Determination of Moisture Sorption Isotherms of Jasmine Rice Crackers Using BET and GAB Models

U. Siripatrawan* and P. Jantawat

Department of Food Technology, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand

Moisture sorption isotherms of Thai Jasmine rice crackers were determined at 30, 45 and 60°C over a water activity range of 0.10 to 0.95 using a static gravimetric technique. Moisture sorption isotherms of rice crackers exhibited the sigmoid (Type II) shape. The moisture content of rice crackers decreased as temperature increased at a given water activity of the storage environment. The Brunauer, Emmett and Teller (BET) and Guggenheim-Anderson-de Boer (GAB) models were applied to fit the experimental data. The isosteric heat of sorption at different moisture levels was also determined using the Clausius–Clapeyron thermodynamic equation. A nonlinear regression analysis method was determined to evaluate the parameters of sorption equations. The criteria used to evaluate the goodness of fit of each model were the mean relative percentage deviation modulus (E) and the percentage root mean square error (RMSE). The more extended range of application of the GAB equation over the BET equation was evident. The GAB model gave the best fit to the experimental sorption data for a wide range of water activity (0.10–0.95) while the BET model gave the best fit for a water activity range of less than 0.60. The GAB model is considered suitable to predict the moisture sorption isotherm of rice crackers since it gave low E and RMSE values. The heat of sorption values of rice crackers were found to be large at low moisture content and decreased with an increase in food moisture content.

Key Words: rice crackers, sorption isotherms, BET model, GAB model

INTRODUCTION

Thai Jasmine rice (Hom Mali) acquired its name through its natural fragrances similar to those of the Jasmine flower. Regarded as the highest quality Thai rice, Jasmine rice is recognised as the favoured rice by consumers both domestically and internationally. Jasmine rice cracker is a tasty and healthy snack item of Thailand and is exported worldwide in particular to Japan and European countries. The quality of this product on storage primarily depends on its water activity which is contingent on the relative humidity and temperature of storage. The moisture sorption isotherm of this product could be valuable information on its storage stability as well as prediction of shelf life since they give information about the humidity–water activity relation, at a given temperature (Al-Muhtaseb et al., 2004; Ayranci and Duman, 2004).

A number of models to describe moisture sorption isotherm have been proposed including kinetic models based on a multilayer (BET and GAB models), semi-empirical (Ferro-Fontan, Henderson and Halsey models) and empirical models (Smith and Oswin models). The BET isotherm model is the most important model for the interpretation of multilayer sorption isotherms, particularly for Type II isotherm characteristics (Anderson, 1946). The GAB model is considered to be the most versatile sorption model available in the literature. BET and GAB models have been adopted as equations by the American Society of Agricultural Engineers for describing sorption isotherms (ASAE, 1995). These models have been widely used in the literature (Mcmin and Magee, 2003; Pahlevanzadeh and Yazdani, 2005; Rohvein et al. 2004).

The isosteric heat of sorption, or latent heat of vaporisation, can be used to estimate the energy requirements of drying and provides crucial information on the state of water in food products (Chen, 2006). The heat of adsorption is a measure of the energy released on sorption and the heat of desorption is the energy requirement to break the intermolecular forces between the molecules of water vapour and the

surface of the adsorbent. Thus, the heat of sorption can be used as indicative of the intermolecular attractive forces between the sorption sites and the water vapour (Kaymak-Ertekin and Gedik, 2004). Sorption isosteric heat of food products can be directly measured using a calorimetric technique. However, this technique requires a precise measurement of small quantities of heat evolved. Hence, calorimetric measurement of isosteric heat of sorption is much less popular than those computed from sorption isotherm data (Chen, 2006). A computation commonly used to determine the heat of sorption is the application of thermodynamic Clausius–Clapeyron equation to the sorption isotherms, at a constant moisture content (Chen, 2006; Kaymak-Ertekin and Gedik, 2004).

Knowledge of the moisture sorption characteristics is crucial for shelf life predictions and determination of critical moisture and water activity for acceptability of products that deteriorate mainly by moisture gain and are important in drying, packaging and storage (Bianco et al., 2001; Palou et al., 1997). The ability to predict the moisture content during storage under a variety of conditions can reduce the cost and the cycle time of product development and shelf life estimation. Although a number of researches have reported sorption isotherms of moisture sensitive foods, such as cereals and snacks, the sorption isotherms of rice crackers have not been investigated.

The objectives of this study were, hence, to determine experimentally the equilibrium sorption isotherm of rice crackers at 30, 45 and 60 °C and to model the sorption characteristics of rice crackers using BET and GAB equations. The isosteric heat of sorption at different moisture levels was also determined at a specific moisture content using the Clausius–Clapeyron equation.

MATERIALS AND METHODS

Sorption Isotherm Determination

Plain Jasmine rice crackers were acquired from a food plant in Samuthprakarn province. Rice crackers have an initial moisture content of 4.72 g/100 g dry basis. Eight saturated salt solutions (LiCl, $KC_2H_3O_2$, $MgCl_2$, K_2CO_3, NaCl, $NaNO_3$, KCl and KNO_3) were used to provide constant water activities ranging from 0.10 to 0.95. Moisture sorption isotherms of rice crackers were determined gravimetrically, in which the weight was monitored continuously within a standard static system of thermally stabilised conditions. Approximately 2–3 g of samples were put in glass dishes and placed inside glass jars containing selected saturated salt solutions. The glass jars were placed in an electric oven at a desired constant temperature of 30, 45 and 60 °C and allowed to equilibrate with the

environment inside the containers. The samples were allowed to equilibrate until there was no discernible weight change, as evidenced by constant (± 0.001 g) weight values.

Sorption Isotherm Models

The data obtained corresponding to the a_w and moisture content at the temperatures studied were adjusted to BET (Brunauer, Emmett and Teller, 1938) and GAB (Anderson, 1946; de Boer, 1995; Guggenheim, 1995) equations in order to determine the best fit.

BET Equation

The BET equation can be expressed as follows:

$$m = \frac{C_B a_w m_0}{(1 - a_w)(1 + (C_B - 1)a_w)} \qquad (1)$$

$$F(BET) \equiv \frac{a_w}{(1 - a_w)m} = \frac{1}{C_B m_0} + \frac{C_B - 1}{C_B m_0} a_w \qquad (2)$$

where m is the amount of sorbate sorbed by 1 g of sorbant at sorbate activity a_w. m_0 is the monolayer moisture content and C_B is the BET constant (Timmermann, 2003).

GAB Equation

The GAB equation was used to model water sorption of rice crackers as follows:

$$m = \frac{C_G K_G a_w m_0}{(1 - K_G a_w)(1 - K_G a_w + C_G K_G a_w)} \qquad (3)$$

where C_G and K_G are GAB constants and are related to monolayer and multilayer properties (Kaymak-Ertekin and Gedik, 2004). The assumption of the GAB model over the BET formulation stating that the sorption state of the sorbate molecules in the layers beyond the first is the same, but different to the pure liquid state, demands the introduction of the additional constant K_G (Timmermann, 2003).

Model Validation

In this research, BET and GAB equations were used to model the moisture sorption isotherms for rice crackers. The experimental data were fitted to the models using a nonlinear regression. All calculations were performed using the routines MATLAB Version 5.3 (Mathworks, Inc., Natick, MA). The coefficient of determination, R^2, was calculated to give a measure of the proportion of variability attributed to the model (Jamali et al., 2006).

In addition to R^2, the criteria used to evaluate the

goodness of fit of each model were the mean relative percentage deviation modulus, E (Kaya and Kahyaoglu, 2005) and the percentage RMSE. The mean relative percentage deviation modulus and RMSE were calculated (Al-Muhtaseb et al., 2004) as follows:

$$E = \frac{100}{N} \sum_{i=1}^{n} \frac{|m_e^i - m_p^i|}{m_e^i} \qquad (4)$$

$$RMSE = \sqrt{\frac{\sum_{i=1}^{N} (m_e^i - m_p^i)}{N}} \qquad (5)$$

where m_e is the experimental value, m_p is the predicted value, and N is the number of experimental data. The mean relative percentage deviation modulus value below 10% indicative of a good fit for practical purposes. The lower the values of E and RMSE, the better the goodness of fit (McMinn and Magee, 2003).

Determination of the Isosteric Heat of Sorption

The isosteric heat of sorption of rice crackers was calculated by applying the Clausius–Clapeyron equation (Equation (6)) to the experimental equilibrium isotherm data.

$$q_{st} = -R \frac{\partial \ln a_w}{\partial (1/T)} \qquad (6)$$

where q_{st} is the isosteric heat of sorption (kJ/mol), R is the universal gas constant (8.314 kJ/mol K), a_w is the water activity, and T is the absolute temperature, Kelvin (Kaymak-Ertekin and Gedik, 2004).

RESULTS AND DISCUSSION

Characteristic of Moisture Sorption Isotherm

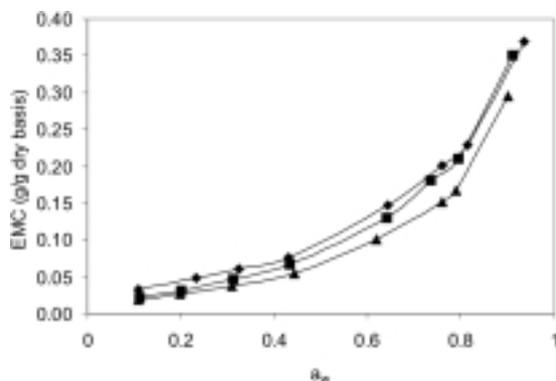The experimental moisture sorption data obtained corresponding to the water activities values ranging

Figure 1. Moisture sorption isotherms of rice crackers at (◆) 30 °C, (■) 45 °C and (▲) 60 °C.

from 0.10 to 0.95 at 30, 45 and 60 °C are presented in Figure 1. Moisture sorption isotherms of rice crackers exhibited the sigmoid (Type II) shape. The effects of temperature shifts on both moisture content and water activity are also displayed in Figure 1.

At a constant water activity, an upward shift in temperature from 30 to 60 °C led to a shift of isotherms towards a lower value for the equilibrium moisture content (EMC). The reason is that as the temperature was increased, the water vapour pressure of the moisture within the rice crackers increased and hastened the transfer of moisture from rice crackers to the surrounding air. Kapsalis (1987) pointed out that temperature affects the mobility of water molecules and the dynamic equilibrium between water vapour and adsorbed phases. Similar findings were also observed for various starchy food products (Barreiro et al., 2003; Iglesias and Chirife, 1982; Rohvein et al., 2004). An increase in temperature causes an increase in the water activity, at the same EMC, which in turn will cause an increase in the chemical and microbiological reaction rate leading to quality deterioration (McMinn and Magee, 2003; Palou et al., 1997).

Modelling of Moisture Sorption Isotherms

The experimental moisture sorption data of rice crackers at 30, 45 and 60 °C were fitted to the BET and GAB equations using nonlinear regression analysis (Figures 2, 3 and 4, respectively). According to Figures 2, 3 and 4, the more extended range of application of the GAB equation over the BET equation is evident. The plots using BET give a good fit at low water activities ($a_w < 0.6$). After which an upward deflection is observed. This deviation indicates that, at higher water activities, less water vapour is absorbed than that indicated by the BET equation using the values of the constants corresponding to the low water activity range. Iglesias and Chirife (1982) stated that the BET model is known to hold for water activities up to about 0.5. In this study, the BET model provided a good description of the isotherms of rice crackers only in the range of water activity <0.6. The GAB model on the other hand produces the best fit throughout the entire range of water activity.

To determine the goodness of fit of BET and GAB models, determination coefficient, mean relative percentage deviation modulus and percentage root mean square error were measured against the experimental isotherm data. Table 1 shows the estimated parameters of model coefficient and the corresponding mean relative percentage deviation modulus and the percentage root mean square error of both the BET and GAB mathematical models that describe the goodness of fit of the isotherms in the water activity and temperature ranges studied.

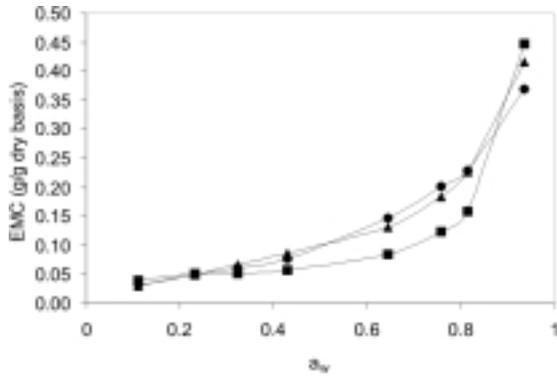Analysis of the rice cracker data showed that at 30,

Figure 2. Comparison between isotherms from experimental data and from BET and GAB models at 30°C. (●) Experimental data, (■) BET, (▲) GAB.
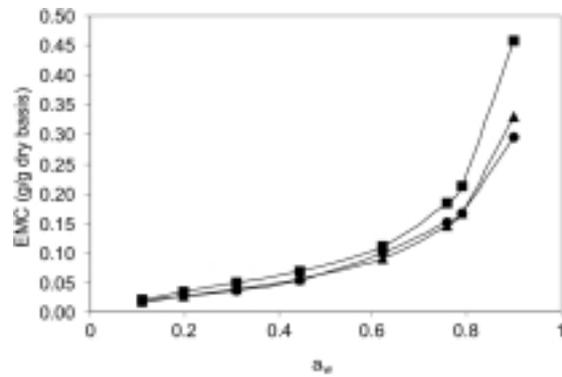

Figure 4. Comparison between isotherms from experimental data and from BET and GAB models at 60°C. (●) Experimental data, (■) BET, (▲) GAB.
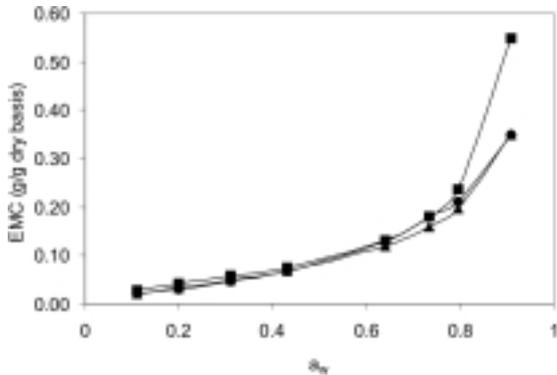

Figure 3. Comparison between isotherms from experimental data and from BET and GAB models at 45°C. (●) Experimental data, (■) BET, (▲) GAB.

45 and 60 C, the GAB equation gave E values ranging from 5.53 to 8.31 while the BET equation predicted the isotherms with E values ranging from 22.55 to 42.61. Generally, a model is considered suitable if the E value is less than 10 (Ayranci and Duman, 2004). Low values of E and RMSE strengthen the usefulness of the GAB

model for studying water vapour sorption of rice crackers. It has also been recognised that the fit become better as the determination coefficient approaches 1. The determination coefficient closer to 1 is evident for the GAB model. Therefore, the GAB equation is optimal to fit the moisture sorption isotherms of rice crackers.

Monolayer Moisture Content

Modelling of sorption data of rice crackers using BET and GAB equations allows the determination of monolayer moisture content values, m_0, which are the measure of sorption possibility of the food material. The monolayer moisture content calculated from the BET and GAB models (Table 1) ranged between 0.047–0.053 g/g (dry basis) and 0.040–0.059 g/g (dry basis), respectively, for the range of temperature considered in this work. Lomauro et al. (1985) reported that the m_0 values of starchy foods generally ranged from 0.032 to 0.160 g/g (dry basis). The m_0 values for rice crackers agree well with the results of Kim et al. (1998), Palou et al. (1997) and Lomauro et al. (1985),

Table 1. Coefficients for BET and GAB isotherms for rice crackers.

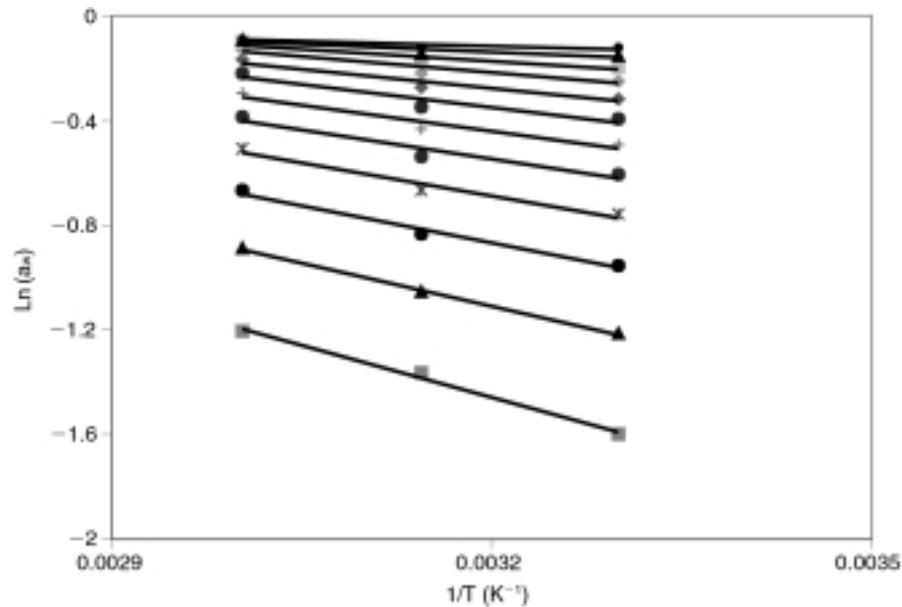| Model	Estimated Parameters	Temperature (°C)		
		30	45	60
BET	m_o	0.0528	0.0500	0.0467
	C_B	12.2970	8.3844	5.7707
	R^2	0.8147	0.9433	0.9796
	%E	42.6120	22.5508	28.5034
	RMSE	5.5045	7.1534	6.1583
GAB	m_o	0.0594	0.0560	0.0501
	C_G	7.4436	4.0314	4.9022
	K_G	0.9200	0.9299	0.9794
	R^2	0.9844	0.9951	0.9923
	%E	8.3088	6.6232	5.5328
	RMSE	1.9136	0.9834	1.2583

Figure 5. ln (a_w) *vs.* $1/T$ plot for rice crackers at a constant moisture content.

who reported m_0 values for wheat crackers, various cookies and corn snacks of 0.040–0.050, 0.037–0.045 and 0.038–0.055 g/g (dry basis), respectively.

The monolayer moisture content showed a tendency to decrease with increasing temperature. The decrease in m_0 reflected a reduction in the number of active sites due to chemical and physical changes induced by temperature (McMinn and Magee, 2003). Similar observations were obtained by Benado and Rizvi (1985) for rice, Barreiro et al. (2003) for barley malt and Kim et al. (1998) for cookies and crackers. The prediction of m_0 values is important since deterioration of foods is very small below m_0, since water is strongly bound to the food below m_0 and is not involved in any deteriorative reaction either as solvent or as one of the substrates (Kaymak-Ertekin and Gedik, 2004).

Isosteric Heat of Sorption

The isosteric heat of sorption values were calculated from Equation (6) by plotting the sorption isotherm as the natural logarithm of water activity ($\ln(a_w)$) against $1/T$, for a specific moisture content using the data derived from the sorption isotherms. q_{st} values were determined from the slope of the line which is equal to $-q_{st}/R$. A typical $\ln(a_w)$ *vs.* $1/T$ plot for rice cracker at a constant moisture content is illustrated in Figure 5.

The maximum q_{st} value of rice crackers (Figure 6) was 24.86 kJ/mol at 0.01 g/g (dry basis) and decreased to 0.05 kJ/mol at 0.28 g/g (dry basis). The maximum q_{st} value of rice crackers (24.86 kJ/mol) was close to that of cookies (28 kJ/mol) as reported by Kim et al. (1998). However, the maximum q_{st} value of rice crackers was different from those reported by Iglesias and Chirife

(1982) for tapioca (12 kJ/mol), Benado and Rizvi (1985) for sorghum (18 kJ/mol) and Kim et al. (1998) for wheat crackers (42 kJ/mol). These differences possibly ascribe to the food composition and their processing treatments (Palou et al. 1997).

The q_{st} values were large at low moisture content and then sharply decrease with an increase in material moisture content. The isosteric heat of sorption has a strong dependence on moisture content, with the energy required for sorption increasing at low equilibrium moisture content. The rapid increase in the heat of sorption at low moisture content was due to the existence of highly active polar sites on the surface of the food material, which are covered with water molecules forming a monomolecular layer. As these sites become occupied, sorption occurs on the less active
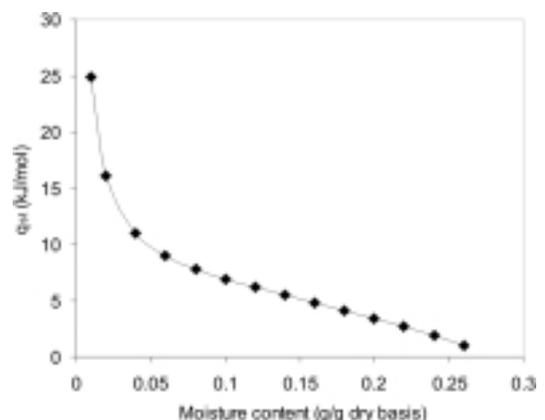

Figure 6. Isosteric heat of sorption of rice crackers as a function of equilibrium moisture content.

sites given lower heats of sorption (Ayranci and Duman, 2004; Iglesias and Chirife, 1982; McMinn and Magee, 2003; Palou et al., 1997). Such a trend was observed in crackers, cookies, rice and many cereal grains (Benado and Rizvi, 1985; Kim et al., 1998; Tolaba et al., 1997).

The magnitude of the heat of sorption, at a specific moisture content, provides a knowledge of the moisture adsorption state and hence, a measure of the physical, chemical and microbiological stability of the food products under given storage conditions (McMinn and Magee, 2003).

CONCLUSION

Rice crackers exhibited Type II isotherms. The equilibrium moisture content decreased with increased temperature at constant water activity, and increased with an increase in water activity, at constant temperature. The GAB model gave the best fit to the experimental sorption data for a wide range of water activity (0.10–0.95) while the BET model gave the best fit for a water activity range of less than 0.60. The GAB model is considered suitable to predict the moisture sorption isotherm of rice crackers since it gave low E and RMSE values. The isosteric heat of sorption was found to be large at low moisture content and then sharply decreased with an increase in food moisture content. The knowledge of the equilibrium moisture content of rice crackers at various temperatures would allow food manufacturers to specify the storage condition for this product.

ACKNOWLEDGEMENTS

REFERENCES

Al-Muhtaseb A.H., McMinn W.A.M. and Magee T.R.A. (2004). Water sorption isotherms of starch powders. Part 1: Mathematical description of experimental data. *Journal of Food Engineering* **61**: 297–307.

Anderson R. (1946). Modifications of the BET equation. *Journal of the American Chemical Society* **68**: 686–691.

ASAE (1995). *Moisture Relationship of Plant-based Agricultural Products*. ASAE Standard D 245.5. ASAE: St. Joseph, MI.

Ayranci E. and Duman O. (2004). Moisture sorption isotherms of cowpea (*Vigna unguiculata* L. Walp) and its protein isolate at 10, 20 and 30 °C. *Journal of Food Engineering* **61**: 192–209.

Barreiro J.A., Fernandez S. and Sandoval A.J. (2003). Water sorption characteristics of six row barley malt (*Hordeum vulgare*). *Lebensmittel-Wissenschaft und-Technologie* **36**: 37–42.

Benado A.L. and Rizvi S.S.H. (1985). Thermodynamic properties of water in rice as calculated from reversible isotherms. *Journal of Food Science* **50**: 101–105.

Bianco A.M., Boente G., Polliop M.L. and Resnik S.L. (2001). Influence of oil content on sorption isotherms of four varieties of peanut at 25 °C. *Journal of Food Engineering* **47**: 327–331.

Brunauer S., Emmett P.H. and Teller E. (1938). Adsorption of gases in multimolecular layers. *American Chemical Society Journal* **60**: 310–319.

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

de Boer J. (1995). The dynamic character of adsorption. In: Rao M. and Rizvi S. (eds), *Engineering Properties of Food*, 2nd edn. New York: Marcel Dekker Inc., pp. 115–251.

Guggenheim E. (1995). Applications of statistical mechanics. In: Rao, M., and Rizvi, S. (eds), *Engineering Properties of Food*, 2nd edn. New York: Marcel Dekker Inc., pp. 115–251.

Iglesias H.A. and Chirife J. (1982). *Handbook of Food Isotherm: Water Sorption Parameters for Food and Food Components*. Food Science and Technology a Series of Monograph, New York: Academic Press.

Jamali A., Kouhila M., Ait Mohamed L., Jaouhari J.T., Idlimam A. and Abdenouri N. (2006). Sorption isotherms of Chenopodium ambrosioides leaves at three temperatures. *Journal of Food Engineering* **72**: 77–84.

Kapsalis J.G. (1987). Influence of hysteresis and temperature on moisture sorption isotherms. In: Rockland, L.B. and Beuchat, L.R. (eds), *Water Activity: Theory and Applications to Food*. New York: Marcel Dekker Inc., pp. 173–207.

Kaya S. and Kahyaoglu T. (2005). Thermodynamic properties and sorption equilibrium of pestil. *Journal of Food Engineering* **71**: 200–207.

Kaymak-Ertekin F. and Gedik A. (2004). Sorption isotherms and isosteric heat of sorption of grapes, apricots, apples and potatoes. *Lebensmittel-Wissenschaft und-Technologie* **37**: 429–438.

Kim S.S., Kim S.Y., Kim D.W., Shin S.G. and Chang K.S. (1998). Moisture sorption characteristics of composite foods filled with strawberry jam. *Lebensmittel-Wissenschaft und-Technologie* **31**: 397–401.

Lomauro C.J., Bakshi A.S. and Labuza T.P. (1985). Evaluation of food moisture sorption isotherms equations. Part II: Milk, coffee, tea, nuts, oilseeds, spices and starchy foods. *Lebensmittel-Wissenschaft und-Technologie* **18**: 118–124.

McMinn W.A.M. and Magee T.R.A. (2003). Thermodynamic properties of moisture sorption of potato. *Journal of Food Engineering* **33**: 227–237.

Pahlevanzadeh H. and Yazdani M. (2005). Moisture

adsorption isotherms and isosteric energy for almond. *Journal of Food Process Engineering* **28**: 331–345.

Palou E., Lopez-Malo A. and Argaiz A. (1997). Effect of temperature on the moisture sorption isotherms of some cookies and corn snacks. *Journal of Food Engineering* **31**: 85–93.

Rohvein C., Santalla E. and Gely M.C. (2004). Note: Estimation of sorption isotherm and the heat of sorption of quinoa (Chenopodium quinoaWilld.) seeds. *Food Science and Technology International* **10**(6): 409–413.

Tolaba M.P., Suarez C. and Viollaz P. (1997). Heats and entropies of sorption of cereal grains: a comparison between internal and differential quantities. *Drying Technology* **15**(1): 137–150.

Timmermann E.O. (2003). Multilayer sorption parameters. *Colloid and Surfaces A: Physicochemical and Engineering Aspects* **220**(1): 235–260.