Table 5.7 Coefficients for BET and GAB isotherms for RS-1

Model	°C	m_0	C	K	R^2	%E	% RMSE
BET	30	0.032	12.297	-	0.892	32.839	4.826
	45	0.050	8.384	-	0.943	22.550	7.153
	60	0.047	5.771	-	0.979	28.503	6.158
GAB	30	0.059	7.443	0.920	0.984	8.308	1.913
	45	0.056	4.031	0.930	0.995	6.623	0.989
	60	0.049	4.902	0.979	0.992	5.532	1.258

Table 5.8 Coefficients for BET and GAB isotherms for RS-2

Model	°C	m_0	C	K	R^2	%E	% RMSE
BET	30	0.030	14.495	-	0.938	16.789	3.331
	45	0.049	5.942	-	0.978	26.584	6.364
	60	0.045	4.704	-	0.993	32.646	5.618
GAB	30	0.035	38.970	1.015	0.988	5.633	1.616
	45	0.034	10.101	1.017	0.978	7.041	1.767
	60	0.029	13.359	1.031	0.980	7.092	2.161

5.4.2 Shelf life determination

The previous experiment (5.4.1) indicates that GAB equation is optimal to fit the moisture sorption isotherms of the samples. Therefore, the shelf life of rice crackers was determined using GAB equation. The moisture content of a packaged product at any time under constant external conditions of temperature and relative humidity depends upon the equilibrium moisture content of the product and the permeability of the package.

Several assumptions have been made for shelf life prediction by simulation model. They include (1) the moisture content of the packaged samples will reach equilibrium rapidly with the relative humidity inside the package; (2) the relative humidity inside the package is determined by the permeability of the package; and (3) the relationship between the moisture content of the product and relative humidty inside the package can be represented by an isotherm equilibrium curve (Hernandez and Giacin, 1998).

The shelf life model was developed based on the package permeability and the moisture absorbed by rice crackers. The shelf life was then calculated using the following equation:

$$\int_{t=0}^{t=t} dt = \frac{lw_d}{PA} \int_{m_1}^{m_c} \frac{dm}{[p_o - p_i]} \tag{5.6}$$

where t is the storage time (days), l is the package thickness, w_d is the dry weight of food product (g), m is the moisture content of the product on % dry basis, m_i is the initial moisture content of the sample, and m_c is the critical moisture content or moisture content at time t, P is the permeability coefficient of polymeric packaging material, A is the exposed surface area of the package (m^2), p_o is the partial pressure of water vapor (mmHg) of storage environment, p_i is the partial pressure of water vapor (mmHg) inside the package head space related to the moisture content of the product determined by GAB model.

When the moisture sorption isotherm is described by GAB model, the shelf life is given by integrating Eq. 5.6 using GAB equation (Eq. 5.3). The calculated shelf life of RS-1 and RS-2 in all packages and stored under different conditions is shown in Tables 5.9 and 5.10, respectively.

Regression analysis was performed between the actual and the GAB predicted shelf lives. Figures 5.6 and 5.7 show the GAB predictions versus actual shelf lives of RS-1 and RS-2, respectively. The determination coefficients, R^2, of RS-1 and RS-2 are 0.7953 and 0.6828, respectively.

Table 5.9 GAB predicted shelf life of RS-1 in the packages at different storage conditions

Temperature	Relative humidity	Package	Mean ± SD
30	75	Bag-1	22 ± 1.8
		Bag-2	26 ± 1.1
		Bag-3	21 ± 2.0
		Bag-4	35 ± 0.5
30	85	Bag-1	16 ± 0.9
		Bag-2	19 ± 0.5
		Bag-3	20 ± 2.9
		Bag-4	55 ± 1.1
45	75	Bag-1	4 ± 0.2
		Bag-2	5 ± 0.2
		Bag-3	3 ± 0.2
		Bag-4	7 ± 0.3

Table 5.10 GAB predicted shelf life of RS-2 in the packages at different storage conditions

Temperature	Relative humidity	Package	Mean ± SD
30	75	Bag-1	24 ± 1.5
		Bag-2	28 ± 0.7
		Bag-3	23 ± 2.1
		Bag-4	37 ± 0.5
30	85	Bag-1	17 ± 1.9
		Bag-2	20 ± 0.6
		Bag-3	22 ± 1.8
		Bag-4	59 ± 1.4
45	75	Bag-1	5 ± 0.2
		Bag-2	5 ± 0.2
		Bag-3	3 ± 0.2
		Bag-4	8 ± 0.3

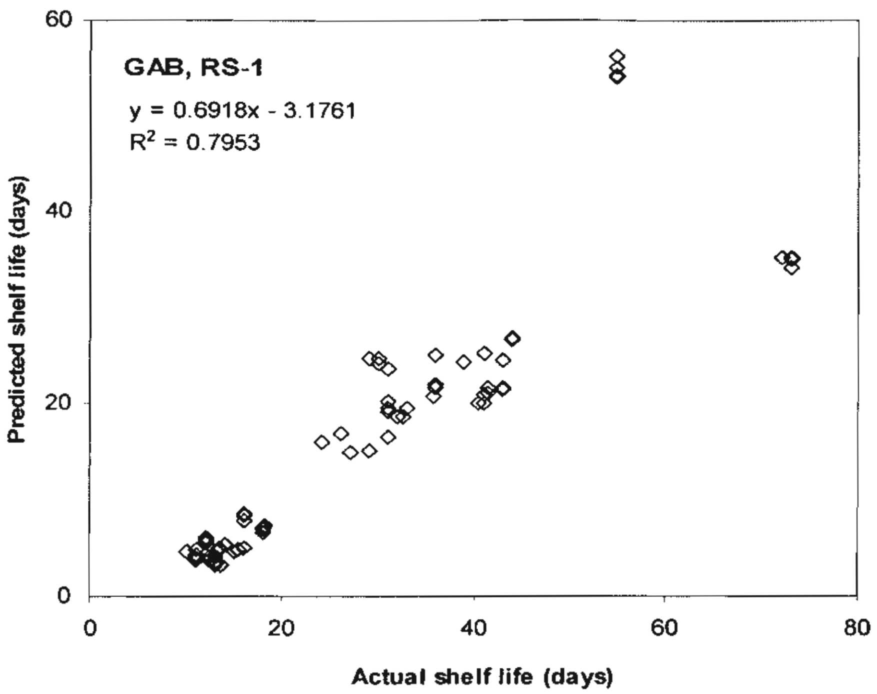

Figure 5.6 The predicted *vs.* actual shelf life of RS-1 using GAB model

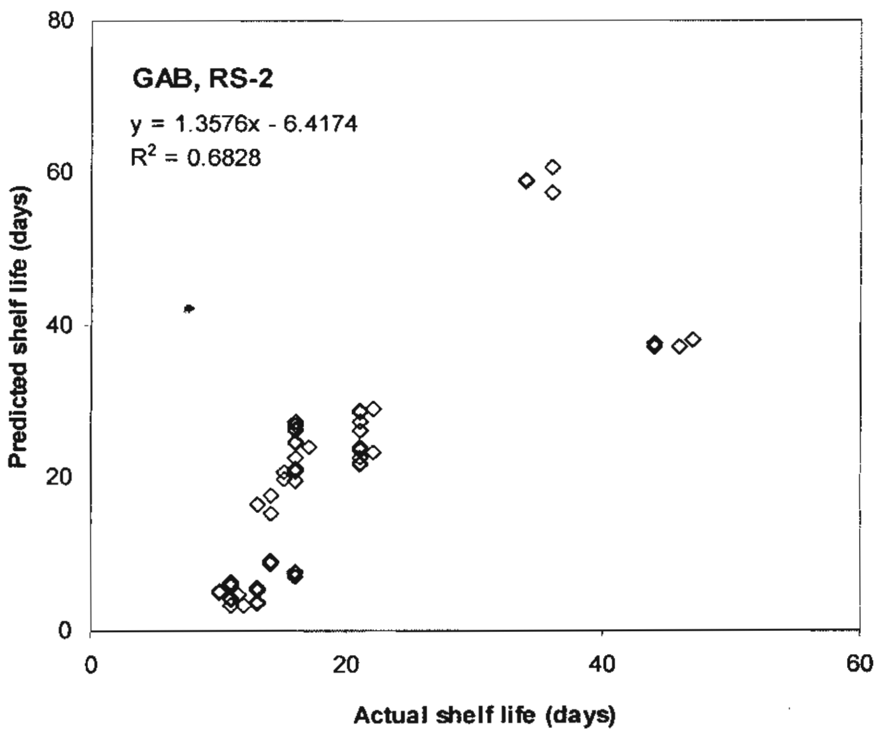

Figure 5.7 The predicted *vs.* actual shelf life of RS-2 using GAB model

5.5 Develop an ANN based model for shelf life prediction of rice crackers

Packaged rice crackers are subject to moisture gain depending on a number of factors: the storage relative humidity; the sorption properties of the product; the water activity gradients relative to the storage atmosphere; and the water vapor permeability of packaging materials. The barrier performance of the packaging system employed can influence the relative importance of each of these factors.

Container moisture permeability is a commonly used criteria for shelf life prediction. However, permeability alone is not sufficient for predicting the rate of moisture uptake as the rate is governed by the environmental conditions and the water activity in the container as well as container permeability. The rate of moisture permeation through a container usually decreases over time as the humidity in the container increases due to the accumulation of moisture in the container. The effect of all these factors must be considered in order to predict the rate of moisture uptake in real life situation.

A MLP neural network based on back propagation was used to predict shelf life of the product from product characteristics, package properties and storage conditions as detailed in Table 5.11. A total of 288 samples were used. For the neural network, three steps were completed, including creating the network object, training the network, validating and testing the network. Using this approach, the data sets were partitioned into three subsets: a training set (a set of samples used to adjusted the network weights), a validation set (a set of samples used to tune the parameters), and a test set (a set of samples used only to assess the performance to new, unseen observations). The performance of the neural network was confirmed by measuring its performance on a third independent set of data called a test set.

The network architecture created for the shelf life data matrix includes an input layer, one hidden layer of neurons, and an output layer. The inputs to a neuron include its bias and the sum of its weighted input. The output of a neuron depends on the neuron's inputs and on its transfer function. The indices j, k, and l refer to the input signals ($j = 1,\ldots, m$) in the input layer, the neurons ($k = 1,\ldots, p$) in the hidden layer, and the neuron ($l = 1,\ldots, q$) in the output layer, respectively. There were 9 neurons ($m = 9$) in the input layer, 9 neurons ($p = 9$) in the hidden layer, and one neuron ($q = 1$) in the output layer. The transfer function, $\varphi(v_k)$, in the hidden layer was a hyperbolic tangent (Eq. 5.7) and a linear function was used in the output layer (Eq. 5.9). The nonlinear hyperbolic tangent function can be calculated as follows.

$$y_k = \varphi(v_k) = \frac{1-\exp(v_k)}{1+\exp(v_k)} \tag{5.7}$$

with v_k being computed as

$$v_k = b_k + \sum_{j=1}^{m} w_{kj} x_j \tag{5.8}$$

where y_k is the output of the hidden layer, $\varphi(v_k)$ is the transfer function associated with the neuron *k* in the hidden layer, v_k is the sum of weighted input of neuron *k*, b_k is the bias, and x_j is the input signal. Use of bias b_k has the effect of applying an affine transformation in the model. A linear function can be calculated as follows.

$$y_l = \varphi(v_l) = b_l + \sum_{k=1}^{p} w_{lk} y_k \tag{5.9}$$

where y_l is the output of the output layer, $\varphi(v_l)$ is the transfer function associated with neuron *l* in the output layer, y_k is the input to the neuron *l*, v_l is the sum of weighted input of neuron *l*, b_l is the bias, and w_{lk} is the weight connection of neuron *k* and neuron *l*.

The ANN was trained using the Bayesian regularization which is used to ovoid overfitting. The training started with different initial random weights, and was optimized during training. The performance function used during training of the feed-forward neural network was the sum square errors (SSE) of the network.

$$\text{SSE} = \sum_{i=1}^{n} (t_i - a_i)^2 \tag{5.10}$$

where *a* = network output, *t* = targets, and *n* = number of samples.

The difference between target value and actual neural output was propagated back through the network to the input. The learning process described herein is referred to as error-correction learning. For error-correction learning, the error was minimized by adjusting the weight. Minimization of the error leads to a learning rule generally referred to as a delta rule. In the learning process, the updated value of weight is computed by

$$w_{kj}(n+1) = w_{kj}(n) + \Delta w_{kj}(n) \quad (5.11)$$

$$\Delta w_{kj}(n) = \eta \ e_k(n) x_j(n) \quad (5.12)$$

where $\Delta w_{kj}(n)$ is the adjustment of weight applied to the synaptic weight at time step n, e_k is the sum square error, x_i is the element of the input vector, and η is the learning rate parameter. The learning rate parameter (η = 0.05) was selected to ensure that the convergence of the learning process was achieved. In order to ensure stability in the network and avoid convergence on a local minimum, the initial weights were randomly assigned to the network. One complete entire training process is called an epoch. The learning process continued epoch-by-epoch until the synaptic weights and bias level of the network stabilized and the sum square error (SSE) over the entire training set converged to the minimum value.

To prevent over training, it is normal practice to train an ANN until the minimum sum squared error for a validation data set has been achieved. Figure 5.8 shows the evolution of training, validation and test errors as a function of the number of learning epochs. The error in the training set decreases as the weights are improved. The network is judged to have converged when the test set error is lowest. The training stopped when the network converged, sum squared error (SSE = 0.7638) is relatively constant over 38 iterations. In this study, the network was trained for 38 epochs to obtain the acceptable output errors. The error on the validation set is monitored during the training process. The validation error normally decreases during the initial phase of training, as does the training set error. The performances of the network were checked on a test set. The errors of the test set were also monitored during the training phase. The test set error is not used during the training, but it is used to compare different models.

The predicted shelf lives of RS-1 and RS-2 using ANN algorithm developed in this study are listed in Table 5.12 and 5.13, respectively. Regression analysis was performed between the network output (predicted shelf lives) and the corresponding targets (actual shelf lives). Figures 5.9 and 5.10 present the ANN predictions versus true shelf lives of RS-1 and RS-2, respectively. The correlation coefficient, R^2, between the outputs and targets was a measure of how well the variation in the output was explained by the targets and outputs. A determination coefficient (R^2 = 0.993 and 0.986 for RS-1 and RS-2, respectively) indicates a very good fit between actual and predicted data.

The performance of ANN algorithm to predict shelf life of rice crackers was compared to that of GAB prediction model. The performance of the trained network was evaluated by measuring the errors in the test sets. Table 5.14 details the statistical performances, including R^2 and RMSE, of the GAB and the ANN predicted shelf life. The results show that ANN algorithm provided dramatically lower prediction errors and gave higher determination coefficients, when compared to GAB model.

The finding in this study suggests that ANN provided a tool that may be used to avoid the shortcomings involved in conventional simulation methods. ANN offers several advantages over traditional digital computations, including faster speed of information processing, learning ability, fault tolerance, and multi-output ability. The additional benefit of ANN is that it enables the simultaneous determination of all packaged products' shelf lives depending on the number of neurons used in the output layer. On the other hand, the shelf life prediction using the conventional GAB equation based prediction model was performed separately for each shelf life.

Table 5.11 Input parameters used for shelf life determination using ANN

Parameter	Input data
Product	food compositions product weight
Package	film thickness permeability package area
Storage condition	temperature relative humidity

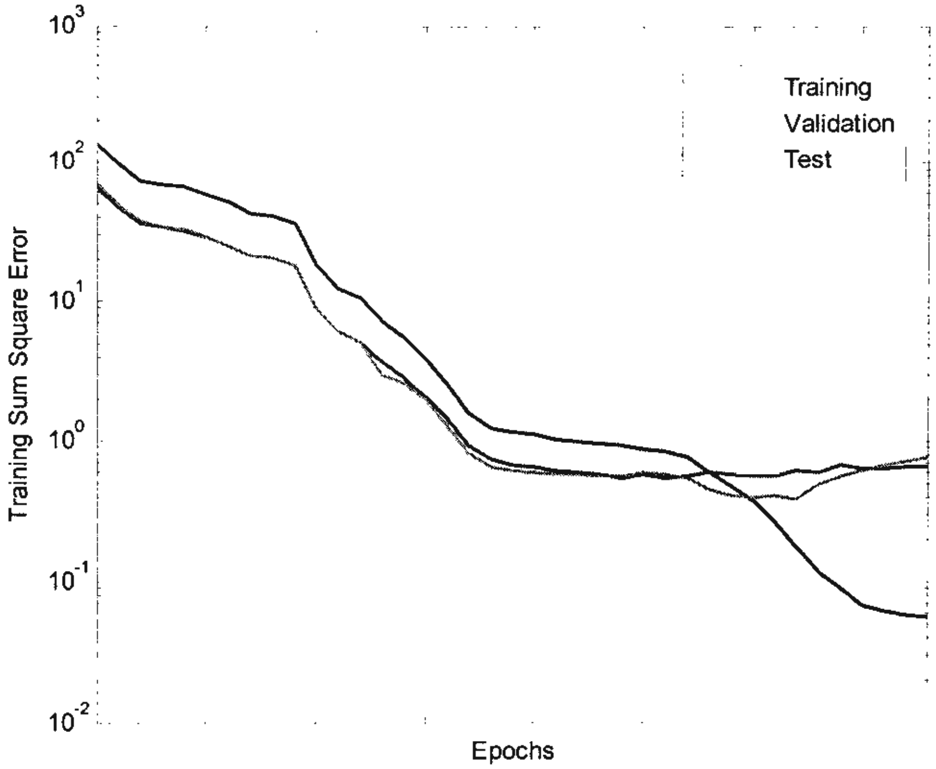

Figure 5.8 Evolution of training, validation and test errors as a function of the number of learning epochs during ANN training

Table 5.12 ANN predicted shelf life of RS-1 in the packages at different storage conditions

Temperature	Relative humidity	Package	Mean ± SD
30	75	Bag-1	37 ± 1.1
		Bag-2	45 ± 1.8
		Bag-3	4[illegible] ± 1.1
		Bag-4	72 ± 0.2
30	85	Bag-1	25 ± 1.4
		Bag-2	31 ± 0.5
		Bag-3	31 ± 0.8
		Bag-4	55 ± 0.4
45	75	Bag-1	12 ± 1.4
		Bag-2	13 ± 0.3
		Bag-3	13 ± 0.1
		Bag-4	19 ± 1.3

Table 5.13 ANN predicted shelf life of RS-2 in the packages at different storage conditions

Temperature	Relative humidity	Package	Mean ± SD
30	75	Bag-1	17 ± 0.7
		Bag-2	22 ± 0.5
		Bag-3	20 ± 0.4
		Bag-4	45 ± 0.2
30	85	Bag-1	14 ± 2.0
		Bag-2	16 ± 0.4
		Bag-3	16 ± 0.7
		Bag-4	34 ± 0.6
45	75	Bag-1	12 ± 0.7
		Bag-2	12 ± 1.3
		Bag-3	11 ± 0.5
		Bag-4	16 ± 1.0

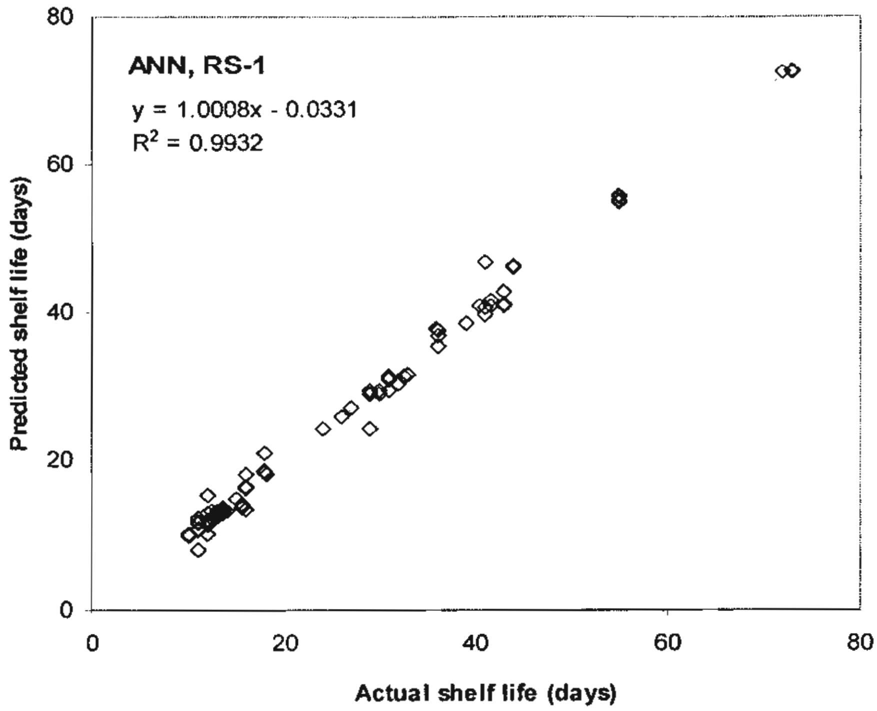

Figure 5.9 The predicted *vs.* actual shelf life of RS-1 using ANN

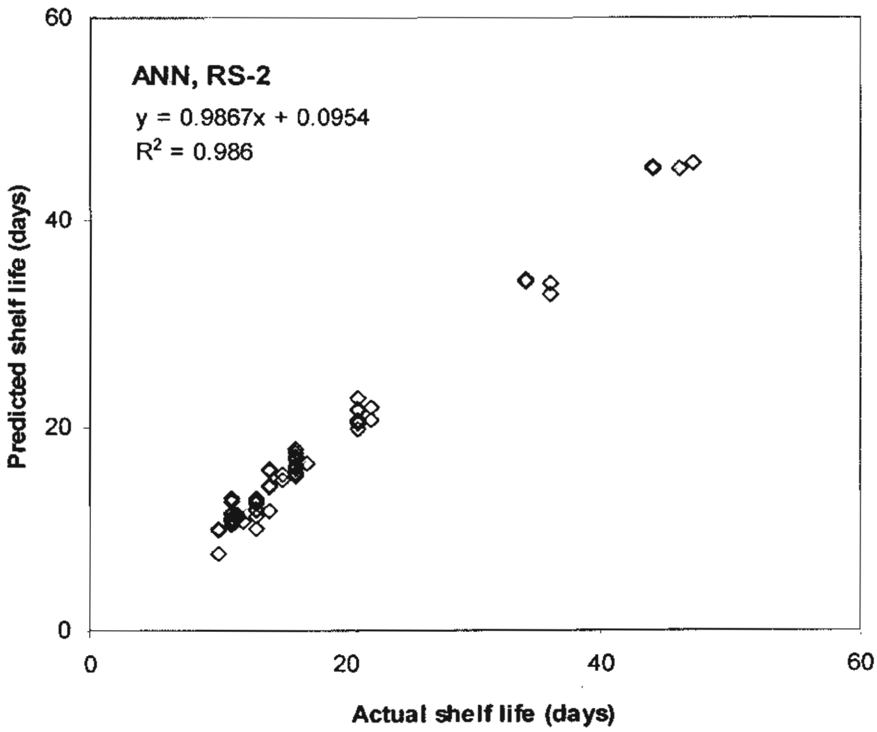

Figure 5.10 The predicted *vs.* actual shelf life of RS-2 using ANN

Table 5.14 Statistical performance of the GAB and the ANN predicted shelf life

Product	Performance	GAB	ANN
RS-1	R^2	0.7953	0.9932
	MSE	193.9458	1.9130
	RMSE	13.9264	1.3831
RS-2	R^2	0.6828	0.9860
	MSE	71.1382	1.0327
	RMSE	8.4343	1.0158
All products	R^2	0.5544	0.9921
	MSE	132.5420	1.4725
	RMSE	11.5127	1.2134

6. CONCLUSION

The experimental moisture sorption data of RS-1 and RS-2 rice crackers at 30, 45 and 60 °C were fitted to the BET and GAB equations using non-linear regression analysis. The more extended range of application of the GAB equation over the BET equation is evident. The plots using BET gave a good fit at low water activities (a_w < 0.6). To determine the goodness of fit of BET and GAB models, determination coefficient (R^2), mean relative percentage deviation modulus (E) and percentage root mean square error (RMSE) were measured against the experimental isotherm data. The GAB equation gives E values ranging from 5.53 to 8.31 and 5.63 to 7.09, while the BET equation gives E values ranging from 22.55 to 32.84 and 16.79 to 32.64 for RS-1 and RS-2, respectively. A good description of an isotherm is considered to be smaller than E value of 10 when the GAB model is applied. Low values of E and RMSE strengthen the usefulness of the GAB model for studying water vapor sorption of rice crackers. GAB equation is optimal to fit the moisture sorption isotherms of the variety of rice crackers under investigation. Therefore, GAB model was used to predict shelf life of the rice crackers.

The GAB shelf life model was developed based on the equilibrium moisture content of rice crackers and the permeability of the packages. When the moisture sorption isotherm is described by GAB model, the shelf life is given by integrating shelf life equation with GAB equation. Regression analysis was performed between the actual and the GAB predicted shelf lives. The correlation coefficients, R^2, of RS-1 and RS-2 are 0.7953 and 0.6828, respectively.

A MLP neural network based on back propagation was developed and used to predict shelf life of the product from product characteristics, package properties and storage conditions. The data sets were partitioned into three subsets: a training set (a set of samples used to adjusted the network weights), a validation set (a set of samples used to tune the parameters), and a test set (a set of samples used only to assess the performance to new, unseen observations). The performance of the neural network was confirmed by measuring its performance on a third independent set of data called a test set.

There were 9 neurons in the input layer, 9 neurons in the hidden layer, and one neuron in the output layer. The transfer function in the hidden layer was a hyperbolic tangent and a linear function was used in the output layer. The ANN was trained using the

Bayesian regularization which is used to ovoid overfitting. The training started with different initial random weights, and was optimized during training. The performance function used during training of the feed-forward neural network was the sum square errors (SSE = 0.7638) of the network. The performance of the trained network was evaluated by measuring the errors in the test sets. A high determination coefficient of ANN predicted shelf lives (R^2= 0.993 and 0.986 for RS-1 and RS-2, respectively) indicates a very good fit between actual and predicted data.

The performance, including R^2 and RMSE, of ANN algorithm to predict shelf life of rice crackers was compared to that of GAB prediction model. The results show that ANN algorithm provided dramatically lower prediction error and gave higher determination coefficient, when compared to GAB model. The finding in this study suggests that ANN provided a tool that may be used to avoid the shortcomings involved in conventional simulation methods. ANN offers several advantages over traditional digital computations, including faster speed of information processing, learning ability, fault tolerance, and multi-output ability. The additional benefit of ANN is that it enables the simultaneous determination of all packaged products' shelf lives depending on the number of neurons used in the output layer. On the other hand, the shelf life prediction using the conventional GAB equation based prediction model was performed separately for each shelf life.

Using the ANN based mathematical model for shelf life determination is expected to be more accurate and convenient than using actual shelf life test or conventional simulation models. Success of this research will provide the food industries with an alternative method for shelf life determination of moisture sensitive food products as well as product/package optimization. The knowledge gained from these studies will reliably promote confidence that the product delivered to the customer is of high quality.

This method is not limited to the aforementioned applications. The system can be applied to other packaged food products in the food industries.

7. BLIBIOGRAPHY

Al-Muhtasep, A. H., W. A. M. McMinn and T. R. A. Magee. 2004. Water sorption isotherms of starch powders Part 1: mathematical description of experimental data. J. of Food Eng. 61: 297-307.

Anderson, R. 1946. Modifications of the BET equation. J. Am. Chem. Soc. 68: 686-691.

AOAC, 1990. Official Methods of Analysis, 13th Edition. Association of Official Analytical Chemists, Washington, DC.

ASAE. Moisture relationship of plant-based agricultural products. ASAE Standard D 245.5. St. Joseph, Michigan, 1995.

ASTM. 1999. Designation D 895-79: standard test method for water vapor permeability of packages. Annual Book of ASTM Standards. American Society of Testing and Materials. Philadelphia, PA.

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

Bianco, A. M., G. Boente, M.L. Polliop and S.L. Resnik. 2001. Influence of oil content on sorption isotherms of four varieties of peanut at 25 °C. J. Food Eng. 47:327-331.

Bila, S., Y. Harkouss, M. Ibrahim, J. Rousset, E. N'Goya, D. Baillargeat, S. Verdeyme, M. Aubourg, and P. Guillon. 1999. An accurate wavelet neural-network-based model for electromagnetic optimization of microwave circuits. Int. J. RF Microw. Comput.-Aided Eng. 93: 297-306.

Brunauer, S., Emmett, P. H., and Teller, E. 1938. Adsorption of gases in multimolecular layers. J. Am. Chem. Soc. 60: 310-319.

Cardoso, G. and T. P. Labuza. 1983. Prediction of moisture gain and loss of packaged pasta subjected to a sine wave temperature/humidity environment. J. Food Technol. 18: 587-606.

Coulibaly, P., B. Bobée, and F. Anctil. 2001. Improving extreme hydrologic events forecasting using a new criterion for artificial neural network selection. Hydro. Proc. 15: 1533-1536.

Coupland, J. N., N. B. Shaw, F. J. Mondahan, E. D. O'Riodan, and M. O'Sullivan. 2000. Modeling the effect of glycerol on the moisture sorption behavior of whey protein edible films. J. Food Eng. 43: 23-30.

de Boer, J. 1953. The dynamic character of adsorption. In: Rao, M., and Rizvi, S. (Eds) 1995. Engineering Properties of Food (2nd ed.). New York: Marcel Dekker Inc. 251pp.

Del Nobile, M. A., P. Fava and L. Piergiovanni. Water transport properties of cellophane flexible films intended for food packaging 2002. applications. J. Food Eng. 53 (4): 295-300.

Devabhaktuni, V., M. C. E. Yagoub, Y. Fang, J. Xu, and Q. Zhang. 2001. Neural networks for microwave modeling: Model development issues and nonlinear modeling techniques. Int. J. RF Microw. Comput.-Aided Eng. 11: 4-21.

Duckworth, R. B. Solute mobility in relation to water content and water activity. In Water Activity: Influences on Food Quality, L. B. Rockland and G.F. Stewart, Eds., Academic Press, New York, 1981, 295-317.

Guggenheim, E. 1966. Applications of statistical mechanics. In Rao, M., and Rizvi, S. (Eds). Engineering Properties of Food (2nd ed.), Marcel Dekker Inc. New York, 1995. 115-251.

Hernandez, R. J. and J. R. Giacin. 1997. Factor affecting permeation, sorption and migration processes in packaged-product systems. In Taub, I. A. and R. P. Singh. Food Storage Stability. CRC Press.

Hikawa, H. 2001. Multilayer neural network with on-chip learning based on frequency-modulated pulse signals and voting neurons. Electr. Commu. Japan. 84 (1): 32-42.

Iglesias, H. A., P. Viollaz, and J. Chirife. 1979. A technique for predicting moisture transfer in mixtures of packaged dehydrated foods. J. Food Sci. 14: 89-92.

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

Jay, J. M. 2000. Determining microorganisms and/or their products in foods. P. 431-449. In Modern food microbiology (6th ed., pp 431-449). Chapman & Hall, New York.

Kaymak-Ertekin, F. and M. Sultanoglu. 2001. Moisture sorption isotherm characteristics of peppers. J. Food Eng. 47: 225-231.

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

Kaya, S. and T. Kahyaoglu. 2005. Thermodynamic properties and sorption equilibrium of pestil. J. Food Eng. 71: 200-207.

Kimura, M. and R. Nakano. 2000. Dynamical systems produced by recurrent neural networks. Syst. Comput. Japan. 31(4): 818-828.

Kwolek, W. F. and G. N. Bookwalter. 1971. Prediction storage stability from time temperature data. Food Technol. 25: 1025-1031.

Pieglovanni, L., P. Fava, and A. Siciliano. 1995. A mathematical model for the prediction of water vapor transmission rate at different temperature and relative humidity. Packag. Technol Sci. 8: 73-78.

Palou, E., A. Lopez-Malo and A. Argaiz. 1997. Effect of temperature on the moisture sorption isotherms of some cookies and corn snacks. J. Food Eng. 31: 85-93.

Martin, M.A., J. P. Santos and J. A. Agapito. 2001. Application of artificial neural networks to calculate the partial gas concentration in a mixture. Sensor Actuator B. 77: 468-471.

McMinn, W. A. M. and T. R. A. Magee. 2003. Thermodynamic properties of moisture sorption of potato. J. Food Eng. 33: 227-237.

Mittal, G. S. and J. Zhang. 2000. Prediction of freezing time for food products using a neural network. Food Res. Int. 32. 557-562.

Nakamura, K., Yoshikawa, T. 2001. Evaluation of recognition ability and inside parameters for a rotation spreading associative neural network. Electr. Commu. Japan. 84 (10): 1-14.

Pahlevanzadeh, H and M. Yazdani. 2005. Moisture adsorption isotherms and isosteric energy for almond. J. Food Process Eng. 28: 331-345.

Rohvein, C., E. Santalla and M. C. Gely. (2004). Estimation of sorption isotherm and the heat of sorption of Quínoa (*Chenopodium quinoa* Willd.) Seeds. Food Sci Technol Int. 10 (6), 409-413.

Sewald, M. and J. DeVries. 2003. Food product shelf life: How long before it's gone? Analytical Progress. Vol.21 (2) A publication of Analytical Progress Press.

Siripatrawan, U. and P. Jantawat. Determination of moisture sorption isotherms of Jasmine rice crackers using BET and GAB models. Food Sci.Technol Int. (*In Press*).

Siripatrawan, U., J. Linz, and B. R. Harte. 2006. Electronic Sensor Array Coupled with Artificial Neural Network for Detection of *Salmonella* Typhimurium. Sensors Actuators B: Chemical. *(In Pess)*.

Siripatrawan, U., J. Linz, and B. R. Harte. 2004. Rapid method for prediction of *Escherichia coli* numbers using an electronic sensor array and an artificial neural network. J. Food Protect. 67: 1604-1609.

Siripatrawan, U., J. Linz, and B. R. Harte. 2004. Solid Phase Microextraction/Gas Chromatograph/Mass Spectrometer Coupled with Discriminant Factor Analysis and Multilayer Perceptron Neural Network for Detection of *Escherichia coli*. J. Food Protect. 67: 1597-1603.

Swicegood, P. and J. A. Clark. Off-site Monitoring Systems for Predicting Bank Underperformance: A Comparison of Neural Networks, Discriminant Analysis, and Professional Human Judgment. Int. J. Intell. Sys. Acc. Fin.Mgmt. 10, 169–186 (2001).

Torrecilla, J.S., L. Otero, and P.D. Sanz. 2004. A neural network approach for thermal/pressure food processing. J. Food Eng. 62 (2004) 89–95.

Tanaka, K. and D. Hasegawa. 2001. On the computational capability of recurrent higher-order neural networks. Syst. Comput. Japan. 32 (10): 42-50.

Terra, M.H. and R. Tinós. 2001. Fault detection and isolation in robotic manipulators via neural networks: A comparison among three architectures for residual analysis. J. Robotic Syst. 18(7): 357-374.

Timmermann, E. O. 2003. Multilayer sorption parameters. Colloid and Surfaces A: Physicochem. Eng. Aspects. 235-260.

Tungangprateep, S. and V.K. Jindal. 2004. Sorption isotherms and moisture diffusivity in fried cassava-shrimp chips. Int. J Food Properties. 7 (2): 215-227.

Watanabe, K., T. Haba, N. Kudo and T. Oohori. 2001. Fluctuation-driven learning rule for continuous-time recurrent neural networks and its application to dynamical system control. Syst. Comput. Japan. 32(3): 14-23.

Output จากโครงการวิจัยที่ได้รับทุนจาก สกอ. และ สกว.

1. ผลงานตีพิมพ์ในวารสารวิชาการนานาชาติ

1.1 บทความเรื่อง "Determination of moisture sorption isotherms of Jasmine rice crackers using BET and GAB models" ได้รับการตอบรับให้ตีพิมพ์ในวารสาร Food Science & Technology International (Impact factor = 0.571) ขณะนี้กำลังอยู่ระหว่างการรอตีพิมพ์ (หนังสือตอบรับ และ Manuscript แสดงไว้ใน Appendix I)

1.2 อยู่ระหว่างเตรียมบทความเรื่อง "Artificial neural network for shelf life prediction of rice crackers" คาดว่าจะนำเสนอในวารสาร Packaging Technology and Science

2. การนำผลงานวิจัยไปใช้ประโยชน์

2.1 นำข้อมูลที่ได้จากงานวิจัยไปใช้ในการเรียนการสอน ในรายวิชา 22314533 Food Packaging และ 2314441 Food Chemistry ภาควิชาเทคโนโลยีทางอาหาร คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

2.2 นำความรู้ที่ได้จากงานวิจัยเพื่อต่อยอดเป็นโครงงานวิจัยสำหรับนิสิตปริญญาตรี ในหัวข้อเกี่ยวกับผลของชนิดบรรจุภัณฑ์ต่ออายุการเก็บของผลิตภัณฑ์ขนมขบเคี้ยว เพื่อแก้ปัญหาให้แก่โรงงานอุตสาหกรรมอาหาร ขณะนี้อยู่ระหว่างเขียนโครงร่างวิจัย

3. การเสนอผลงานในที่ประชุมวิชาการ

3.1 นำเสนอผลงานเรื่อง "Modeling of moisture sorption isotherm of a crispy rice snack using BET and OSWIN equations" ในการประชุมสัมมนาวิชาการอุตสาหกรรมเกษตร ครั้งที่ 8 (Food Innovations) Conference Bangkok, THAILAND ระหว่างวันที่ 15-16 มิถุนายน 2006 โดยมีการรวบรวมผลงานใน proceedings ในรูปแบบ CD ผลงานที่นำเสนอได้แสดงไว้ใน Appendix II

3.2 นำเสนอผลงาน "Brunauer, Emmett and Teller (BET) model to determine moisture sorption isotherms of rice crackers" ในที่ประชุม International Agricultural Engineering Conference Bangkok, THAILAND ระหว่างวันที่ 6 – 9 December 2005 โดยมีการรวบรวมผลงานใน proceedings ในรูปแบบ CD

<u>หมายเหตุ</u> ตามที่ได้ระบุไว้ในรายงานรอบ 18 เดือน บทความใน 3.2 ได้รับการตอบรับให้นำเสนอผลงานในที่ประชุม และผลงานถูกรวบรวมไว้ใน proceedings ในรูปแบบ CD แต่เนื่องจากในระหว่างที่มี Conference ผู้วิจัยติดภาระกิจ ไม่สามารถเข้าร่วมประชุมได้ จึงไม่สามารถนับเป็น output ได้

APPENDIX

Appendix I : Manuscript "Determination of moisture sorption isotherms of Jasmine rice crackers using BET and GAB models"

Appendix II : Manuscript "Modeling of moisture sorption isotherm of a crispy rice snack using BET and OSWIN equations"

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RESEARCH PAPER

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

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ABSTRACT

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 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 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 contents and decreased with an increase in food moisture content.

Keywords: BET model, GAB model, Sorption isotherms, Rice crackers

INTRODUCTION

Thai Jasmine (Hom Mali) rice has its name through its natural fragrances similar to those of Jasmine flower. Regarded as the highest quality Thai rice, Jasmine rice is recognized as the favored 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. 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-Muhstaseb et al., 2004; Ayranci and Duman, 2005).

A number of models to describe moisture sorption isotherm have been proposed including kinetic models based on a multilayer (Brunauer, Emmett and Teller (BET) model and Guggenheim-Anderson-de Boer (GAB) model), 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 Types II isotherm characteristic (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 literatures (Mcmin and Magee, 2003; Pahlevanzadeh and Yazdani, 2005; Rohvein et al. 2004).

The isosteric heat of sorption, or latent heat of vaporization, 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 vapor 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 vapor (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 Claussius-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 been reported on the studies of 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 Clausius-Clapeyron equation.

MATERIALS & 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 stabilized 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 (±0.001g) 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 one gram of sorbant at sorbate activity a_w. m_0 is the monolayer moisture content and C_B is BET constant (Timmermann, 2003).

GAB equation

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

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

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 root mean square error (RMSE). The mean relative percentage deviation modulus and RMSE were calculated (Al-Multaseb et al., 2004) as follow:

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

$$RMSE = \sqrt{\frac{\sum_{i=1}^{N} (m_e^i - m_p^i)^2}{N}} \quad (5)$$

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.

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

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 (K) (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 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 observed 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 vapor 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 vapor 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 & Magee, 2003; Palou et al., 1997).

Modeling 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 non-linear 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 vapor is absorbed than that indicated by the BET equation using the values of the constants corresponding to the low water activity range. Iglesia 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 shows that at 30, 45, and 60 °C, the GAB equation gives E values ranging from 5.53 to 8.31 while the BET equation predicted the isotherms gives E values ranging from 22.55 to 42.61. A good description of an isotherm is considered to be smaller than E value of 10.0 when the GAB model is applied. 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 vapor sorption of rice crackers. It has also been recognized that the fit become better as the determination coefficient approaches to 1. The determination coefficient closer to 1 is evident for GAB model. Therefore, GAB equation is optimal to fit the moisture sorption isotherms of rice crackers.

Monolayer Moisture Content

Modeling 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) range 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. (1998) and Lomauro et al. (1985), 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 shows a tendency to decrease with increasing temperature. The decrease in m_0 reflects 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, Barreriro 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 variation of the heat of sorption of the samples with moisture content is shown in Figure 6. In this study, the maximum q_{st} value of rice crackers is 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) is close to that of cookies (28 kJ/mol) as reported by Kim et al. (1998). However, the maximum q_{st} value of rice crackers is 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 disparities possibly ascribe to the differences in food compositions and processing treatments of these food products (Palou et al. 1997).

As illustrated in Figure 6, the q_{st} values are 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 is 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 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 increase in water activity, at a 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 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 contents 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

The authors would like to thank The Thailand Research Fund for providing full financial support to this project under funding no. MRG4780202.

REFERENCES

Al-Muhtasep, 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. St. Joseph, Michigan.

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.

Barreriro, 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 ed.), New York: Marcel Dekker Inc. pp. 115-251.

Guggenheim, E. (1995). Applications of statistical mechanics. In: Rao, M., & Rizvi, S. (eds), Engineering Properties of Food (2nd ed.). New York, USA: 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, Academic Press: New York.

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. PartII, 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 M. C. 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 creal graines: a comparison between interal an ddifferential quanitites. Drying Technology 15(1): 137-150.

Timmermann, E. O. (2003). Multilayer sorption parameters. Colloid and Surfaces A: Physicochem. Eng. Aspects 235-260.

LEGENDS TO FIGURES

Figure 1 Moisture sorption isotherms of rice cracker at 30, 45 and 60 °C

Figure 2 Comparison between isotherms from experimental data and from BET and GAB models at 30 °C

Figure 3 Comparison between isotherms from experimental data and from BET and GAB models at 45 °C

Figure 4 Comparison between isotherms from experimental data and from BET and GAB models at 60 °C

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

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

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	12.297	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	0.920	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 1

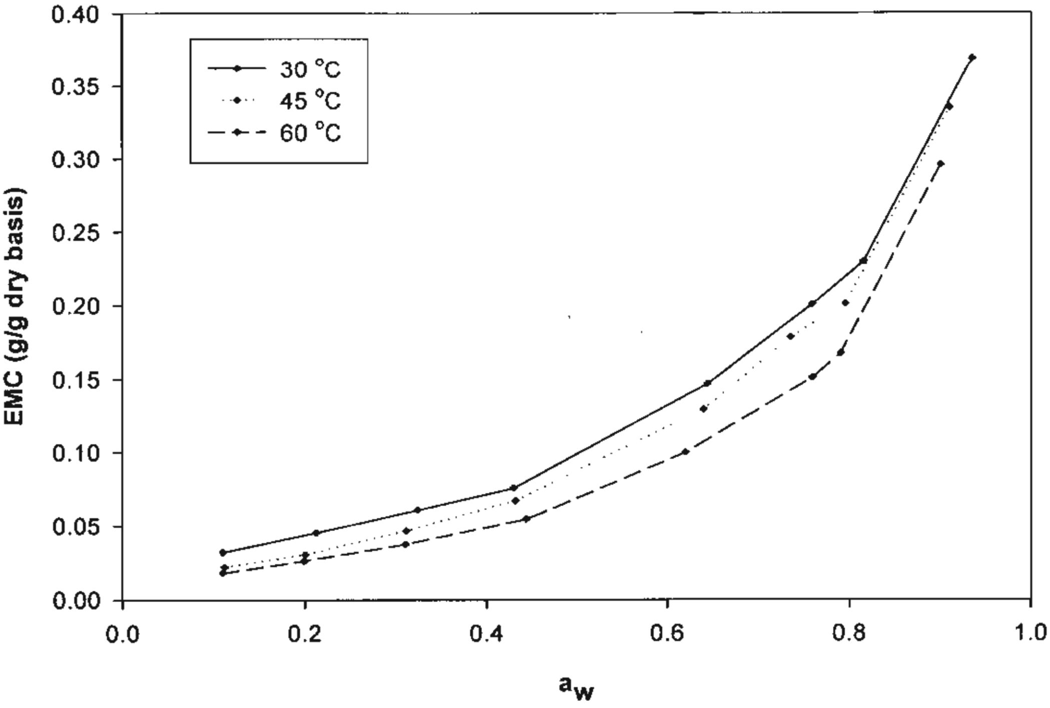


Figure 2

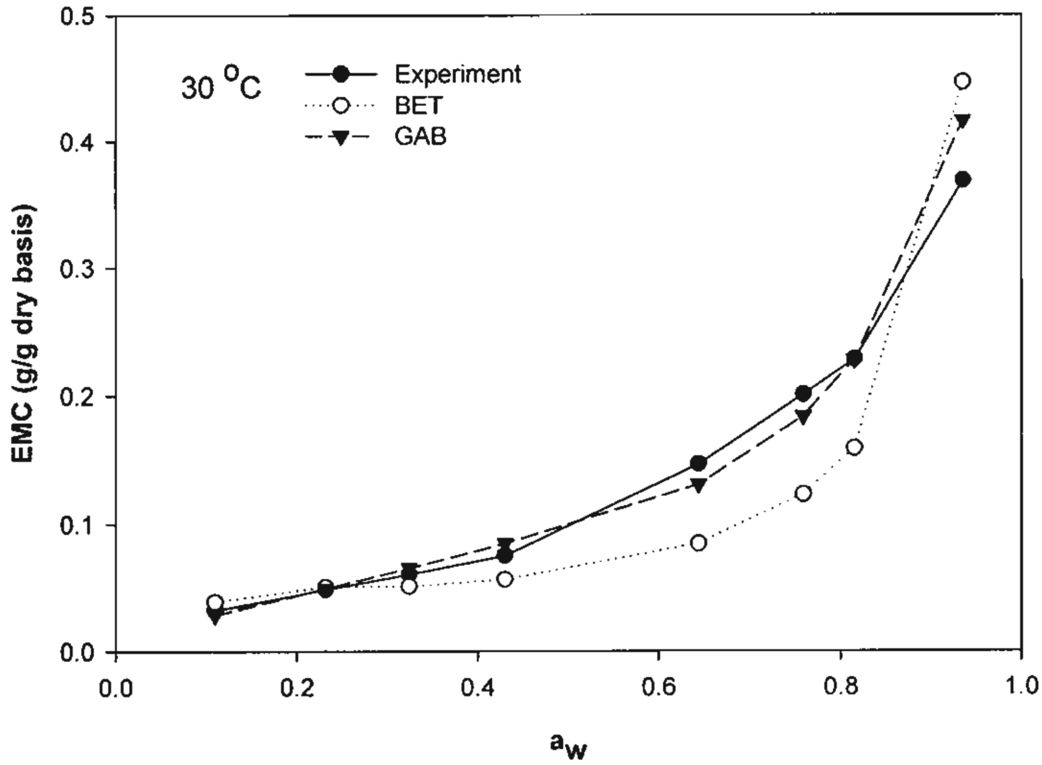


Figure 3

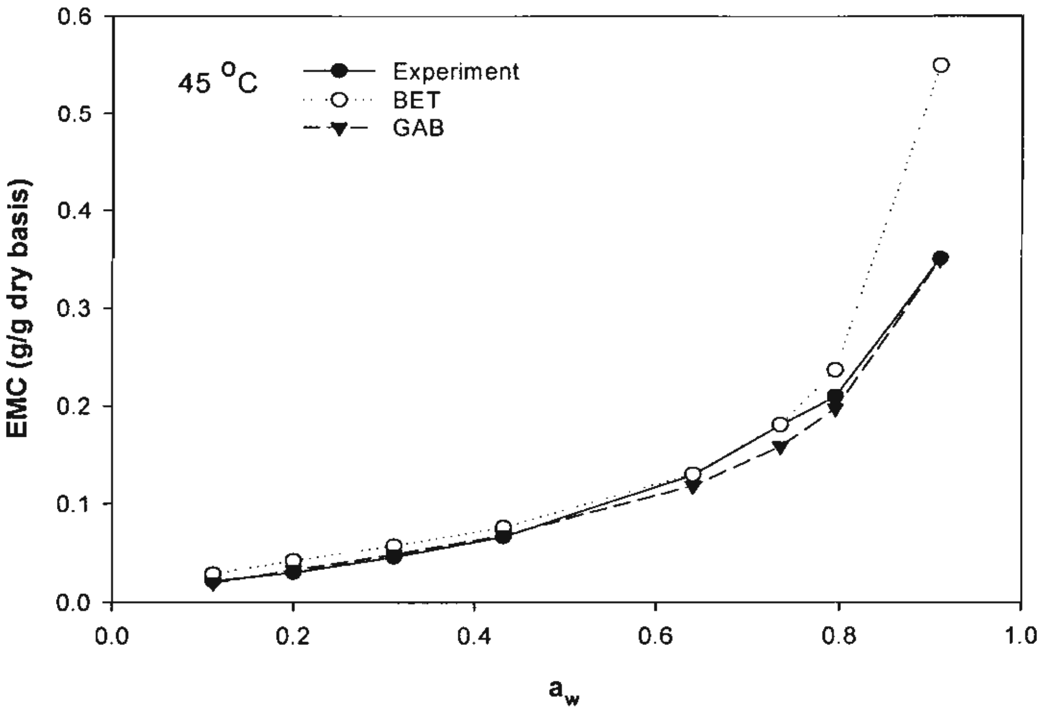

45 °C
Experiment
BET
GAB
EMC (g/g dry basis)
a_w

Figure 4

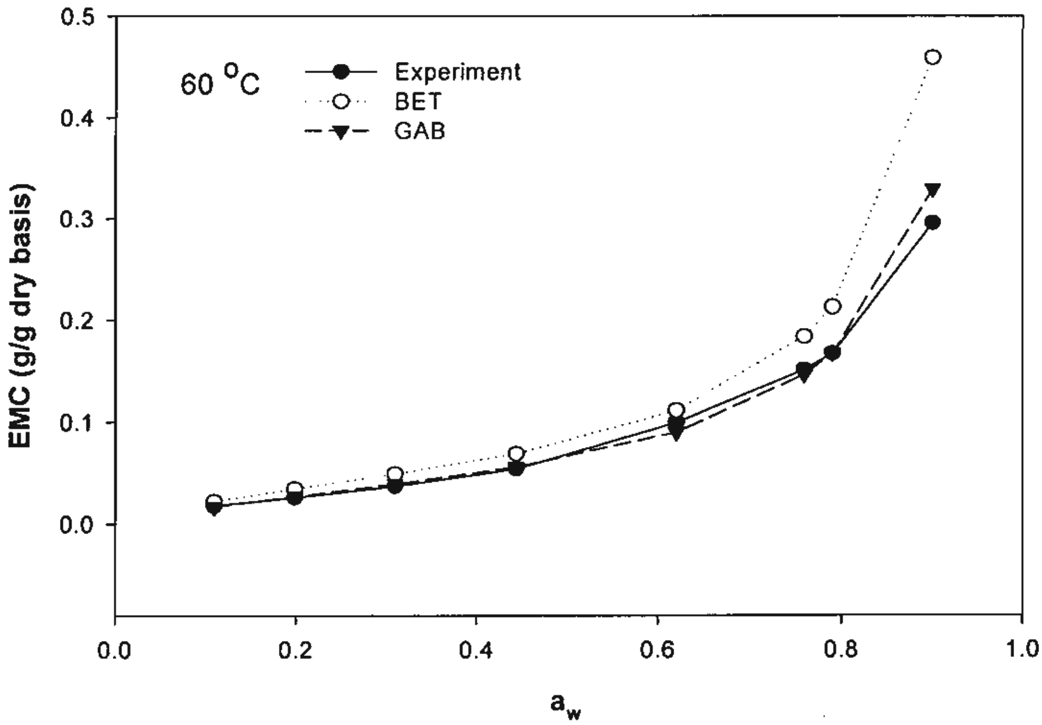

60 °C
Experiment
BET
GAB
EMC (g/g dry basis)
a_w

Figure 5

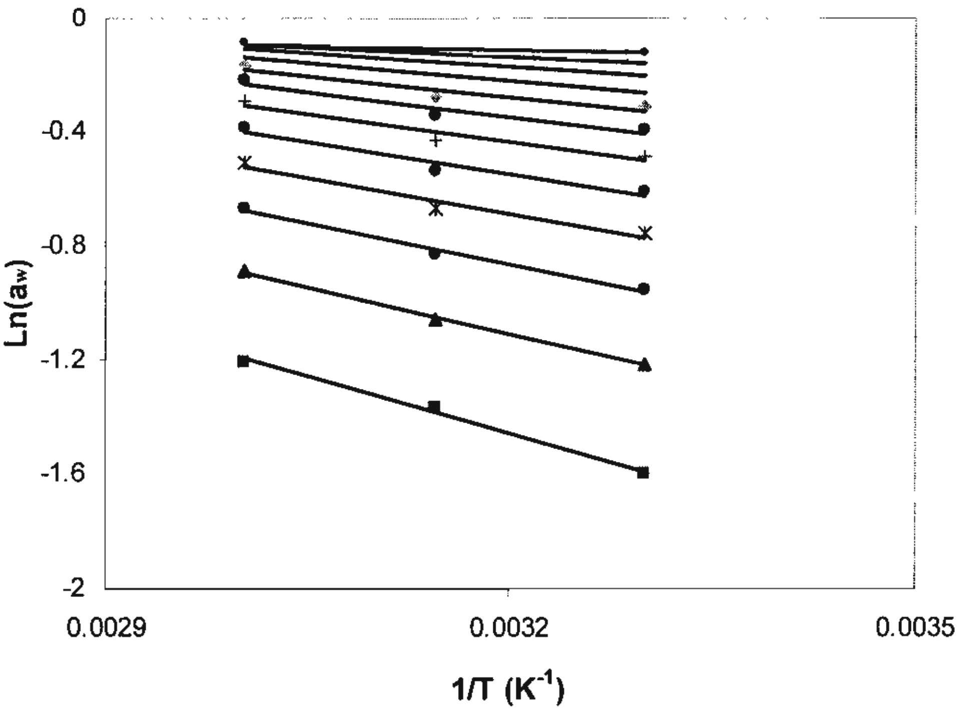
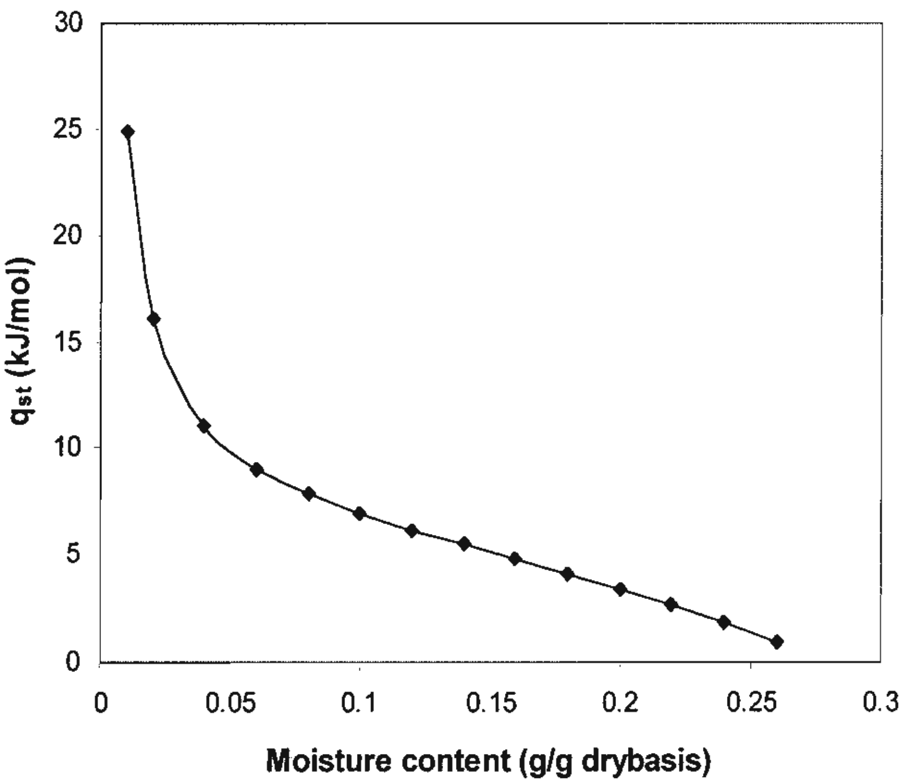


Figure 6



MODELING OF MOISTURE SORPTION ISOTHERM OF A CRISPY RICE SNACK USING BET AND OSWIN EQUATIONS

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ABSTRACT

Moisture sorption isotherm of a rice snack was determined at 30 °C over a water activity range of 0.10 to 0.95 using a static gravimetric technique. Moisture sorption isotherms of the snack exhibited the sigmoid (Type II) shape. The Brunauer, Emmett and Teller (BET) and OSWIN models were applied to fit the experimental data. 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 OSWIN equation over the BET equation was evident. The OSWIN model gave the best fit to the experimental sorption data for a wide range of water activity (0.10-0.95) while BET model gave the best fit for a water activity range of less than 0.60. The OSWIN model is considered suitable to predict the moisture sorption isotherm of rice snack since it gave low E and RMSE values.

Keywords—Moisture sorption isotherm, BET model, OSWIN model, Rice snack

ACKNOWLEDGEMENTS

The authors would like to thank the Thailand Research Fund for providing full financial support to this project under funding no. MRG4780202.

Introduction

Many foods absorb moisture during long term storage as commonly used packaging materials are permeable to moisture. Moisture content can be used as the critical criteria for judging the quality of foods that are graded by moisture. Moisture sorption isotherm equations are useful for prediction of water sorption properties of foods which, in turn, affect acceptability, shelf life and packaging requirements. A number of models to describe moisture sorption isotherm have been proposed including kinetic models based on a mono-layer (Brunauer, Emmett and Teller (BET) model), semi-empirical (Ferro-Fontan, Henderson and Halsey models) and empirical models (Smith and Oswin models). The objective of this study was to determine experimentally the equilibrium sorption isotherm of rice snack at 30 °C using BET and OSWIN equation.

Methodology

Sorption Isotherm Determination

Plain rice snack was acquired from a food plant in Samuthprakarn province. Saturated salt solutions (($LiCl$, $KC_2H_3O_2$, $MgCl_2$, K_2CO_3, Na_2NO_3, KCl and KNO_3)) were used to provide constant water activities ranging from 0.10 to 0.95 at a desired constant temperature. Moisture sorption isotherm of rice snacks was determined gravimetrically.

Sorption Isotherm Models

The data were adjusted to BET (Brunauer, Emmett and Teller, 1938) and OSWIN (Oswin, 1946) equations in order to determine the best fit.

BET equation

The BET equation can be expressed as follows:

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

where m is the amount of sorbate sorbed by one gram of sorbant at sorbate activity a_w. m_0 is the monolayer moisture content and C_B is BET constant.

OSWIN equation

OSWIN equation (Oswin, 1946) can be expressed as follows:

$$m = \alpha\left[\frac{a_w}{(1-a_w)}\right]^{\beta} \quad (2)$$

where m is moisture content of the product and α and β are constants.

Experimental moisture sorption data can be described by sorption models. In this study, three models including BET and OSWIN were used to fit the experimental sorption data and the parameters of the models were established using non-linear regression analysis. All calculations were performed using the routines MATLAB Version 5.3 (Mathworks, Inc., Natick, MA).

Model validation

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 root mean square error (RMSE). The mean relative percentage deviation modulus and RMSE were calculated (Al-Multaseb et al., 2004) as follow:

$$E = \frac{100}{N}\sum_{i=1}^{N}\frac{\left|m_e^i - m_p^i\right|}{m_e^i} \quad (3)$$

$$RMSE = \sqrt{\frac{\sum_{i=1}^{N}(m_e^i - m_p^i)^2}{N}} \quad (4)$$

where m_e is the experimental value, m_p is the predicted value, and N is the number of experimental data.

Result & Discussion

Determination of sorption isotherm

The experimental sorption isotherm of a rice snack follows the characteristic shape of type II isotherms. The EMC of the samples increased with the increase in the water activity at constant temperature.

Figures 1 and 2 show the sorption isotherms of the samples at 30 °C using BET and OSWIN equations, respectively. The plots using BET give an apparently linear part at low activities (a_w < 0.6). After which an upward curvature is observed. This deviation shows that, at higher activities, less water vapor is sorbed than that indicated by the BET equation using the values of the constants corresponding to the low activity range.

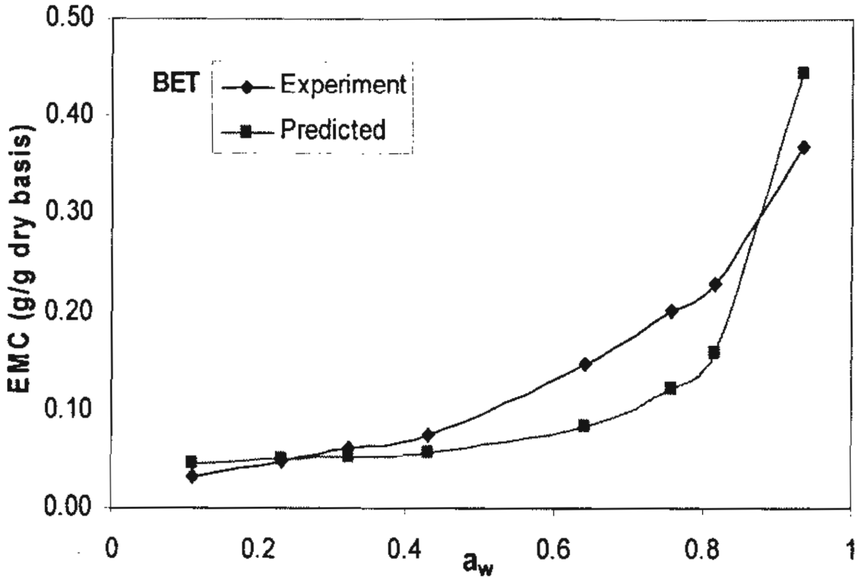

Figure 1 Sorption isotherm of RC at 30 °C using BET model

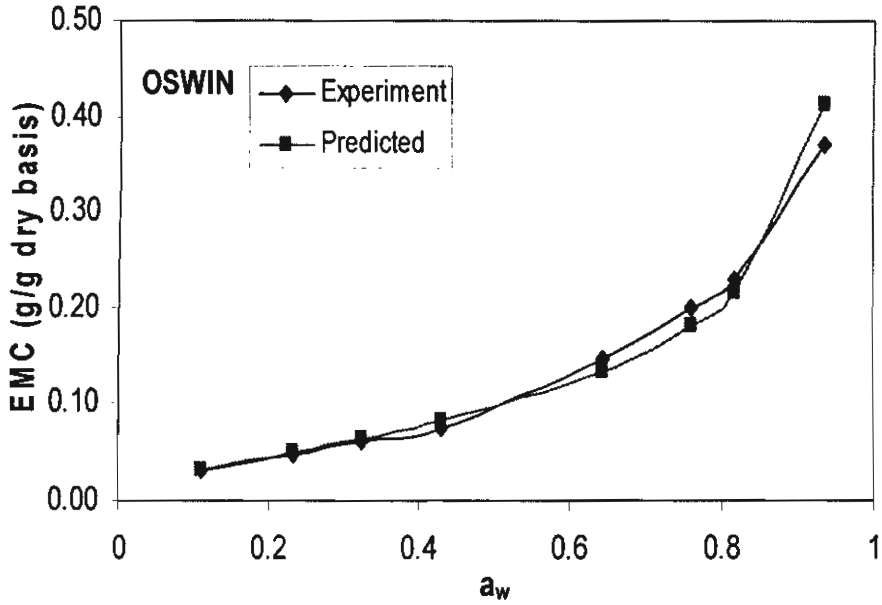

Figure 2 Sorption isotherm of RC at 30 °C using OSWIN model

Comparison of BET and OSWIN models

Figures 3 and 4 show the predicted and experimental EMC of the rice snack using BET and OSWIN models, respectively. The estimated parameters of the sorption models including monolayer moisture content (m_0) and model constant (C) are given in Table 1. The coefficient of determination

(R^2), together with the mean relative percentage deviation modulus and the root mean square error values are also given in Table 1.

The lower the values of E and RMSE, the better the goodness of fit (McMinn and Magee, 2003). The BET model provided a good description of the isotherms of the rice snack in the range of $a_w < 0.6$. The same conclusion was also drawn on the sorption isotherm of peppers by Kaymak-Ertekin and Sultanoglu (2001). OSWIN model on the other hand produced the best fit throughout the entire range of water activity. OSWIN model was found to be suitable for describing the sorption behavior of the samples.

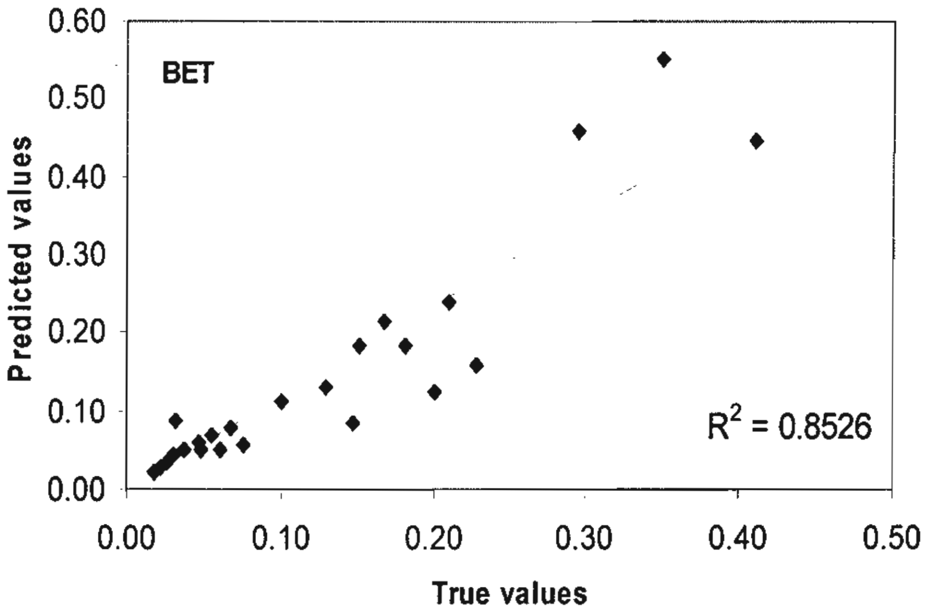

Figure 4 Predicted and experimental EMC of rice snack using BET model

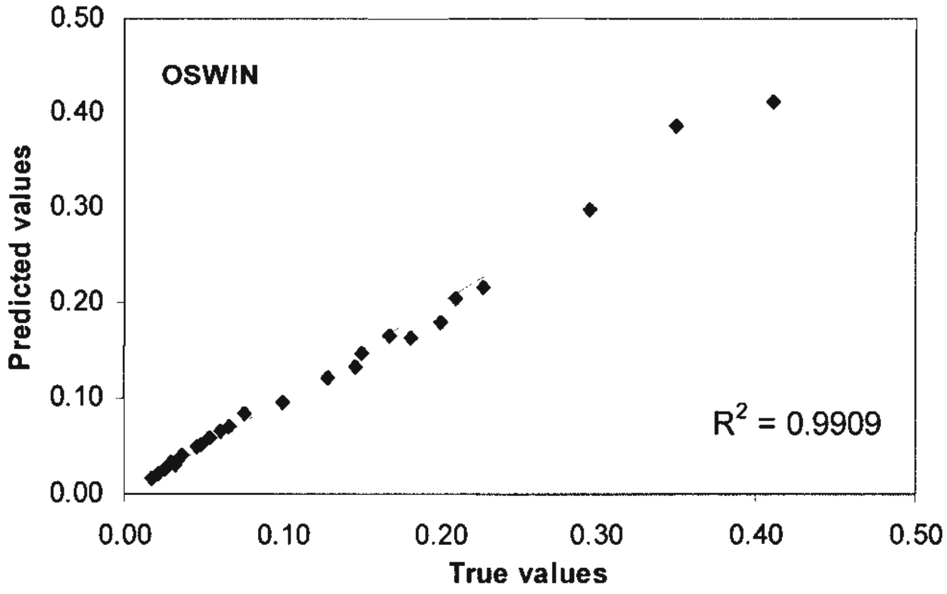

Figure 4 Predicted and experimental EMC of rice snack using OSWIN model

Table 1 Estimated parameters of BETand OSWIN models

Model	Estimated parameters	
BET	m_o	0.0588
	C_B	-12.297
	R^2	0.8147
	E	43.612
	RMSE	5.5045
OSWIN	α	0.0964
	β	0.5449
	R^2	0.9799
	E	7.4312
	RMSE	1.8369

Conclusion

Rice crackers exhibited Type II isotherms. The OSWIN model gave the best fit to the experimental sorption data for a wide range of water activity (0.10-0.95) while 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 the rice snack since it gave low E and RMSE values.

References

Al-Muhtasep, A. H., W. A. M. McMinn and T. R. A. Magee. 2004. Water sorption isotherms of starch powders Part 1: mathematical description of experimental data. J. Food Engineering. 61: 297-307.

Kaya, S. and Kahyaoglu, T. 2005. Thermodynamic properties and sorptin equilibrium of pestil. J. Food Engineering. 71: 200-207.

Kaymak-Ertekin, F. and Sultanoglu, M. 2001. Moisture sorption isotherm characteristics of peppers. J Food Engineering. 47: 225-231.

Oswin, C.R. 1946. The kinetics of packing life. The isotherm. Journal of Chemical Industry. 65: 419-423.