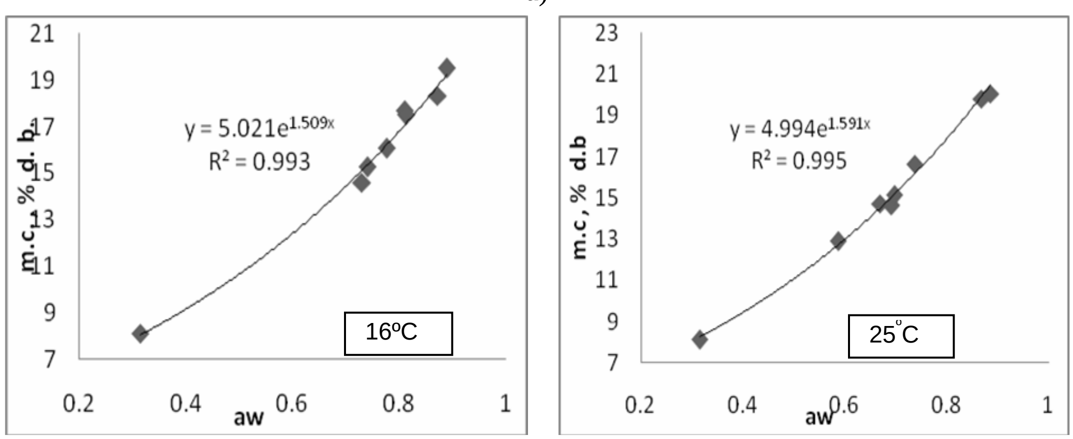
where $M_{ei}$ and $M_{ci}$ are the experimental and predicted moisture content values, respectively, and N is the number of experimental data. A model is considered acceptable if it has a P value lower than 10%.

## 3. Results and discussions

The adsorption and desorption isotherms at 16, 25°C are shown in Figure 1. The isotherms have a sigmoid shape depicting an increase in the equilibrium moisture content with $a_w$. These are typical Type II isotherms (Deming, et al., 1940) and have been reported for starchy products such as potato and wheat starch (Igbeka, et al., 1975).




a)




b)

**Figure 1.** Adsorption isotherms a) wheat, b)barley

The correlation between $a_w$ and moisture content for wheat at 25°C is significant ($R^2$=0.989), while the correlation coefficients for wheat at 16°C and barley at 16 and 25°C is highly significant. ($R^2$=0.99). An exponential equation was used to depict the relationship between moisture and $a_w$ content.

The temperature dependence of the sorption isotherms is shown in Figure 2 where the equilibrium moisture content is observed to decrease during a temperature decrease, at the same $a_w$, and $a_w$ decrease during a temperature increase, for the same equilibrium moisture content. This indicates that the wheat and barley become less hygroscopic when temperature is increased.

For example, for wheat at 16.07% dry base the $a_w$ is of 0.777 at 16°C and of 0.722 at 25°C.

Tables 2 and 3 show the coefficients of the models fitted to the experimental adsorption data by non-linear regression and *P* (%)- the mean relative percentage deviation modulus. The correlation coefficients ($R^2$) were in all cases higher than 0.985.

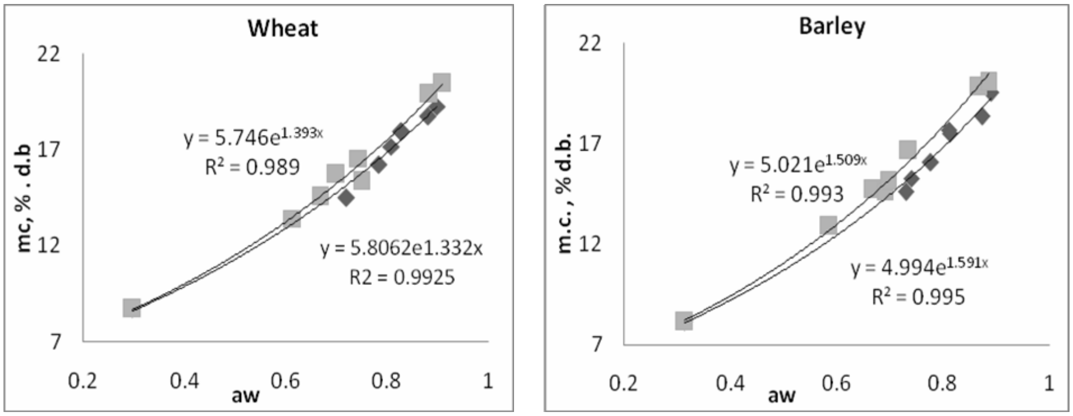



**Figure 2.** Adsorption isotherms for wheat and barley at 16 (◆) and 25ºC(■)

**Table 2.** Mathematical models for the adsorption isotherms of wheat

| Model | Temperature(°C) 16 | 25 |
|---|---|---|
| GAB | | |
| *C* | 19.7036 | 13.8212 |
| *K* | 0.6433 | 0.6253 |
| *m₀* | 8.5221 | 9.3396 |
| *P(%)* | 1.70 | 1.78 |
| $R^2$ | 0.999 | 0.999 |
| Polynomial | | |
| *a* | 83420 | 6.9412 |
| *b* | -4.3753 | 1.7329 |
| *c* | 18.6443 | 14.4240 |
| *P(%)* | 1.48 | 1.63 |
| $R^2$ | 0.988 | 0.980 |

**Table 3.** Mathematical models for the adsorption isotherms of barley

| Model | Temperature(°C) 16 | 25 |
|---|---|---|
| GAB | | |
| *C* | 11.2086 | 7.0985 |
| *K* | 0.6531 | 0.6093 |
| $m_0$ | 8.6527 | 10.4305 |
| *P(%)* | 1.69 | 1.26 |
| $R^2$ | 0.999 | 0.999 |
| Polynomial | | |
| *a* | 7.3102 | 5.14345 |
| *b* | -3.5005 | 5.3715 |
| *c* | 19.1945 | 13.1132 |
| *P(%)* | 1.54 | 1.24 |
| $R^2$ | 0.985 | 0.993 |

Both models have P <10%, so they can be considered reliable to describe the correlation between $a_w$ and moisture content at 16ºC and 25ºC, for both wheat and barley. Moreover, the statistical parameters computed for the model and $R^2$ indicate a good estimation of the parameters for the experimental values.

The estimated monolayer moisture content ($m_0$) from the adsorption isotherms using GAB equation is of 8.5221 and 9.3395 kg/100 kg for wheat at 16 and 25 ºC. The moisture content for barley is higher than the one for wheat, and is of 9.3395 and 10.4305 kg/100 kg at 16 and 25 ºC respectively. These values are in line with the values reported by Yanniotis (1994) for high starchy foods between 20 and 30ºC (7.36 kg/100kg). The accuracy of the models and its concomitant parameters were evaluated plotting the experimental values versus the predicted ones for each studied temperature (16 and 25ºC).

From the Figures 3 and 4, a good correlation between predicted and experimental values was noticed.

Moreover, the deviation of the bisector line can be considered an indicator for the model fitness. Since a concentration of the data can be noticed alongside the bisector line, we can conclude that the two models used (GAB and Polynomial) accurately described the experimental data behavior. Hence, it could be concluded that the proposed models and its parameters correctly described the adsorption isotherms for both wheat and barley.

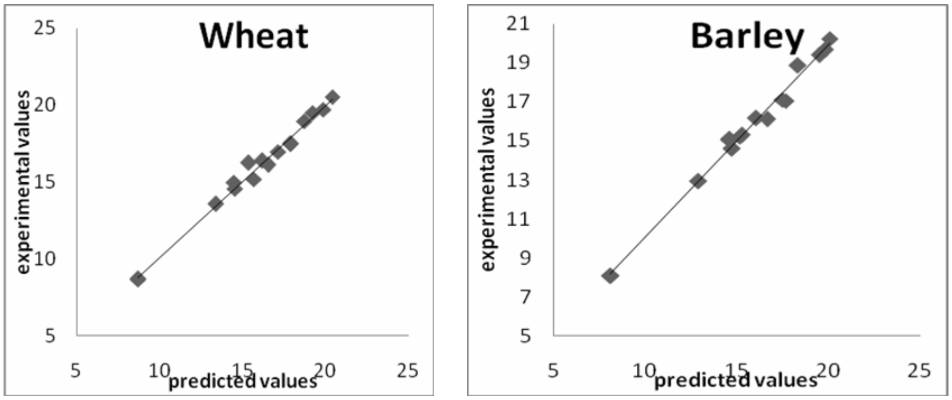



***Figure 3*** *Relationship between the experimental and predicted relative humidity values for GAB model*

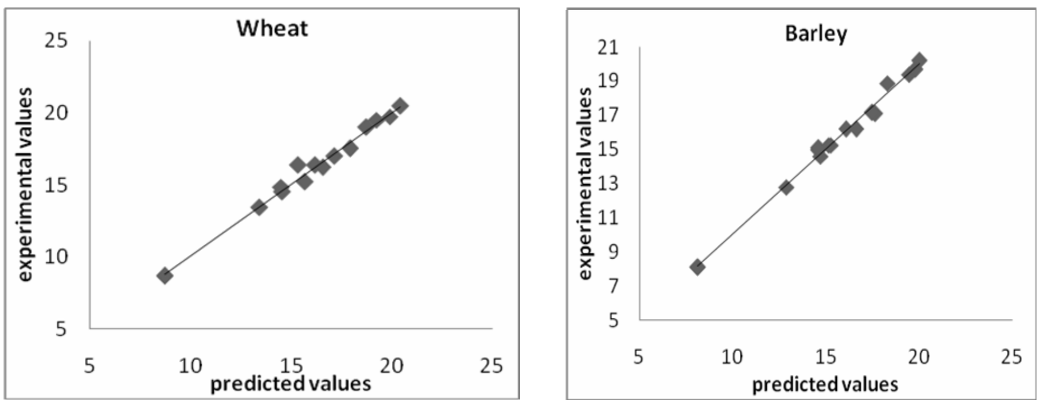



***Figure 4*** *Relationship between the experimental and predicted relative humidity values for the Polinomial model*

Graphics of the residual values (differences between experimental and predicted values) shows no signs of bias as results from Figures 5 and 6.

The random distribution of residuals for wheat and barley is an indicator of the correspondence between theoretical and experimental values.

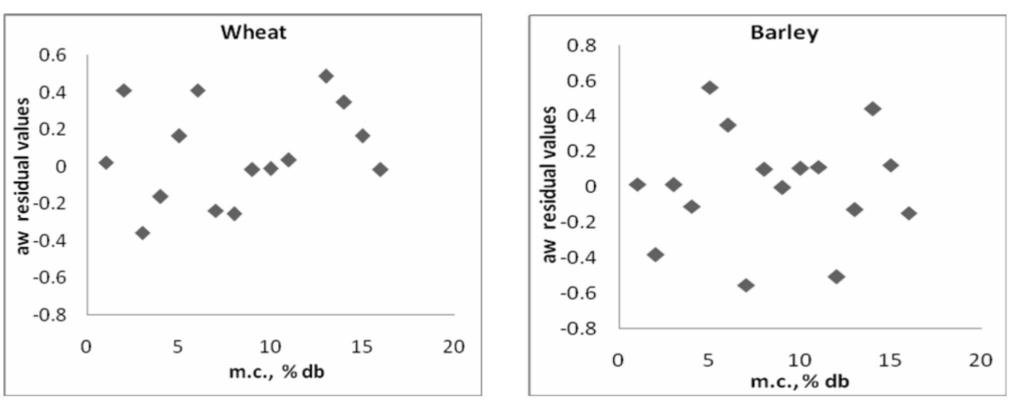



***Figure 5.*** *Residual $a_w$ values for Polinomial model*

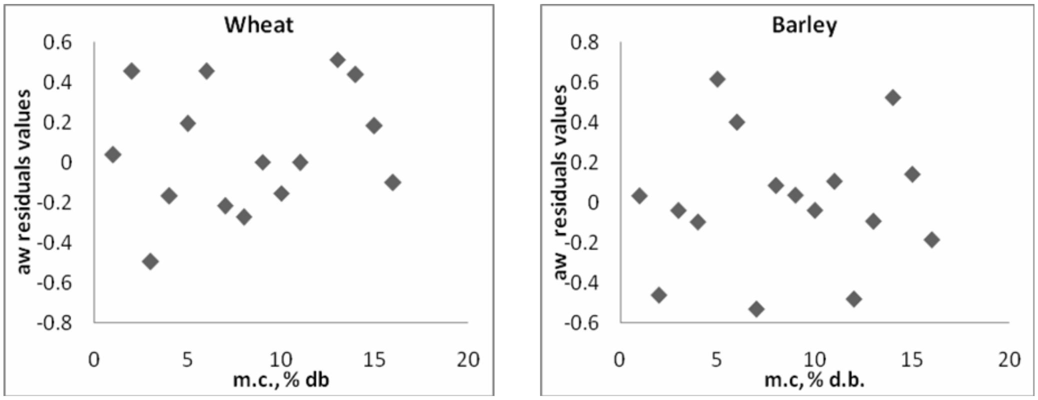



***Figure 6.*** *Residual $a_w$ values for GAB model*

## 4. Conclusions

Adsorption isotherms for wheat and barley, at 16 and 25 ºC have sigmoid shape and behave like Type II isotherms. Temperature has a significant influence on sorption isotherms, and an increase in $a_w$ values was noticed for the same humidity content with temperature decrease.

The experimental values could be modelled using GAB and Polinomial models using the non linear regression.

For all the cereals tested and all the experimental temperatures, the nonlinear models applied showed that convergence criteria were met.

The estimated parameters are in line with other similar researches for other cereals.

The relationship diagrams of the experimental and predicted values, the residual distribution charts and the correlation coefficients ($R^2$) and P(%) were appropriate and indicate good accuracy of the models used.

### References

Al-Muhtaseb, A.H., McMinn, W.A.M., Magee, T.R.A.,. 2002, Moisture sorption isotherm characteristics of food products: a review. *Transactions of the Institute of Chemical Engineers*, **80**, 118–128.

Aviara, N.A., Ajibola, O.O., Aregbesola, O.A., Adedeji, M.A., 2006, Moisture sorption isotherms of sorghum malt at 40 and 50°C *Journal of Stored Products Research*, **42**, 290–301.

Chowdhury, M.M.I., Huda, M.D., Hossain, M.A., Hassan, M.S., 2005, Moisture sorption sotherms for mungbean (Vigna radiata L). *Journal of Food Engineering*, **74**, 462–467.

Deming, L. S., Deming, W. E., Troller, E., 1940. 1940, On the theory of Van der Waals adsorption of gases*. Journal of the American Chemical* Society, **62**, 1723-173.

Igbeka, J.C., Blaisdell, J.L., Herum, F.L., Hamdy, M.Y., 1975, Equilibrium moisture content of cassava and potato. *American Society of Agricultural Engineers*, 75–6527.

Labuza, T. P.,. 1984, Moisture sorption: Practical aspects of isotherm measurement and use. St. Paul, MN: *American Association of Cereal Chemists*.

Ngoddy, P.O., Bakker-Arkema, F.W. 1975, A theory of sorption hysteresis in biological materials. *Journal of Agricultural Engineering Research*, **20**, 109–121.

Samapundo, S., Devlieghere, F., De Meulenaer, B. and Debevere, J. M., 2007, Sorption isotherms and isosteric heats of sorption of whole yellow dent corn. *Journal of Food Engineering*, **79(1)**, 168-175.