Modeling of heat and entropy sorption of maize (cv. Sc704): neural network method

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Abstract

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Equilibrium moisture content of maize affects its values of dehydration heat and entropy. Precise prediction of heat and entropy with regard to its equilibrium moisture content is a simple and fast method for proper estimation of energy required for dehydration of maize and simulation of dried maize storage. Artificial neural network and thermodynamic equations for computation of maize heat and entropy of sorption were used, as a new method. The artificial neural network method for prediction of the equilibrium moisture content of maize was utilized. The heat of sorption of maize is predicted by a power model. After well training of equilibrium moisture content data sets using the artificial neural network models, predictive power of the model was found to be high (R^2 = 0.99). A power regression model was also developed for entropy of sorption. At moisture content above 11% (d.b.) the heat and entropy of sorption of maize decreased smoothly and they were highest at moisture content about 8% (d.b.).

Keywords: maize; back propagation; entropy; isosteric heat; sorption isotherm

Moisture content and temperature of maize seed affect its storage life. Increasing these factors causes an increase in maize seed respiration and enzymes production. This phenomenon tends to decrease food storage of seed and germination (Copeland, McDonald 1995).

Equilibrium moisture content (*EMC*) of food and agricultural products is a durability criterion and any change in the quality during drying, storage and packaging is crucial and important (Veltchev, Menkov 2000). Fundamental relationship between air temperature, air relative humidity and *EMC* of food and agricultural products is known as sorption isotherms. Adsorption and desorption characteristics of food and agricultural products are used for designing, modeling and optimizing some post-harvest processes such as drying, aeration and storage (Labuza 1975; Bala 1997).

Drying time and energy consumption of drying process with regard to final moisture content are important indices for selection of a dryer or type of drying process. Safe storage and packaging as well as keeping the quality of harvested maize, considering its high moisture content at harvesting time, is very important. Maize *EMC,* that is defined as its moisture content in equilibrium with particular environmental conditions (air temperature and air relative humidity) is a vital parameter in studying the drying and storage processes. Studies showed that if the two environmental factors were not controlled, the mold activities increased. (Brooker et al. 1992).

Chen and Morey (1989) studied the sorption isotherm curves of yellow dent maize at the air temperature boundary of 5°C to 45°C. Their results showed that sorption isotherm curves are different for maize cultivars; also air relative humidity and air temperature are the most effective factors on these curves. Sopade and Ajisegiri (1994) studied on the moisture sorption isotherms of maize at the air temperature boundary of 20°C to 40°C and air water activity of 0.1–0.98. They applied six mathematical models of sorption to fit experimental data. Results showed that the Henderson model was the best for prediction of maize sorption isotherm.

Many studies were reported to suggest numerous sorption isotherm models for food and agricultural materials (Kaymak-Ertekin, Gedik 2004; Lahsasni et al. 2004; Reddy, Chakraverty 2004; Janjai et al. 2006; Phomkong et al. 2006). The GAB (Guggenheim, Anderson and de Boer) model commonly presented the best results. Sorption isotherms of agricultural and food products are usually sigmoid-shaped curves which are even difficult to draw and manipulate. Several complex mathematical models were developed to describe these curves (Bala 1997). Non-linear direct optimization techniques required for estimation of these model parameters, accuracy and shape of the isotherms and also reliability of the predictions over the whole range of the air relative humidity limited by these estimations. Therefore, finding an alternative computational model is necessary to calculate the relationship of isotherms of agricultural and food products to increase accuracy and reliability in predictions. Artificial neural network (ANN) method can be an alternative for this purpose.

An ANN consists of processing units, named neurons. They are related with special arrangement. Neurons are in layers and every neural network includes some neurons in input layer, one or more neurons in output layer and neurons in one or more hidden layers. Algorithms and architectures of ANNs are different through variation in neuron model and type of relationship between neurons, and their weights. The learning purpose in ANNs is weight updating, so that desired outputs are obtained with presenting a set of inputs. Many researchers applied the ANN models for sorption isotherm modeling of agricultural and food products, such as black tea (Pancharyia et al. 2002) and maize starch (Peng et al. 2007). In all of these studies the ANN models were better than mathematical models.

Heat of sorption is an important parameter for drying and storage of maize and is an index for water-solid binding strength. It can be used to determine storage condition, energy requirements and state of water within the dried material. Moisture content level of maize at which the heat of sorption reaches the value of latent heat of sorption is often considered as the indication of the amount of bound water existing in maize (Wang, Brennan 1991).

Many exponential relationships were proposed between the heat of sorption and material moisture content for some fruits (Tsami 1994). Entropy of maize is proportional to the number of sites at a specific energy level (Madamba et al. 1996). Many researchers find the relationship between entropy and heat of sorption versus moisture content (Madamba et al. 1996; McMinn et al. 2004).

The objectives of this study were the application of the ANN method for modeling of maize sorption isotherm, finding an improved empirical model for maize heat of sorption and also a new empirical model for maize entropy based on the ANN method.

MATERIAL AND METHODS

Experiments

Maize Sample (cv. SC704) was supplied from the Kermanshah province, Iran. Moisture content of samples was about 35% (d.b.). To establish a fixed air relative humidity at water activity domain of 9.30–90.45%, five salt-saturated solutions including lithium chloride, potassium acetate, potassium carbonate, sodium nitrate, and potassium chloride (all made by the MERK Company) were utilized. Creation of such air relative humidity by the saturated solutions was reported through the literature (Bala 1997). In addition, these values were also checked using a hygrometer.

Gravimetric method was used for *EMC* determination of maize samples; because it has high precision and does not need a complex implement (Spiess, Wolf 1983). After cleaning the maize samples, several kernels of maize with about 10 g in weight were used in each experimental unit. Maize samples were placed into a desiccator and kept for six weeks while they were weighed every single day. Equilibrium in moisture content was derived when the difference of any successive weighings was lower than 0.001 g (Gabas et al. 1999).

The air temperature needed for the experiment (25, 35, 45, and 55°C) was provided by the use of

Table 1. Input parameters for ANNs and their boundaries for prediction of equilibrium moisture content in maize

Variables	Maximum	Minimum	Levels
Water activity (%)	90.45	9.30	5
Air temperature (°C)	55	25	4

an incubator with an electrical heater and an electronic air temperature controller to maintain the air temperature. An electrical fan was fitted to circulate the air inside the sample box to accelerate moisture transfer between the samples and air inside the sample box. Three to four weeks were needed for the samples to reach equilibrium. Lower air relative humidity and upper experimental air temperature cause a decrease in the time required for the equilibrium. In order to determine the final moisture content, the equilibrated samples were placed in an oven (103°C) for 72 h. All the experiments were conducted in three replications. The common mathematical model of modified GAB (Guggenheim, Anderson and de Boer) was used for prediction of maize sorption isotherms in this study as follows (Simal et al. 2007; Cervenka et al. 2008; Fasina 2008):

$$EMC = ABa_w \frac{\left(\frac{C}{T}\right)}{(1 - Ba_w + \left(\frac{C}{T}\right)Ba_w)(1 - Ba_w)} \quad (1)$$

where:

a_w – water activity
EMC – equilibrium moisture content (% d.b.)
T – absolute temperature (K)
A, B, and C – constants for different materials calculated by experimental method

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

Neural networks modeling

Feed-Forward Backpropagation (FFBP) and Cascade-Forward Backpropagation (CFBP) neural networks were utilized for training of experimental data set. FFBP consists of one input layer, one or several hidden layers and one output layer. For learning FFBP, back propagation (BP) learning algorithm is usually used. In BP algorithm, the first output layer weights were updated. A desired value (target) exists for each neuron of output layer. The weight coefficients were updated using these values and learning rules. During training the FFBP, calculations were conducted from input of network toward output and then error values were propagated to previous layers. CFBP is similar to FFBP network in weights updating and the BP algorithm, but the main symptom of CFBP is that each layer of neurons relates to all previous layers of neurons. Two training algorithms including Bayesian Regulation (BR) backpropagation and Levenberg-Marquardt (LM) algorithms were used for updating network weights.

Applying two inputs (air relative humidity and air temperature) in all experiments, the *EMC* values were derived for different conditions. Neural networks with two neurons in the input layer (air relative humidity and air temperature) and one neuron in the output layer (*EMC*) were designed. Levels and boundaries of input parameters are shown in Table 1. Neural network toolbox (ver. 4.1) of the Matlab software was used in this study.

The increasing method was used in order to proper select layers and neurons number for evaluation of various topologies. By this method, when the selected topology of neural network is trapped into the local minimum, new neuron was added to the network. This method has more practical power to detect the optimum size of the neural network. Threshold functions of purelin, logsig and tansig were utilized to reach the optimized status (Demuth, Beale 2003).

Experimental data of 25, 35, and 55°C were selected for training network with suit topology and training algorithm. Also the data obtained from experiment of 45°C used for testing of trained network. The following criterion of mean square error was defined to minimize the training error (Demuth, Beale 2003):

$$MSE = \frac{1}{MN}\sum_{p=1}^{M}\sum_{i=1}^{N}(S_{ip} - T_{ip})^2 \quad (2)$$

where:

MSE – mean square error
S_{ip} – network output in i^{th} neuron and p^{th} pattern
T_{ip} – target output at i^{th} neuron and p^{th} pattern
N – number of output neurons
M – number of training patterns

To optimize the selected network from the previous stage, the secondary criteria were used as follows:

$$R^2 = 1 - \frac{\sum_{k=1}^{n}[S_k - T_k]}{\sum_{k=1}^{n}[S_k - \frac{\sum_{k=1}^{n} S_k}{n}]} \quad (3)$$

$$E_{mr} = \frac{100}{n}\sum_{k=1}^{n}\left|\frac{S_k - T_k}{T_k}\right| \quad (4)$$

$$SE = \sum_{k=1}^{n}\sqrt{\frac{(S_k - T_k)^2}{d.f.}} \quad (5)$$

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

To increase the accuracy and processing velocity of neural networks, input data were normalized at the boundary of [0, 1].

Thermodynamic properties (theoretical principle)

The heat of sorption can be computed by the following equation (Phomkong et al. 2006):

$$\frac{\partial \ln(RH)}{\partial T_{ab}} = \frac{\Delta H}{R_o T_{ab}^2} \quad (6)$$

where:
RH – air relative humidity (%)
T_{ab} – absolute air temperature (K)
ΔH – heat of sorption (kJ/mol)
R_o – universal gas constant (8.315 kJ/kmol K)

Integrating Eq. (6) and assuming that the heat of sorption (ΔH) is independent of air temperature, gives the Eq. (7) as follow:

$$\ln(RH) = -(\frac{\Delta H}{R_o})\frac{1}{T_{ab}} + C \quad (7)$$

where:
C – intercept of the Eq. (7)

The value of ΔH is computed from the slope of the Eq. (7), as a following relationship in thermodynamics (Rizvi 1995):

$$\Delta G = \Delta H - T_{ab}\Delta S \quad (8)$$

where:
ΔG – Gibbs free energy (J/mol)
ΔS – entropy (J/mol K)

For moisture sorption, it can be shown that:

$$\Delta G = -R_o T_{ab} \ln(RH) \quad (9)$$

Substituting ΔG from Eq. (8) into Eq. (9), the following equation is obtained:

$$-\ln(RH) = (\frac{\Delta H}{R_o})\frac{1}{T_{ab}} - \frac{\Delta S}{R_o} \quad (10)$$

when:
$\ln(RH)$ – plotted against $1/T_{ab}$

A straight line graph is obtained with the y-intercept of $\Delta S/R_o$. From the values of this y-intercept and R_o, ΔH, and ΔS can be computed.

RESULTS AND DISCUSSION

The average *EMC* of maize samples in three replications as well as water activities of salt solutions are shown in Fig. 1. These curves are *EMC* of maize samples at four air temperature levels of 25, 35, 45, and 55°C in the range of 9.30% to 90.45% air relative humidity. Increasing air temperature in the air relative humidity decreases the samples *EMC*. Increasing in air relative humidity caused an increase in maize *EMC* at all of air temperatures. This smooth change in all air temperatures is obvious. This change is due to high starch percentage and high density of maize.

The best results of neural network modeling together with various compositions of topologies are represented in Table 2. The best results were obtained at FFBP network, tansig-tansig-tansig threshold function and 2-3-2-1 topology. This composition produced MSE = 0.0000403, R^2 = 0.9996, E_{mr} = 1.297%, and SE = 0.378 converged in 19 epochs. The predicted data of optimized ANN versus experimental one is in Table 3. Application result of GAB model showed that R^2 = 0.9752, E_{mr} = 6.237%, and SE = 1.234. Therefore the optimized artificial neural network topology gave better results and was used for prediction of maize heat and entropy of sorption.

The optimized neural network model was used to compute the maize equilibrium moisture content

Table 2. Training algorithm for different neurons and hidden layers for the networks

Network	Training algorithm	Threshold function	No. of layers and neurons	*MSE*	R^2	E_{mr}	*SE*	Epoch
FFBP	LM	tansig-tansig-tansig	2-3-2-1	0.0000403	0.9996	1.297	0.378	19
	BR	logsig-tansig-purelin	2-3-3-1	0.0000883	0.9951	3.521	0.645	27
CFBP	LM	tansig-tansig-logsig	2-3-3-1	0.0000751	0.9968	3.108	0.489	33
	BR	logsig-logsig-purelin	2-4-2-1	0.000763	0.9905	6.33	0.825	42

Table 3. Real and normal predicted and experimental values of maize *EMC* using ANNs for testing data set at 45°C

Real experiment	Normal experiment	Real predict	Normal predict
5.83	0.0427	5.78	0.0400
8.88	0.1996	8.72	0.1916
11.39	0.3287	11.32	0.3250
15.28	0.5288	14.91	0.5100
22.07	0.8780	21.89	0.8688

values at four air temperature levels (25, 35, 45, and 55°C) and five moisture levels (8, 11, 14, 17, and 20%). Values of ln(*RH*) versus function of $1/T_{ab}$ were depicted for maize at constant moisture content (Table 4). These values were predicted by the optimized ANN. The slope of the fitted lines at constant moisture contents were the maize heat of sorption. The slopes were calculated by linear regression analysis. The maize heat of sorption for different moisture content levels is presented in Fig. 2.

Maize heat of sorption was found to be decreased with increasing *EMC* at low moisture content. Water was absorbed on the most accessible locations of maize exterior surface. As the maize moisture content increased, the solid material swells and therefore, new high-energy places are opened up for moisture to get bound to. This causes maize heat of sorption to increase as with moisture content decrease. This trend is identical to those reported in studies on agricultural and food products as well as medical and aromatic plants (Lahsasni et al. 2004; Phomkong et al. 2006). Maize heat of sorption was found to be fitted a power model. The following equation was developed for maize:

$$\Delta H = 429.74 EMC^{-1.523}$$
$$R^2 = 0.9906 \qquad (11)$$

This relationship showed that maize heat of sorption increased following a power relationship; it provided a better result compared with exponential relation previously developed by Janjai et al. (2006) for Longan. The maximum values of heat of sorption for some agricultural products compared with maize are represented in Table 5. The lower values of maize heat of sorption compared with the other agricultural products might be due to its starchy and soft structure. The heat of sorption of maize is significantly high, while the *EMC* is lower than 11% (d.b.). The reason for this trend is that at moisture content above 11% (d.b.) the water loosely

Table 4. Obtaining ln(*RH*) as a function of $1/T_{ab}$ at different moisture contents in maize using neural network method

Moisture content (% d.b.)	8		11		14		17		20	
Parameter	$1/T_{ab}$	ln(*RH*)	$1/T_{ab}$	ln(*RH*)	$1/T_{ab}$	ln(*RH*)	$1/T_{ab}$	ln(*RH*)	$1/T_{ab}$	ln(*RH*)
	2.8094	0.003356	3.6376	0.003356	4.0383	0.003356	4.2166	0.003356	4.3240	0.003356
	3.0782	0.003247	3.7629	0.003247	4.1247	0.003247	4.2892	0.003247	4.3895	0.003247
	3.2936	0.003145	3.8795	0.003145	4.2053	0.003145	4.3568	0.003145	4.4502	0.003145
	3.5139	0.003049	4.0157	0.003049	4.2877	0.003049	4.4185	0.003049	4.5008	0.003049
	2.8094	0.003356	3.6376	0.003356	4.0383	0.003356	4.2166	0.003356	4.3240	0.003356

Table 5. Maximum value of maize heat of sorption compared with the other agricultural products

Sample type	*EMC* (%, d.b.)	Heat of sorption (kJ/mol)	Reference
Maize	8	18.94	This Study
Mango	30	18	Janjai et al. (2007)
Longan	40	19.5	Janjai et al. (2006)
Litchi	20	32	Janjai et al. (2009)

binds in maize. This implies that maize needs less energy at higher moisture content (above 11% d.b.) for drying but more energy is needed at lower moisture contents, especially for storage. After processing, dried maize with 15% (d.b.) moisture content is stored (Brooker et al. 1992).

Maize entropy of sorption is presented in Fig. 2. It is a function of moisture content and the following power model is fitted to data:

$$\Delta S = 300.4EMC^{-0.6077}$$

$$R^2 = 0.9873 \qquad (12)$$

The fitted curve for prediction of maize entropy has good values compared with the experimental one. These results showed that the maize entropy decreases with increase in moisture content. Similar trends

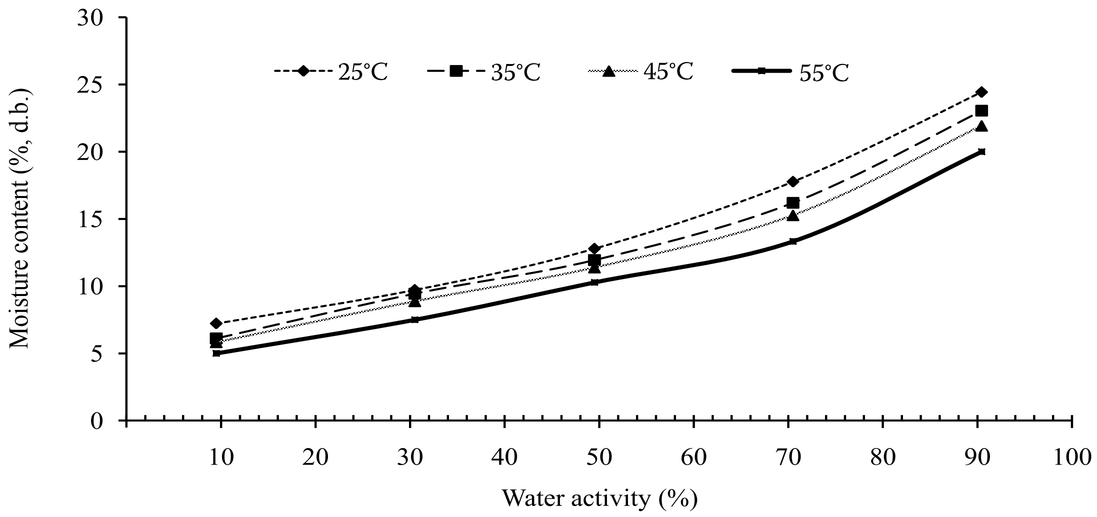

Fig. 1. Moisture content values as a function of air temperature and water activity of maize

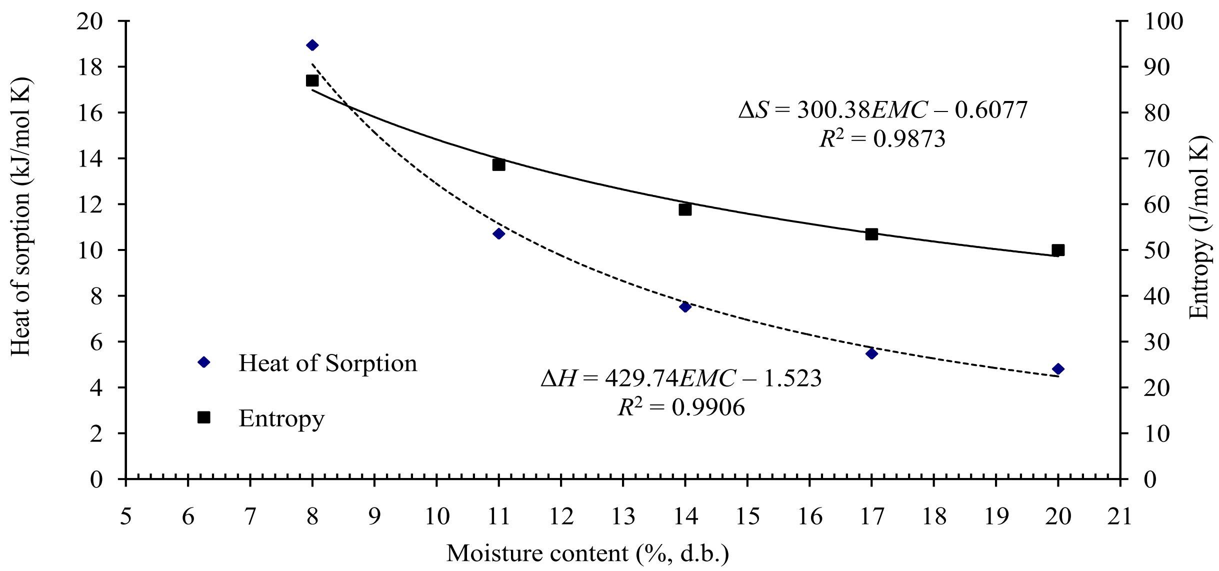

Fig. 2. Experimental values and power model of maize heat and entropy of sorption at different equilibrium moisture contents

were reported on the entropy of some agricultural products such as potato, melon seeds and cassava (McMinn, Magee 2003; Aviara, Ajibola 2002).

Heat and entropy of sorption equations are necessary for calculation of humidity during drying and storage of maize. These results showed that the ANN method has adequate accuracy to develop precise equations for heat and entropy of sorption modeling.

CONCLUSIONS

1. The best artificial neural network model for data training of maize equilibrium moisture content belonged to FFBP network, tansig-tansig-tansig threshold function and 2-3-2-1 topology.
2. The relationship between moisture content and heat and entropy of sorption in maize are power models. The optimized fitted models have high precision for prediction of heat and entropy of sorption.
3. The upper values of maize heat of sorption compared with the agricultural products might be due to the starchy and soft structure of maize. The heat of sorption of maize is significantly high, while the equilibrium moisture content is lower than 11% (d.b.). This implies that maize need less energy at higher moisture content (above 11% d.b.) for drying and storage, but at lower moisture contents more energy was needed.

List of selected symbols:

C – intercept
d.f. – degree of freedom
E_{mr} – mean relative error
EMC – equilibrium moisture content (% d.b.)
M – number of training patterns
N – number of output neurons
n – number of training patterns
MSE – mean square error
S_{ip} – network output in i^{th} neuron and p^{th} pattern
T_{ip} – target output at i^{th} neuron and p^{th} pattern
R^2 – determination coefficient
RH – air relative humidity (%)
R_o – universal gas constant (8.315 kJ/kmol K)
SE – standard error
S_k – network output for k^{th} pattern
T_k – target output for k^{th} pattern,
T_{ab} – absolute air temperature (K)
ΔH – heat of sorption (kJ/mol)
ΔG – gibbs free energy (J/mol)
ΔS – the entropy (J/mol K)

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