Int. Agrophys., 2010, 24, 213-218

INTERNATIONAL
Agrophysics
www.international-agrophysics.org

Mathematical modelling of corn thermodynamic properties for desorption energy estimation

R. Amiri Chayjan[1]**, J. Amiri Parian*[1]*, M. Esna-Ashari*[2]*, and M.H. Peyman*[3]

[1]Department of Mechanics of Agricultural Machinery Engineering, [2]Department Horticulture Science,
Faculty of Agriculture, Bu-Ali Sina University, 6517833131, Hamedan, Iran
[3]Department Agricultural Mechanization, Faculty of Agriculture, Guilan University, 41635-1314, Rasht, Iran

Received August 22, 2009; accepted September 12, 2009

Abstract. Two thermodynamic properties of net isosteric heat and entropy of sorption of corn were obtained by thermodynamic equations and mathematical models. Mathematical models were used to predict the equilibrium moisture content (*EMC*) of corn. The modified Oswin model was the best for prediction of the *EMC* of corn with R^2=0.9910. The isosteric heat of sorption of corn is predicted by a power model applied in this study. After finding the best model (modified Oswin), predictive power of the model was found to be high (R^2=0.99). Also a regression model was developed for entropy of sorption. The maximum value of net isosteric heat of sorption of corn is lower than those of some the other agricultural products, which might be due to soft and starchy tissue of corn. At moisture content above 11% (d.b.) the isosteric heat and entropy of sorption of corn decrease smoothly and they are the highest at moisture content of about 8% (d.b.). Isosteric heat and entropy would be useful in the simulation of storage of dried corn. The modified Oswin model predicts corn *EMC* more accurately than the other mathematical models. Hence better equations are developed for prediction of heat of sorption and entropy based on data from modified Oswin model.

Keywords: modified Oswin model, entropy, isosteric heat, sorption isotherm, corn

INTRODUCTION

Safe storage and keeping the quality of harvested corn, with attention to high moisture content of corn at harvesting time, is very important. Drying of corn is the most important stage in its processing chain. Energy consumption of the drying process with regard to the final moisture content is an index for selection of dryer or type of drying process. The equilibrium moisture content (*EMC*) that is defined as the moisture content of a hygroscopic material in equilibrium with particular environmental conditions (temperature and relative humidity) is a vital parameter in studying the drying process. Research has proved that, if the two mentioned environmental factors are not controlled, mould activities increases. In this condition, the embryo is the first part of the seed that will be attacked by mould (Brooker *et al*., 1992).

Temperature and moisture content of seed have an effect on its shelf life. Increase in the mentioned factors causes increasing seed respiration and enzyme production. This phenomenon tends to decrease the storage durability of seed and seed germination (Copeland and McDonald, 1995). *EMC* is a durability criterion and any change in the quality of food and agricultural products during storage and packaging is of crucial importance (Veltchev and Menkov, 2000). The fundamental relationship between *EMC* and relative humidity of food products is known as sorption isotherms (Palipane and Driscroll, 1992). Sorption characteristics of food and agricultural products are used for designing, modelling and optimising some processes such as drying, aeration and storage (Labuza, 1975; Bala, 1997).

Sopade and Ajisegiri (1994) studied the moisture isotherms of corn within the temperature range of 20-40°C and water activity of 0.1-0.98. They applied six models for fitting the experimental data. The results showed that the Henderson model was the best for the desorption isotherm. Chen and Morey (1989) derived the sorption isotherm curves of yellow-dent corn for the temperature range of 5-45°C. Their results showed that the curves are different for various cultivars, also that temperature and relative humidity are the most effective factors on the curves.

---

*Corresponding author's e-mail: amirireza@basu.ac.ir

Many studies have been reported to suggest numerous isotherm models for food materials (Kaymak-Ertekin and Gedik, 2004; Lahsasni *et al*., 2004; Lomauro *et al*., 1985; Mir and Nath, 1995; Reddy and Chakraverty, 2004). Of these models the GAB (Guggenheim, Anderson and de Boer) model is the most widely used and versatile model.

Phomkong *et al*. (2006) fitted the Chung Pfost, Oswin and GAB models to desorption isotherm data of peach, plum and nectarine and the GAB model was found to give the best representation of the data. Janjai *et al*. (2006) determined the isotherm data of longan using the dynamic method and fitted data to five selected mathematical models. The GAB model was found to be the best to fit the experimental isotherm data of longan.

Isotherms of agricultural products are usually sigmoid-shape curves which are even difficult to draw and manipulate (Bala, 1997). Several complex mathematical models have been developed to describe these curves (Janjai, 2006). For the estimation of the parameters of these models, non linear direct optimization techniques are required.

The net isosteric heat equation is suggested for use in the computation of heat of sorption of corn, while both the isosteric heat and entropy equations are essential to compute the humidity during simulation of stored dried corn. If mathematical models are developed using experimental equilibrium moisture content data of corn, the models developed can be used to predict the equilibrium moisture contents using computer and also can be used to predict the isosteric heat and entropy for modelling and simulation of drying and storage of corn. The net isosteric heat of sorption is an important parameter for drying and is a measure of the water-solid binding strength. It can be used to determine the energy requirements and show the state of water within the dried material. The moisture content level of a material at which the net isosteric heat of sorption reaches the value of latent heat of sorption is often considered as the indication of the amount of bound water exiting in the material (Wang and Brennan, 1991).

Researchers proposed an empirical exponential relationship between the net isosteric heat of sorption and material moisture content for some fruits (Tsami, 1994) and a power function between them for pineapple (Hossain *et al*., 2001). The differential entropy of a material is proportional to the number of sites at a specific energy level (Madamba *et al*., 1996). Many researchers studied the relationship between net isosteric heat of sorption and moisture content. Madamba *et al*. (1996) adopted an exponential relation to describe the entropy of garlic sorption as a function of moisture content. McMinn *et al*. (2004) reported that the net isosteric heat of sorption and differential entropy of potato decreased with increase in moisture content and were adequately characterized by a power law model.

No study has been reported about sorption isotherm of corn (cv. SC704) by mathematical models. Also net isosteric heat of sorption and differential entropy of corn is not available. The objective of this study was to develop a mathematical model on experimental data of sorption of corn, an improved empirical model for the net isosteric heat of sorption and also a new empirical model for the net isosteric heat of entropy for corn.

MATERIAL AND METHODS

Corn samples (cv. SC704) were supplied from Kermanshah province, Iran. Salt saturated solutions including lithium chloride, potassium acetate, magnesium chloride, potassium carbonate and potassium chloride (all made by MERK Company) were used to provide needed relative humidity.

One of the most common methods used for *EMC* determination is gravimetric, as it has high precision and does not need a complex implement (Spiess and Wolf, 1983). After preparation, the corn kernels were used in each 5 g experimental sample. The samples were placed into three Petri dishes (90 mm in diameters). The dishes were then transferred into a desiccator and kept for six weeks, being weighed every single day. Equilibrium was achieved when the difference between any successive weighing was lower than 0.001 g (Ayranchi *et al*., 1990; Gabas *et al*., 1999).

To establish a fixed relative humidity at water activity domain of 9.30-90.45%, five salt saturated solutions were used. Creation of such relative humidity using saturated salt solutions has been reported in literature (Bala, 1997). In addition, these values were also checked by using a hygrometer.

The temperature needed for the experiment was provided by the use of an incubator with an electrical heater and an electronic temperature controller to maintain the temperature. An electric fan was fitted to circulate the air inside the sample box to accelerate moisture transfer between the samples and the air inside the sample box. Three to four weeks were needed for the samples to reach equilibrium. Lower relative humidity and upper experimental temperature caused a decrease in the time required for reaching the equilibrium. In order to determine the final moisture content, the equilibrated samples were placed in an oven (103°C) for 72 h. Boundaries and levels of input parameters are shown in Table 1. All the experiments were conducted in three replications.

Table 1. Input parameters for mathematical models and their boundaries for prediction of corn equilibrium moisture content

Parameters	Min	Max	No. of levels
Air temperature (°C)	25	55	4
Relative humidity (%)	9.30	90.445	5

Some of the most common mathematical models that are used for prediction of sorption isotherms of agricultural products are:

$$EMC = \frac{1}{\mathrm{B}} \ln\left[-\frac{T+\mathrm{C}}{\mathrm{A}} \ln a_w\right] \text{ (Chung-PFost)}, \tag{1}$$

$$EMC = \left[\frac{-1}{\mathrm{A}(T+\mathrm{C})} \ln(1-a_w)\right]^{\frac{1}{B}} \text{ (Modified Henderson)}, \tag{2}$$

$$EMC = (\mathrm{A}+\mathrm{B}T)\left[\frac{a_w}{1-a_w}\right]^{\frac{1}{\mathrm{C}}} \text{ (Modified Oswin)}, \tag{3}$$

where: *EMC* is equilibrium moisture content (% d.b.); a_w is water activity; *T* is absolute temperature (K). A, B, and C are constants for different materials calculated by experimental method. Supremacy of each model for prediction of *EMC* is expressed by three indices of coefficient of determination (R^2), mean relative error ($\mathrm{E_{mr}}$) and standard error (SE). These indices are defined as follows:

$$\mathrm{R}^2 = 1 - \frac{\sum_{k=1}^{n}\left[S_k - T_k\right]}{\sum_{k=1}^{n}\left[S_k - \frac{\sum_{k=1}^{n} S_k}{n}\right]}, \tag{4}$$

$$\mathrm{E_{mr}} = \frac{100}{n}\sum_{k=1}^{n}\left|\frac{S_k - T_k}{T_k}\right|, \tag{5}$$

$$\mathrm{SE} = \sum_{k=1}^{n}\sqrt{\frac{(S_k - T_k)^2}{d.f.}}, \tag{6}$$

where: R^2 – the determination coefficient, $\mathrm{E_{mr}}$ – the mean relative error, SE – the standard error, S_k – the network output for *k*th pattern, T_k – the target output for *k*th pattern, *d.f.* – degree of freedom and *n* – the number of patterns.

The fit was performed by non-linear regression based on minimization of the square sum by means of the software Statistica 8.

The net isosteric heat of sorption can be determined by the Clausius-Clayperon equation (Hossain *et al.*, 2001; Phomkong *et al.*, 2006):

$$\frac{\partial \ln(RH)}{\partial T_{ab}} = \frac{\Delta H}{\mathrm{R_o} T_{ab}^2}, \tag{7}$$

where: *RH* is the relative humidity (%), T_{ab} is the absolute temperature (K), ΔH is the isosteric heat of sorption (kJ $\mathrm{mol^{-1}}$) and $\mathrm{R_o}$ is the universal gas constant (8.315 kJ $\mathrm{kmol^{-1}\ K^{-1}}$).

Integrating Eq. (7) and assuming that the isosteric heat of sorption (ΔH) is independent of temperature gives the Eq. (8) as follows:

$$\ln(RH) = -\left(\frac{\Delta H}{\mathrm{R_o}}\right)\frac{1}{T_{ab}} + C, \tag{8}$$

where *C* is the intercept of the Eq. (8).

The value of ΔH is computed from the slope of Eq. (8) and following this the relationship in thermodynamics is (Rizvi, 1995):

$$\Delta G = \Delta H - T_{ab}\Delta S, \tag{9}$$

where: ΔG is the Gibbs free energy (J $\mathrm{mol^{-1}}$) and ΔS is the entropy (J $\mathrm{mol^{-1}\ K^{-1}}$). For moisture sorption, it can be shown that:

$$\Delta G = -\mathrm{R_o} T_{ab} \ln(RH). \tag{10}$$

Substituting from Eq. (9) into Eq. (10), the following equation is obtained:

$$-\ln(RH) = \left(\frac{\Delta H}{\mathrm{R_o}}\right)\frac{1}{T_{ab}} - \frac{\Delta S}{\mathrm{R_o}}, \tag{11}$$

when ln(*RH*) are plotted against $1/T_{ab}$, a straight line graph is obtained with the y-intercept of $\Delta S/\mathrm{R_o}$. From the values of this y-intercept and $\mathrm{R_o}$, ΔH and ΔS can be computed.

RESULTS AND DISCUSSION

Equilibrium moisture content of corn was determined experimentally using a dynamic method. The average *EMC* as well as water activities of salt solutions are shown in Fig. 1. These curves are the moisture sorption isotherms of corn at four temperature levels of 25, 35, 45 and 55°C in the range of 9.30-90.45% relative humidity. Increasing temperature in a water activity decreases the *EMC*. Increasing in water activity caused an increase in corn *EMC*

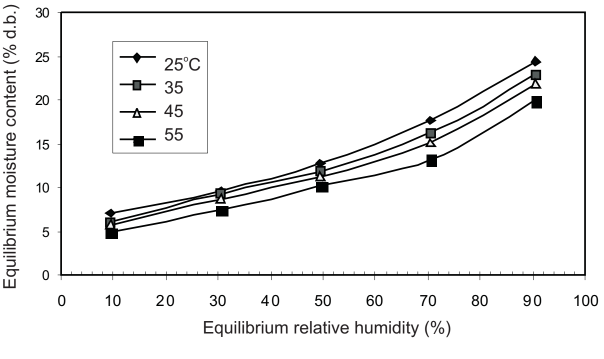

Fig. 1. Sorption isotherm of corn from the experiments at different temperature.

at all of the temperatures. This smooth change in all temperatures is obvious. This change is because of high density and high starch percentage of corn.

Mathematical models of Chung-Pfost, modified Henderson and modified Oswin were used for corn *EMC* empirical data fitting. Non-linear regression method with software was used for fitting the data. Three indices of coefficient of determination (R^2), mean relative error (E_{mr}) and standard error (SE) were used for appropriate fit determination. The results of empirical models fitting at the temperature levels tested are shown in Table 2. For those temperatures the modified Oswin model produced the best result. The best result was $R^2 = 0.9910$, $E_{mr} = 5.521\%$ and SE = 0.965. Therefore this model produced the best results for the four temperature levels that could be used for the estimation of corn, net isosteric heat of sorption and net isosteric entropy of sorption at various temperatures and water activities. Any empirical model has an equation with constants (A, B, C).

Equilibrium moisture content values of corn at the four temperature levels (25, 35, 45 and 55°C) and five moisture content levels (8, 11, 14, 17 and 20%) were computed using the modified Oswin model. Values of ln(*RH*) versus function of $1/T_{ab}$ were plotted for corn (cv. SC704) at constant moisture content (Fig. 2). These values were estimated by the modified Oswin model. The slope of the lines at constant moisture contents were the net isosteric heat of sorption of corn. The slopes were determined by linear regression analysis. The heat of sorption for corn at different moisture contents is presented in Fig. 3.

The net isosteric heat of sorption was found to decrease with increase in moisture content. At low moisture content, water is absorbed on the most accessible locations on the exterior surface of the solid. As the moisture content increases the material swells and, therefore, new high-energy sites are opened up for water to get bound to. This causes the net isosteric heat of sorption to increase as with moisture content decrease. This trend is similar to those reported in studies on agricultural, food and medical and aromatic plants (Hossain *et al.*, 2001; Lahsasni *et al.*, 2004; Phomkong *et al.*, 2006). The net isosteric heat of sorption was found to fit a power law relation. The following equations was developed for corn:

$$\Delta H = 512.46 MC^{-1.6009} \quad R^2=0.9832. \tag{12}$$

This relation showed that the net isosteric heat of sorption of corn increases following a power law relationship. This relation has a better fit than the exponential relation previously developed by Janjai *et al.* (2006) for Longan. The maximum values of isosteric heat of sorption for some agricultural products that have been reported by researchers, compared to corn (this study), are represented in Table 3. The lower values of heat of sorption of corn compared to the other agricultural products might be due to the soft and starchy structure of corn. The isosteric heat of sorption of corn is high, significantly, while the equilibrium moisture content is lower than 11% (d.b.). This can be explained by the fact that at moisture content above 11% (d.b.) water is loosely bound in corn. This implies that corn needed less energy at higher moisture content (above 11% d.b.) for

Table 2. Constants and outputs of mathematical models for corn

Model	Constants			R^2	E_{mr}	SE
	A	B	C			
Chung-PFost	521.880	19.012	48.845	0.9900	5.670	1.046
Modified Oswin	0.152	-0.00079	3.321	0.9910	5.521	0.965
Modified Henderson	0.840	2.154	42.897	0.9880	7.002	1.186

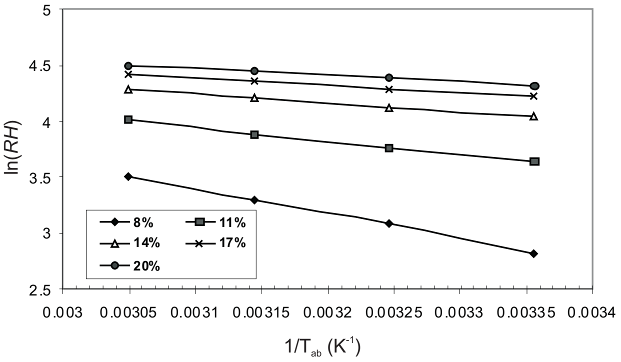

Fig. 2. ln(RH) as a function of $1/T_{ab}$ at different moisture content for corn.

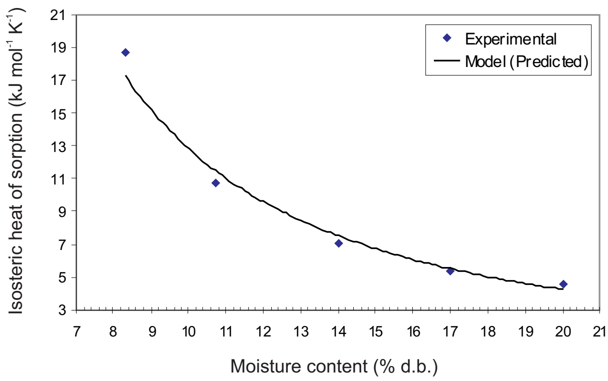

Fig. 3. Isosteric heat of corn sorption at different equilibrium moisture contents.

T a b l e 3. Input parameters and their boundaries for prediction of corn equilibrium moisture content

Products	$EMC_{\min}$ (%, d.b.)	Isosteric heat of sorption (kJ mol^{-1})
Longan[1]	40	19.5
Litchi[2]	20	32
Mango[3]	30	18
Corn (cv. SC704)	8	18.68

[1]Janjai *et al*. (2006), [2]Janjai *et al*. (2010), [3]Janjai *et al*. (2007).

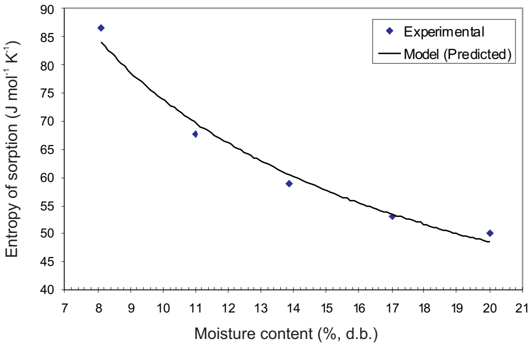

Fig. 4. Entropy of corn sorption at different equilibrium moisture contents.

drying, but more energy at lower moisture contents was needed, especially for storage. After processing, dried corn with 15% (d.b.) moisture content is stored (Brooker *et al*., 1992).

Entropy of sorption of corn (cv. SC704) is presented in Fig. 4. It is a function of moisture content and the following power law model is fitted to data:

$$\Delta H = 301.23\,MC^{-0.6104} \quad R^2=0.9802. \qquad (13)$$

The fitted curves for prediction of entropy have good values compared to the experimental one. These results proved that the entropy decreases with increase in moisture content. Similar trends have been reported on the entropy of potato and melon seed and cassava (Aviara and Ajibola, 2002; McMinn and Magee, 2003).

The derived equations for isosteric heat and entropy of sorption are necessary for calculation of humidity during storage of corn. These results showed that the modified Oswin model has supremacy over the other models because it provides more accurate data to develop better equations for isosteric heat and entropy of sorption.

CONCLUSIONS

1. Application of mathematical models showed that the modified Oswin model produced the best results for corn (cv. SC704) with $R^2 = 0.9910$, $E_{mr} = 5.521$ and $SE = 0.965$.

2. The net isosteric heat of sorption of corn was computed by the Clausius-Clapeyron equation. This method proved that the relation between moisture content and net isosteric heat and entropy of sorption is a power law model. The isosteric heat of sorption of corn was characterized by a power law model developed in this study with above 0.98. Entropy of sorption of corn was also determined by a power model. The power model for corn has about 0.98.

3. The power law relations for net isosteric heat and entropy of sorption of corn showed that the net isosteric heat of sorption increases following a power law relationship. The lower values of heat of sorption of corn compared to other agricultural products might due to the soft and starchy structure of corn. The isosteric heat of sorption of corn is high, significantly, while the equilibrium moisture content is lower than 11% (d.b.). This can be explained by the fact that at moisture content above 11% (d.b.) water is loosely bound in. This implies that corn needs less energy at higher moisture content (above 11% d.b.) for drying and storage, but more energy at lower moisture contents is needed.

REFERENCES

Aviara N.A. and Ajibola O.O., 2002. Thermodynamics of moisture sorption in melon seed and cassava. J. Food Eng., 55, 107-113.

Ayranchi E., Ayranchi G., and Dogantan Z., 1990. Moisture sorption isotherms of dried apricot, fig and raisin at 20°C and 36°C. J. Food Sci., 55, 1591-1593.

Bala B.K., 1997. Drying and Storage of Cereal Grains. Oxford-IBH Press, New Delhi, India.

Brooker D.B., Bakker-Arkema F.W., and Hall C.W., 1992. Drying and Storage of Grain and Oilseeds. AVI Press, New York, USA.

Chen C. and Morey R.V., 1989. Equilibrium relative humidity (ERH) relations for yellow-dent corn. Trans. ASAE, 32(3), 999-1006.

Copeland L.O. and McDonald M.B., 1995. Seed Science and Technology. Chapman and Hall Press, New York, USA.

Gabas A.L., Telis-Romero J., and Menegalli F.C., 1999. Thermodynamic models for water sorption by grape skin and pulp. Drying Techol., 17, 961-974.

Hossain M.D., Bala B.K., Hossain M.A., and Mondol M.R.A., 2001. Sorption isotherm and heat of sorption of pineapple. J. Food Eng., 48, 103-107.

Janjai S., Bala B.K., Tohsing K., Mahayothee B., Heawsungcharen M., Muhlbauer W., and Muller J., 2006. Equilibrium moisture content heat of sorption of longan (*Dimocarpus longan*). Drying Technol., 24, 1691-1696.

Janjai S., Bala B.K., Tohsing K., Mahayothee B., Heawsungcharen M., Muhlbauer W., and Muller J., 2007. Moisture sorption isotherms and heat of sorption of mango. Int. Agric. Eng. J., 16(3-4), 159-168.

Janjai S., Bala B.K., Tohsing K., Muller J., and Muhlbauer W., 2010. Moisture sorption isotherms of litchi. Int. J. Food Properties, 13(2), 251-260.

Kaymak-Ertekin F. and Gedik S., 2004. Sorption isotherms and isosteric heat of sorption for grapes, apricots, apples and potatoes. Lebensm.-Wiss. Tech., 37, 429-438.

Labuza T.P., 1975. Interpretation of sorption data in relation to the state of constituent water. In: Water Relations of Foods (Ed. R.B. Duchworth,). London Academic Press, London, UK.

Lahsasni N., Kouhila M., and Mahrouz M., 2004. Adsorpion-desorption isotherms and heat of sorption of pickly pear fruit. Energy Conv. Manag., 45, 249-261.

Lomauro C.J., Bakshi A.S., and Labuza T.P., 1985. Evaluation of food moisture sorption isotherm equations. Part 1. Fruit, vegetable and meat products. Lebensm.-Wiss. Tech., 18, 111-117.

Madamba P.S., Driscoll R.H., and Buckle K.A., 1996. Enthalpy-entropy compensation models for sorption and browning of garlic. J. Food Eng., 28, 109-119.

McMinn W.A.M., Al-Muhtaseb A.H., and Magee T.R.A., 2004. Moisture sorption characteristics of starch gels. Part II: Thermodynamic properties. J. Food Proc. Eng., 27, 213-227.

McMinn W.A.M. and Magee T.R.A., 2003. Thermodynamic properties of moisture sorption of potatoes. J. Food Eng., 60, 157-165.

Mir M.A. and Nath N., 1995. Sorption isotherms of fortified mango bars. J. Food Eng., 25, 141-150.

Palipane K.B. and Driscoll R.H., 1992. Moisture sorption characteristics of in-shell macadamia nut. J. Food Eng., 18, 63-76.

Phomkong W., Srzednicki G., and Driscoll R.H., 2006. Desorption isotherms of stone fruit. Drying Technol., 24(2), 201-210.

Reddy B.S. and Chakraverty A., 2004. Equilibrium moisture characteristics of raw and parboiled paddy, brown rice and bran. Drying Technol., 22(4), 837-851.

Rizvi S.S.H., 1995. Thermodynamics of food and dehydration. In: Engineering Properties of Foods (Eds M.A. Rao, S.S.H. Rizvi). Marcel Dekker Press, New York, USA.

Spiess W.E.L. and Wolf W., 1983. The results of the COST 90 projects on water activity. In: Physical Properties of Foods (Ed. R. Jowitt). Applied Sci. Press, London, UK.

Sopade P.A. and Ajisegiri E.S., 1984. Moisture sorption study on Nigerian foods: maize and sorghum. J. Food Proc. Eng., 17(1), 33-56.

Tsami E.D., 1994. Net isosteric heat of sorption in dried fruit. J. Food Eng., 4(4), 327-335.

Veltchev Z.N. and Menkov N.D., 2000. Desorption isotherm of apples at several temperatures. Drying Technol., 18, 1127-1137.

Wang N. and Brennan J.G., 1991. Moisture sorption isotherm characteristics of potatoes at four temperatures. J. Food Eng., 14, 269-282.