รายงานวิจัยฉบับสมบูรณ์

โครงการ การทำนายอายุการเก็บของผลิตภัณฑ์ที่เสื่อมคุณภาพเนื่องจากความชื้นโดยใช้ Artificial Neural Network

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Shelf Life Prediction of a Moisture Sensitive Food Product Using Artificial Neural Network

Ubonrat Siripatrawan and Pantipa Jantawat

ABSTRACT

Actual storage shelf life test by storing a packaged product under typical storage conditions is costly and time consuming. Hence, a rapid and cost effective shelf life prediction models was established for a packaged moisture sensitive food product. Artificial neural network (ANN) algorithm was developed to predict the shelf life of 2 varieties of rice crackers (RS-1 and RS-2) packaged in 4 types of packaging materials (Bag-1, Bag-2, Bag-3 and Bag-4) and stored at 30 °C and 75% RH, 30 °C and 85% RH and 45 °C and 75% RH, comparable to tropical storage conditions. ANN based prediction model was compared to the conventional shelf life simulation model based on Guggenheim-Anderson-de Boer (GAB) equation as well as actual shelf life testing. The performance of ANN and GAB models was measured using regression coefficient, R^2, and root mean square error, RMSE. The GAB model for shelf life prediction of rice crackers was carried out using the relationship between water activity of food product and barrier property of packaging material. Using ANN algorithm, many factors could be incorporated into the model including food characteristics, package properties, and storage environments. On the other hand, complicated theoretical isotherms, such as the GAB equation, does not take into account the different between food compositions. The ANN developed for shelf life prediction of rice crackers is based on back-propagation. The neural network comprised an input layer, one hidden layer and an output. The network was trained using Bayesian regularization. The ANN algorithm gave R^2 of 0.993 and 0.986, and RMSE of 1.3831 and 1.0158, while the GAB model gave R^2 of 0.7953 and 0.6828, and RMSE of 13.9264 and 8.4343 for RS-1 and RS-2, respectively. The result indicated that the ANN could predict shelf life better than the GAB model. Shelf life prediction using the simulation model is possible within a reasonable time and provides a powerful support tool for packaging development. ANN offers several advantages over conventional digital computations, including faster speed of information processing, learning ability, fault tolerance, and multi-output ability.

Keywords : Shelf life prediction, ANN algorithm, GAB equation

การทำนายอายุการเก็บของผลิตภัณฑ์ที่เสื่อมคุณภาพเนื่องจากความชื้นโดยใช้ Artificial Neural Network

อุบลรัตน์ สิริภัทราวรรณ และ พันธิพา จันทวัฒน์

บทคัดย่อ

การกำหนดอายุการเก็บของอาหารที่เสื่อมเสียเนื่องจากความชื้นตามวิธีปกติ โดยเก็บรักษาอาหารไว้ที่ภาวะการเก็บรักษาจริงและตรวจสอบเป็นระยะจนกระทั่งอาหารหมดอายุ เป็นวิธีที่ใช้เวลานานและสิ้นเปลืองค่าใช้จ่ายเนื่องจากอาหารที่มีความชื้นต่ำสามารถเก็บรักษาได้นาน งานวิจัยนี้ศึกษาการทำนายอายุการเก็บของ rice crackers 2 ชนิด (RS-1 และ RS-2) ในบรรจุภัณฑ์ 4 ชนิด (Bag-1, Bag-2, Bag-3 and Bag-4) และเก็บรักษาที่ภาวะต่าง ได้แก่ 30 °C 75% RH, 30 °C 85% RH และ 45 °C 75% RH โดยการใช้แบบจำลองทางคณิตศาสตร์ที่พัฒนาจาก artificial neural network (ANN) และเปรียบเทียบกับการใช้ Guggenheim-Anderson-de Boer (GAB) model ควบคู่กับการหาอายุการเก็บจริงของอาหาร (actual shelf life testing) การทำนายอายุการเก็บโดยใช้ GAB model ใช้ข้อมูลความสัมพันธ์ระหว่างค่า water activity ของอาหารในบรรจุภัณฑ์ กับค่าการซึมผ่านของบรรจุภัณฑ์ (water vapor permeability) ที่อุณหภูมิและความชื้นสัมพัทธ์ของการเก็บรักษา ส่วนการใช้ ANN algorithm ที่พัฒนาขึ้นใช้ในงานวิจัยนี้ ใช้ข้อมูลทั้งจากองค์ประกอบของอาหาร คุณสมบัติของบรรจุภัณฑ์ และภาวะในการเก็บรักษา ซึ่ง ANN algorithm ที่พัฒนาขึ้นใช้ในการทำนายอายุการเก็บคือ back propagation multilayer perceptron และใช้ Bayesian regularization ในการฝึกฝนการเรียนรู้ของ ANN algorithm การวัดประสิทธิภาพของ ANN algorithm และ GAB equation ทำโดยวัดค่า regression coefficient (R^2) และ mean square error (MSE) เปรียบเทียบกับอายุการเก็บจริงของผลิตภัณฑ์ พบว่า ANN ที่พัฒนาขึ้นสามารถทำนายอายุการเก็บของ RS-1 และ RS-2 ในภาวะต่าง ๆ ได้โดยให้ค่า R^2 เท่ากับ 0.993 และ 0.986 และค่า RMSE เท่ากับ 1.3831 และ 1.0158 ส่วน GAB model ให้ค่า R^2 เท่ากับ 0.7953 และ 0.6828 และค่า RMSE เท่ากับ 13.9264 และ 8.4343 ตามลำดับ ANN ที่พัฒนาขึ้นสามารถทำนายอายุการเก็บได้ถูกต้องกว่าการใช้ GAB equation การใช้ ANN เพื่อทำนายอายุการเก็บอาหารช่วยให้อุตสาหกรรมอาหารสามารถประเมินอายุการเก็บของอาหารได้รวดเร็ว มีความถูกต้องสูง และไม่สิ้นเปลืองค่าใช้จ่าย โดยไม่จำเป็นต้องใช้เวลานานในการทดลองเก็บรักษาอาหารจริง

คำหลัก การทำนายอายุการเก็บอาหาร, ANN, GAB

EXECUTIVE SUMMARY

โครงการ การทำนายอายุการเก็บของผลิตภัณฑ์ที่เสื่อมคุณภาพเนื่องจากความชื้นโดยใช้ ANN

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JUSTIFICATION

During storage and distribution, undesirable transport phenomena such as permeation of moisture, oxygen, or volatile compounds through the packaging material affect the quality of foods including taste, aroma, texture or appearance that are deemed unacceptable. For the delivery of a product with maximum quality, the shelf life of a packaged food product should be determined. The shelf life determination may also be required when there are changes in product design, food formulation, package, or storage system. Therefore, establishing the shelf life of food product becomes important for the food industry. Actual storage shelf life test by storing a packaged product under typical storage conditions is costly and time consuming. Therefore, a rapid and cost effective shelf life simulation models have been established. Shelf life prediction using the simulation model is possible within a reasonable time and provides a powerful support tool for reducing the cost and the cycle time of product development and for packaging development. Shelf life modeling is of particular interest for predicting shelf life of foods.

Simulation models such as GAB model which have been used to indicate the shelf life of packaged moisture sensitive foods are based on the relationship between water activity of food product and barrier property of packaging material. These conventional approaches are useful. However, they are not necessarily accurate when applied to foods with complex compositions and are not applicable when there are differences in processing conditions, packaging properties, and storage systems. Besides food product's water activity and barrier property of the package, other factors can also significantly influence the shelf life characteristics of the packaged foods. Numerous variables must be considered in the experimental design of the shelf life study to obtain a useful result. To date, there is no exact mathematical solution available for predicting the shelf life of the packaged moisture sensitive foods. In this research, hence, ANN algorithm was developed and used as a practical tool for shelf life prediction of a packaged moisture sensitive food product. Incorporation of various factors including food product compositions, package properties, and storage condition data into a single model can be achieved when artificial neural network (ANN) algorithm is used.

OBJECTIVE

The overall objective of this research is to develop a general and effective shelf life prediction model based on ANN algorithm incorporating the information of product characteristic, package properties, and storage conditions to predict shelf life of a moisture sensitive product.

METHODOLOGY

The methodology was divided into 5 major activities : (1) Determination of 2 varieties of rice cracker (RS-1 and RS-2) characteristics and package (Bag-1, Bag-2, Bag-3 and Bag-4) properties; (2) Determination of moisture sorption isotherm of the products at 30, 45 and 60 ^{o}C; (3) Determination of the actual shelf life of the product at 30 ^{o}C and 75% RH, 30 ^{o}C and 85% RH and 45 ^{o}C and 75% RH, comparable to tropic environment; (4) Determination of the product shelf life using a conventional mathematical model; (5) Development of an ANN algorithm for shelf life prediction of the products.

RESULTS

Sorption isotherm characteristics of two varieties of rice crackers (RS-1 and RS-2) were examined in light of their influence on the storage stability of rice crackers and prediction of shelf life. The moisture content decreased as temperature increased at a given relative humidity of the storage environment. Conventional mathematical models including Brunauer, Emmett and Teller (BET) and Guggenheim-Anderson-de Boer (GAB) equations were used to predict the moisture sorption isotherms of rice crackers. The criteria to evaluate goodness of fit of each model were the coefficient of determination (R^2), the mean relative deviation modulus (E), and the root mean square error (RMSE). The result shows the BET model provided a good description of the isotherms of rice crackers in the range of water activity < 0.60. The GAB model on the other hand produced the best fit throughout the entire range of water activity with low values of E and RMSE. GAB model was then used for shelf life prediction of rice crackers.

GAB model for shelf life prediction of rice crackers was carried out using the relationship between water activity of food product and barrier property of packaging material. The GAB model gave R^2 of 0.7953 and 0.6828, and RMSE of 13.9264 and 8.4343 for RS-1 and RS-2, respectively. The performances, including R^2 and RMSE, of GAB model to predict shelf life of rice crackers was compared to that of ANN algorithm.

ANN based on back-propagation was developed for shelf life prediction of rice crackers. Incorporation of various factors including food product compositions, package properties, and storage condition data into a single model can be achieved when artificial neural network (ANN) algorithm is used. The neural network comprised an input layer, one hidden layer and an output. The network was trained using Bayesian regularization. The determination 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. The 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 ANN algorithm gave RMSE of 1.3831 and 1.0158 for RS-1 and RS-2, respectively. The results indicates that ANN algorithm provided dramatically lower prediction errors and gave higher determination coefficients, when compared to the GAB model.

ANN provided a tool that may be used to avoid the shortcomings involved in conventional simulation methods. ANN offers several advantages over conventional digital computations, including faster speed of information processing, learning ability, fault tolerance, and multi-output ability. The additional benefit of ANN is that it enable 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 model was performed separately for each shelf life.

SIGNIFICANCE

Using the ANN algorithm, shelf life prediction is expected to be more rapidly and conveniently comparable with that from actual experimental testing and conventional shelf life simulation model. Successive of the research will provide the food industries with an alternative method for shelf life analysis of moisture sensitive food products as well as product/package optimization. This method is not limited to the aforementioned applications. The system can be applied to other packaged food products in the food industries.

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1. INTRODUCTION

During storage and distribution, undesirable transport phenomena such as permeation of moisture, oxygen, or volatile compounds through the packaging material affect the quality of foods including taste, aroma, texture or appearance that are deemed unacceptable. For the delivery of a product with maximum quality, the shelf life of a packaged food product should be determined. The shelf life determination may also be required when there are changes in product design, food formulation, package, or storage system. Therefore, establishing the shelf life of food product becomes important for the food industry. Actual storage shelf life test by storing a packaged product under typical storage conditions is costly and time consuming. Therefore, a rapid and cost effective shelf life simulation models have been studied. Shelf life prediction using the simulation model is possible within a reasonable time and provides a powerful support tool for packaging development.

Simulation models which have been used to indicate the shelf life of packaged moisture sensitive foods are based on the relationship between water activity of food product and barrier property of packaging material. These conventional approaches are useful. However, they are not necessarily accurate when applied to foods with complex compositions and are not applicable when there are differences in processing conditions, packaging characteristics, and storage systems. Besides the water activity of food product and the barrier property of packaging material, other factors can also significantly affect the shelf life characteristics of the packaged foods. Numerous variables must be considered in the experimental design of the shelf life study to obtain a useful result. Incorporation of various factors including food product compositions, package properties, and storage condition data into a single model can be achieved when artificial neural network (ANN) algorithm is used. ANN is a mathematical model whose structure and function are inspired by the organization and function of human brain (Coulibaly, Bobée and Anctil, 2001). ANN provides several advantages over conventional digital computations because of its faster speed of data processing, learning ability, fault tolerance (Bila et al., 1999; Devabhaktuni, 2001).

In this research, Jasmine rice crackers were studied as a representative sample of moisture sensitive food products. Jasmine rice cracker is a tasty and healthy snack item of Thailand and is exported worldwide in particular to Japan and European countries. This product usually encounters loss of crispness due to moisture gain during storage and distribution, with subsequent deterioration in, and loss of, product. Actual shelf life test and conventional simulation model were performed parallel to one another. ANN algorithm for shelf life prediction of rice crackers was developed. Product characteristics, package properties and storage conditions were incorporated into a single ANN model. The performance of ANN algorithm was then compared to a conventional prediction model based on GAB equation.

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.

2. LITERATURE REVIEW

2.1 Shelf life stability of moisture sensitive food products

Shelf life is a measure of how long after production and packaging that a food product remains optimal or acceptable under specified environmental conditions. At the end of shelf life, food quality undergoes various changes in taste, aroma, texture or appearance that are deemed unacceptable or undesirable (Cardoso and Labuza, 1983).

Shelf life is a function of the product, the package, and the environment through which the product is transported, stored, and sold. During the storage, a number of deterioration processes including taste, aroma, texture or appearance take place together (Jay, 2000). For a moisture sensitive food product, there is exchange of moisture between the atmosphere and the food during the storage. This exchange continues until the food reaches equilibrium with the atmosphere (Cardoso and Labuza, 1983; Hernandez and Giacin, 1997). Food packaging plays an important role in the control of moisture which has a significant effect on shelf life. The optimal packaging material that is chosen should be compromise between protective requirements, shelf life, aesthetics, and cost. For the delivery of a product with maximum quality, the shelf life of a packaged food product should be established. The determination of shelf life may also be required when there are changes in product design, food formulation, package, or storage system. Therefore, establishing the shelf life of food product becomes important for the food industry (Hernandez and Giacin, 1997; Jay, 2000).

2.2 Factors Affecting Food Shelf Life

2.2.1 Food characteristics

Water level affects the characteristics of many foods. Water is essential for microbial growth, and if the amount of free water changes, a food's susceptibility to spoilage may change. Crispness of moisture sensitive foods is affected by water content and it may be lost as a result of plasticization of the physical structure by temperature or water. Crispness is essential to the quality of various low moisture cereal and snack foods.

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. When a foodstuff is in equilibrium with its surroundings, the water vapor pressure of the food is equal to the partial pressure of water vapor in the atmosphere, hence the water activity in the foodstuff is equal to the equilibrium relative humidity of the air (Arslan and Togrul, 2005; Aryanci and Duman, 2004).

Water activity, a_w, (Eq. 2.1) is the ratio of the vapor pressure in a solution or a food material, p , and that of pure water at the same temperature, p_s . Therefore, the equilibrium or steady state a_w is related to equilibrium relative humidity (ERH) of the surrounding atmosphere, and a_w can be considered to be a temperature dependent property of water which is used to characterize the equilibrium or steady sate of water within a food material (Corzo and Fluentes, 2004).

$$a_w = \frac{p}{p_s} \qquad (2.1)$$

Stability of a moisture sensitive food product requires the determination of the relationship between water activity and equilibrium moisture content, known as the water sorption isotherm. The water activity of low moisture foods products is dependent on storage relative humidity and temperature. The gravimetric method is the most common for obtaining water sorption isotherms (Corzo and Fluentes, 2004).

Determination of sorption isotherms is necessary for the determination of stability at various storage conditions and requirements for packaging materials to ensure product shelf life (Aryanci and Duman, 2004). Several mathematical models exist to describe water sorption isotherms of food materials, however, no one equation gives accurate results throughout the whole range of water activities, or for all types of foods since the water is associated with the food matrix by different mechanisms in different water activity regions (Al-Muhtaseb et al., 2004).

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., 2004; Siripatrawan and Jantawat, 2006).

2.2.2 Packaging Considerations

Shelf life is a complex concept depending on the nature of the food product under consideration, the preservation technologies applied, and the environmental conditions to which the food product is exposed. Food packaging plays a crucial role in the control of moisture, and has a significant effect on shelf life (Tung, Britt, and Yada, 2000).

Proper selection and optimizing of packaging are of great importance to food manufacturers due to aspects such as economy, marketing, logistics, distribution, consumer demands, and the environmental impact of the packaging. The barrier properties of flexible films play a major role in determining the shelf life of packaged food products. In fact, polymeric films controlling the rate at which small molecular weight compounds permeate into or outside the package can slow down the detrimental phenomena responsible for the unacceptability of the packaged product (Del Nobile, Fava and Piergiovanni, 2002).

In terms of packaging considerations, the water activity of a food product, at various moisture contents and temperatures, will determine whether the product will gain or lose moisture when exposed to an atmosphere of a given relative humidity. Water activity can be related to moisture content of a food through moisture sorption isotherms. The permeability of packaging materials to moisture is a critical factor in controlling changes in the moisture content and water activity of packaged foods and, hence, their shelf life (Tung, Britt, and Yada, 2000).

2.2.3 Environmental Factors

The climatic environment (e.g., relative humidity, oxygen, light, temperature) as well as the physical distribution and storage environment are major extrinsic factors involved in numerous deteriorative reactions and physical damage that can lead to losses in food quality and decrease shelf life (Tung, Britt, and Yada, 2000).

One of the most common shelf life stability concerns in relation to packaging and mass transfer arises from the exchange of water vapor between the food and the surrounding atmosphere. Difference among the water activities of food and the environment outside the package introduces a driving force for water transport. Therefore, exchange of moisture between the atmosphere and the food occurs. This exchange continues until the food reaches equilibrium with the atmosphere. Moisture transfer can result in a number of undesirable changes depending on the specific product and whether moisture is gained or lost. These changes could include; physical processes such as caking of powders and loss of crispness resulting from moisture sorption; microbial spoilage resulting from increased availability of water due to moisture sorption and chemical processes which can be enzymatic or non-enzymatic.

2.3 Shelf life testing and prediction

Actual storage shelf life test by storing a packaged product under typical storage conditions is costly and time consuming. Therefore, shelf life simulation models have been established. Shelf life prediction using the simulation model is possible within a reasonable time and provides a powerful support tool for packaging development.

Determination of shelf life of food products has been studied using models based on the deterioration of food products as a function of storage temperature (Iglesias, Viollaz and Chirife, 1979; Kwolek and Bookwalter, 1971). Only a few works have performed the shelf life of moisture sensitive foods as a function of more than one environmental factor. Cardoso and Labuza (1983) used Arrhenius relationship based mathematical model to predict shelf life of food product as a function of temperature and relative humidity. Pierglovanni, Fava, and Siciliano (1995) developed a more general mathematical model for food shelf life prediction based on product's water activity and barrier properties of the package at different temperature and relative humidity.

The simulation models widely used to determine the shelf life of packaged food products are theoretically based on the Brunauer, Emmett and Teller equation and the

Guggenheim-Anderson-de Boer equation (Brunauer, Emmett and Teller, 1938; Coupland et al., 2000; Mittal and Zhang, 2000). These conventional methods calculate the shelf life by using the relationship between moisture uptake behavior of food product and barrier property of packaging material. However, Hernandez and Giacin (1997) indicated that shelf life of the packaged food product is generally controlled by product characteristic, environment of storage condition, and package property.

A basic model has been reported by Labuza et al. (1972) to calculate the moisture uptake by a single component. But, iterative approximation procedures have to be carried out when the product isotherm is not linear. Since most food products do not have a linear moisture isotherm products may consist of multiple components, more simplification and approximations have to be made in order to apply this basic model.

To date, there is no exact mathematical solution available for predicting the moisture uptake by packaged products.

2.4 Artificial Neural Network

An artificial neural network (ANN) can be referred to as a neurocomputer with parallel distributed processors. ANN is a mathematical model whose structure and function are inspired by the organization and function of human brain (Bila et al., 1999). A neural network is a massively parallel distributed processor made up of simple processing units, which has a natural propensity for storing experiential knowledge and making it available for use. It resembles the brain in 2 aspects: knowledge is acquired by the network from its environment thought a learning process, and interneuron connection strengths, known as synaptic weights, are used to store the acquired knowledge. Neural networks have the advantage that they can handle nonlinear data and are more tolerant to noise of the system, and tend to produce lower prediction error rates than chemometric techniques (Packianather et al., 2000; Terra et al., 2001).

The most common neural network approach to regression-type problems is multilayer perceptrons (MLP) (Coulibaly, Bobée and Anctil, 2001; Martin, Santos and Agapito, 2001). The basic idea is to find a model that will correctly associate the inputs with the outputs. The learning data is used to train the system and to set the calibration model. The test data are then passed through the calibration model in order to obtain the model's predicted results. This technique has the advantage of producing low prediction errors (Coulibaly, Bobée and Anctil, 2001; Siripatrawan et al., 2004; Siripatrawan et al., 2006).

The primary element of an ANN is the neuron. These neurons are arranged in input and output layers of one or more hidden processing layers. Neurons can be thought of as weighted transfer functions (Nakamura and Yoshikawa, 2001). The most common neural network approach to regression-type problems is multilayer perceptrons (MLP). The popular algorithm is known as a back propagation algorithm (Martin, Santos, and Agaptito, 2001). Figure 2.1 shows the architectural graph of multilayer perceptrons with one hidden layer and an output layer. The input signal is a function signal that comes through the input end of the network, propagates neuron by neuron through the network, and emerges at the output end of the network as an output signal. The function signal is presumed to perform a useful function at the output of the network and at each neuron of the network through which a function signal passes, the signal is calculated as a function of the inputs and associated weights applied to that neuron (Hikawa, 2001; Swicegood and Clark , 2001; Tanaka and Hasegawa, 2001).

The majority of published work uses a feed forward net with back propagation for training. 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 (Devabhaktuni et al., 2001; Kimura and Nakano, 2000; Watanabe et al., 2001). In mathematical terms, a neuron *k* can be described by

$$u_k = \sum_{j=1}^{m} w_{kj} x_j \qquad (2.2)$$

$$y_k = \varphi(u_k + b_k) \qquad (2.3)$$

where $x_1,\ldots,x_m$ are the input signals; $w_{k1},\ldots,w_{km}$ are the weights of neuron k; u_k is the linear combiner output due to the input signals; b_k is the bias; $\varphi(.)$ is the activation function; and y_k is the output signal of the neuron.

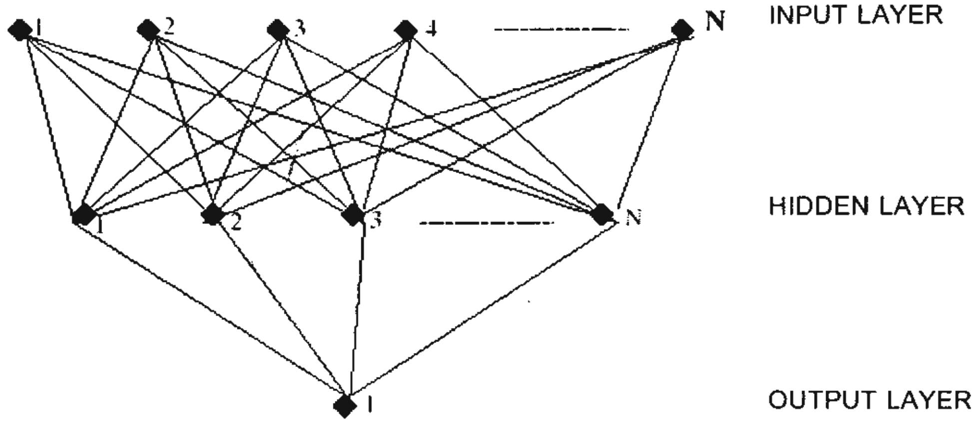


Figure 2.1 Artificial neural network architecture

The important property of a neural network is its ability to learn to improve its performance. The network ideally becomes more knowledgeable about its environment after each iteration of the learning process. Learning is defined as changing in the synapses weights.

The learning techniques can be classified into two categories, supervised and unsupervised learning. Multilayer perceptron neural networks use error-correction learning (supervised learning procedure). Error-correction learning adjusts the weights connected between neurons in proportion to the errors of each neuron. The corrective adjustments are calculated to make the output come closer to the desired value in a step by step manner. For error-correction learning, minimization of the error leads to a learning rule generally referred to as the Widrow-Hoff rule or delta rule (Terra et al., 2001).

Neural networks have been applied to a wide variety of applications including, dynamic system control (Watanabe et al., 2001), predicting process parameters involved in thermal/pressure food processing (Torrecilla, Otero and Sanz, 2004), prediction of *E. coli* growth in nutrient media (Siripatrawan, Linz and Harte, 2004), and hydrologic events forecasting (Coulibaly et al., 2001).

3. OBJECTIVES

The overall objective of this research is to establish a general and effective ANN algorithm incorporating the information of product characteristic, package properties, and storage conditions to predict shelf life of a moisture sensitive product (rice crackers). The specific objectives include:

1. To determine moisture sorption isotherms of a moisture sensitive food product
2. To determine the actual shelf life of a moisture sensitive food product
3. To predict shelf life of a moisture sensitive food product using a conventional shelf life simulation model
4. To develop an ANN algorithm for shelf life prediction of a moisture sensitive food product

4. MATERIAL & METHODS

4.1 Determination of product and package characteristics

4.1.1 Determination of product characteristic

Plain Jasmine rice crackers were studied as a representative sample of moisture sensitive food products. Two varieties of rice crackers (RS-1 and RS-2) were used in this study. The composition of rice crackers was determined following the AOAC (1995) methods including: moisture content (AOAC 24.035 method); ash content determined by dry-ashing method (AOAC 24.036); protein (AOAC 42.016) using 6.25 as the conversion factor; and fat content (AOAC 24.005). Carbohydrate content was calculated by difference according to the following formula: 100-(moisture + protein + fiber + lipid + ash).

4.1.1 Determination of package characteristics

Different commercially available non-polar hydrocarbon packaging materials (Bag-1, Bag-2, Bag-3 and Bag-4) were used to form into 100 x 100 mm^2 packages. The thickness of all packages was measured using a digital micrometer (Mitutoyo Absolute, Tester Sangyo Co., Ltd., Tokyo, Japan). The water vapor permeability of the packages was determined following ASTM standard test method (ASTM, 2003).

4.2 Study of moisture sorption isotherm of the products

Eight saturated salt solutions (LiCl, $KC_2H_3O_2$, $MgCl_2$, K_2CO_3, $NaNO_3$, NaCl, $(NH_4)_2SO_4$ and KNO_3) were used to provide constant water activities ranging from 0.10 to 0.95. 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 and 45 ^oC and allowed to equilibrate with the environment inside the containers. 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. The equilibrium moisture contents

(EMC) of the samples were evaluated in various controlled relative humidity chambers ranging from ~10 % to ~95 % RH at 30, 45 and 60 ^{o}C.

4.3 Study of actual shelf life of the products

4.3.1 Determination of critical moisture content of rice crackers

This step was performed to determine the moisture level at which a product is no longer acceptable. The products were placed in an airtight chamber containing a dish of water and stored at 30 $\pm$ 2 ^{o}C and periodically examined for changes in texture (the critical attribute) until it becomes unacceptable. Sensory evaluation was carried out by fifteen trained panelists to determine the product quality. The assessors rated the samples organoleptically and the moisture level at which the product is not acceptable was determined. The critical water activity of the samples was measured using a water activity analyzer (Aqua Lab, Model Series 3 TE, Decagon Devices, Inc, USA). The critical moisture contents (CMC) of each sample was then determined at the specific critical water activity.

4.3.2 Determination of the actual shelf life of the products

Approximately 10 g of products were packaged in selected packaging materials (Bag-1, Bag-2, Bag-3 and Bag-4) formed into 100 x 100 mm^{2} bags and heat sealed using an impulse sealer. The products were stored at 30 ^{o}C and 75% RH, 30 ^{o}C and 75% and 45 ^{o}C and 75 % RH and periodically examined until the critical moisture content was reached. These storage conditions represent a practical range for the tropical storage conditions.

4.4 Study of food shelf life simulation using conventional mathematical algorithm

4.4.1 Modeling of Sorption isotherms

Moisture sorption isotherms of rice crackers were determined gravimetrically, at various constant water activities ranging from 0.10 to 0.95, at in which the weight was monitored continuously within a standard static system of thermally stabilized conditions.

A knowledge of the equilibrium moisture content *m* corresponding to water activity a_w at constant temperature requires a knowledge of the food isotherm. The data (from 4.2) obtained corresponding to the a_w and moisture content at the temperatures studied were adjusted to Brunauer Emmet and Teller (BET) equation (Brunauer, Emmett and Teller, 1938) and Guggenheim-Anderson-de Boer (GAB) equation (Anderson, 1946; de Boer, 1953; Guggenheim, 1966) in order to determine the best fit.

The experimental data were fitted to the models using a nonlinear regression. All calculations were performed using the routines MATLAB Version 7.1 (Mathworks, Inc., Natick, MA) as written by the authors. The criteria used to evaluate the goodness of fit of each model were the coefficient of determination, R^2, the mean relative percentage deviation modulus (E) and the percentage root mean square error (RMSE).

4.4.2 Shelf life determination

The best model from 4.4.1 that gave the best fit to the moisture sorption isotherm was used for shelf life determination. The data necessary for shelf life calculation included critical moisture content of the product and the package permeability.

4.5 Develop an ANN based model for shelf life prediction of the packaged samples

Artificial neural network was used to predict shelf life of rice crackers. The data of food product compositions, packaging characteristics, and storage conditions were used as an input data for the ANN calculation. All the data required to develop the ANN model were collected. A total of 288 samples were used. 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 ANN was trained using selected parameters from data set and was subsequently validated using independent data set. All matrix calculations were performed using the routines MATLAB Version 7.1 (Mathworks, Inc., Natick, MA).

5. RESULTS & DISCUSSION

5.1 Product and package characteristics

5.1.1 Determination of product characteristics

Compositions of RS-1 and RS-2 rice crackers are presented in Table 5.1. The main composition differences in the analyzed crackers were in their fat content, 1.27 % for RS-1 and 21.09 % for RS-2, and total carbohydrate content, 85.82 % for RS-1 and 68.39 % for RS-2.

Table 5.1 Compositions of RS-1 and RS-2 rice crackers

Composition[a] g/100 g sample	Sample Code RS-1	Sample Code RS-2
Moisture	4.72 $\pm$ 0.34	1.28 $\pm$ 0.18
Protein	6.72 $\pm$ 0.28	6.31 $\pm$ 0.10
Fat	1.27 $\pm$ 0.14	21.09 $\pm$ 0.23
Fiber	0.32 $\pm$ 0.07	0.49 $\pm$ 0.09
Ash	1.17 $\pm$ 0.11	1.36 $\pm$ 0.15
Carbohydrate[b]	85.82	69.39

[a]All results are means of triplicate determinations

[b]Calculated by differences.

5.1.2 Determination of package properties

The water vapor transmission rate (WVTR) of the packages (Bag-1, Bag-2, Bag-3 and Bag-4) was determined following ASTM standard test method (ASTM, 2003). The permeability coefficient of the packages was calculated using the following equation:

$$P = WVTR\frac{x}{\Delta p} \qquad (5.1)$$

where P is the permeability coefficient (g.mil. $m^{-2}.d^{-1}.mmHg^{-1}$), x is the film thickness, Δp is the partial vapor pressure gradient, *WVTR* ($g.m^{-2}.s^{-1}$) is the water vapor transmission rate correspond to the amount of water vapor (Δw) transferred through a film area (A) during a definite time (Δt). Thickness and permeability coefficient of each packaging material are presented in Table 5.2.

Table 5.2 Thickness and permeability coefficient of packaging materials

Material code	**Thickness** (mil)	**Permeability*** ($g.mil.m^{-2}day^{-1}mmHg^{-1}$)
Bag-1	1.70 $\pm$ 0.11	0.136 $\pm$ 0.007
Bag-2	2.32 $\pm$ 0.14	0.151 $\pm$ 0.003
Bag-3	1.38 $\pm$ 0.09	0.089 $\pm$ 0.006
Bag-4	2.80 $\pm$ 0.07	0.109 $\pm$ 0.001

* @ 30 ^{o}C, 75% RH

5.2 Characteristics of moisture sorption isotherm

The experimental moisture sorption data of RS-1 and RS-2 obtained corresponding to the water activities ranging from 0.10 to 0.95 at 30, 45, and 60 ^{o}C (Table 5.3) are presented in Figures 5.1 and 5.2, respectively. The effects of temperature shifts on both moisture content and water activity are also observed in Figures 5.1 and 5.2. Moisture sorption isotherms of RS-1 in Figure 1 exhibited the sigmoid (Type II) shape. The equilibrium moisture content of RS-2 increased slowly over lower range of a_w (0.1 – 0.6) and showed a sharp rise thereafter at higher water activity levels. RS-2 gave the sorption isotherm with a shape similar to the isotherm, which is commonly obtained for foods with high fat content (Tungsangprateep and Jindal, 2004). These results are similar to moisture adsorption isotherms reported previously in literature for snack foods with high fat content, such as corn snacks (Palou et al., 1997) and cassava-shrimp chips (Tungsangprateep and Jindal, 2004).

RS-1 characterized a greater sorption of water at the same water activity in comparison to RS-2 for the a_w range of 0.30-0.70, indicating the less hygroscopic nature of RS-2 (Bianco et al., 2001). Pukacka et al., (2003) investigated the effect of lipid content in beech seeds on water sorption isotherm and concluded that the moisture content of seeds at a given water activity decreases with an increase in lipid content. Pollio, Chirife and Resnik (1984) also found that soybeans and sunflower samples with higher oil content have lower equilibrium moisture values. Therefore, the higher water sorption of RS-1 is probably attributed to the lower level of lipid content in RS-1 (1.27 %) when compared to RS-2 (21.09 %). The differences in water sorption between RS-1 and RS-2 are of great importance for their stability during storage, which is known to depend on moisture content and temperature.

An upward shift in temperature from 30 to 60 °C, led to a shift of isotherms towards a lower value for the EMC. The values for the EMC of rice cracker decreased with increased temperature at constant water activity. The reason is that as the chamber 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. These results indicate that temperature affects the mobility of water molecules and the dynamic equilibrium between water vapor and adsorbed phases (Kapsalis, 1987). 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. The decrease in the EMC with the increased temperature was also observed for cookies and corn snacks (Palou, Lopez-Malo, and Argaiz, 1997).

Table 5.3 Relative humidity (%) at 30, 45 and 60 °C

Salt solutions	**Temperature (°C)**		
	30	**45**	**60**
LiCl	11.1	10.2	9.0
$KC_2H_3O_2$	22.1	21.6	19.8
$MgCl_2$	33.3	32.7	31.0
K_2CO_3	44.9	44.3	43.1
$NaNO_3$	63.6	62.7	62.5
NaCl	75.5	76.0	76.0
$(NH_4)_2SO_4$	81.5	79.5	79.0
KNO_3	93.5	93.3	90.0

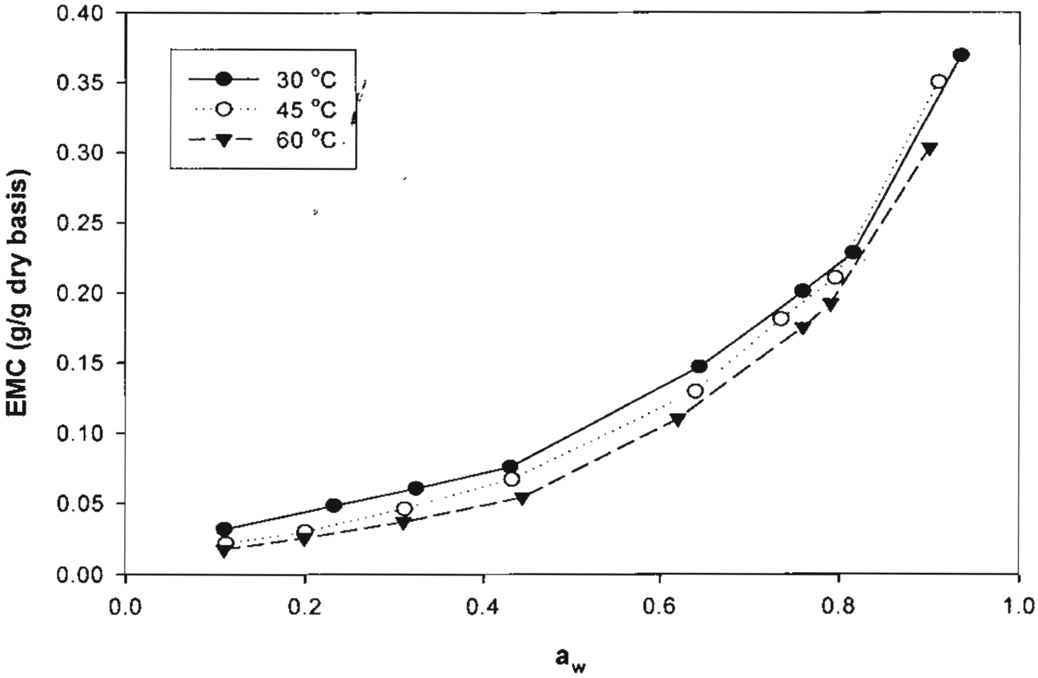


Figure 5.1 Moisture sorption isotherms of RS-1 at 30, 45 and 60 °C

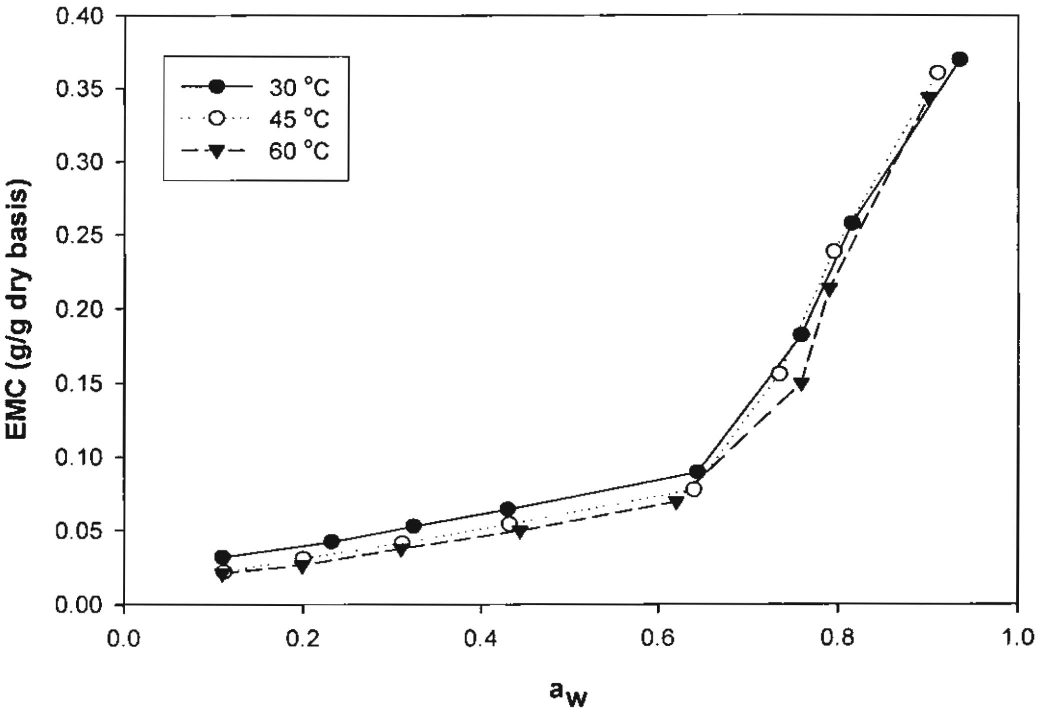


Figure 5.2 Moisture sorption isotherms of RS-2 at 30, 45 and 60 °C

5.3 Study of actual shelf life of the products experimentally

5.3.1 Determination of critical moisture content of rice crackers

This is to determine the moisture level at which a product is no longer acceptable. In this study, the critical attribute of moisture sensitive rice crackers was their texture which becomes unacceptable when the texture changes due to moisture absorption. The break point analysis was conducted to identify the moisture content at which the product quality becomes unacceptable from an organoleptic point of view. The critical water activities and critical moisture content of the samples were shown in Table 5.4. The results suggested that for RS-1 and RS-2 the critical moisture level are 8.97 and 6.83% g/g dry basis, respectively. This was then used to indicate the shelf life.

Table 5.4 Critical water activity and moisture contents of RS-1 and RS-2

Product	Critical a_w	Critical moisture content (% g/g dry basis)
RS-1	0.43 $\pm$ 0.01	8.97 $\pm$ 0.09
RS-2	0.39 $\pm$ 0.02	6.83 $\pm$ 0.02

5.3.2 Experimentally determination of the actual shelf life of the products

Approximately 10 g of products were packaged in selected pouches (having different permeability). The samples were placed in different packaging material formed into 100 mm x 100 mm pouch and heat sealed. The products were stored at 30 ^{o}C and 75% RH, 30 ^{o}C and 85% RH, and 45^{o}C and 75% RH and periodically examined until the critical moisture content was reached. In this study, temperatures of 30 and 45 ^{o}C were chosen, comparable to the tropical storage conditions. Actual shelf life of RS-1 and RS-2 in different packages and stored under different conditions are shown in Tables 5.5 and 5.6, respectively.

Shelf lives of the packaged rice crackers varied with the packaging materials and the storage conditions. Shelf lives of the packaged rice crackers decreased with an increase in storage temperature. 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 and permeated through the packaging material. These results indicate that temperature affects the mobility of water molecules and the dynamic equilibrium between water vapor and adsorbed phases (Kapsalis, 1987).

The relative humidity of storage condition slightly affected the product shelf lives. Hernandez and Giacin (1997) stated that low a_w foods packaged in plastic containers are subject to moisture gain depending on the storage relative humidity, the sorption characteristics of the packaged food, the water activity gradients relative to the storage atmosphere, and the water vapor permeability of packaging materials.

Table 5.5 Actual shelf life of RS-1 in the packages at different storage conditions

Temperature	Relative humidity	Package	Mean ± SD
30	75	Bag-1	36 ± 0.1
		Bag-2	43 ± 1.4
		Bag-3	40 ± 0.9
		Bag-4	73 ± 0.5
30	85	Bag-1	27 ± 1.2
		Bag-2	32 ± 0.9
		Bag-3	31 ± 0.0
		Bag-4	55 ± 0.0
45	75	Bag-1	13 ± 0.4
		Bag-2	14 ± 0.3
		Bag-3	13 ± 0.3
		Bag-4	18 ± 0.1

Table 5.6 Actual shelf life of RS-2 in the packages at different storage conditions

Temperature	Relative humidity	Package	Mean ± SD
30	75	Bag-1	16 ± 0.5
		Bag-2	21 ± 0.5
		Bag-3	21 ± 0.0
		Bag-4	45 ± 1.5
30	85	Bag-1	14 ± 0.8
		Bag-2	16 ± 0.0
		Bag-3	16 ± 0.5
		Bag-4	35 ± 1.2
45	75	Bag-1	11 ± 0.3
		Bag-2	13 ± 0.0
		Bag-3	12 ± 1.0
		Bag-4	16 ± 0.0

5.4 Study of food shelf life model using conventional mathematical algorithm

5.4.1 Determination of the best isotherm model

5.4.1.1 BET equation

The BET equation (Kaymak-Ertekin and Sultanoglu, 2001) can be expressed as follows:

$$m = \frac{C_B a_w m_0}{(1-a_w)(1+(C_B-1)a_w)} \quad (5.2)$$

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).

5.4.1.2 GAB equation

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

$$m = \frac{C_G K_G a_w m_0}{(1-K_G a_w)(1-K_G a_w + C_G K_G a_w)} \quad (5.3)$$

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).

BET and GAB models were used to fir the moisture sorption isotherms for rice crackers. The experimental data were fitted to the models using a nonlinear regression. 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:

$$E = \frac{100}{N}\sum_{i=1}^{N}\frac{|m'_e - m'_p|}{m'_e} \quad (5.4)$$

$$RMSE = \sqrt{\frac{\sum_{i=1}^{N}(m'_e - m'_p)^2}{N}} \quad (5.5)$$

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).

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 are detailed in Figures 5.3, 5.4 and 5.5, respectively. According to Figures 5.3, 5.4 and 5.5, 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.

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 5.7 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. In all cases the correlation coefficients obtained are higher than 0.90.

Analysis of the rice cracker data shows that at 30, 45, and 60 ^{o}C, 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. 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. 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 cracker in 5.4.2.

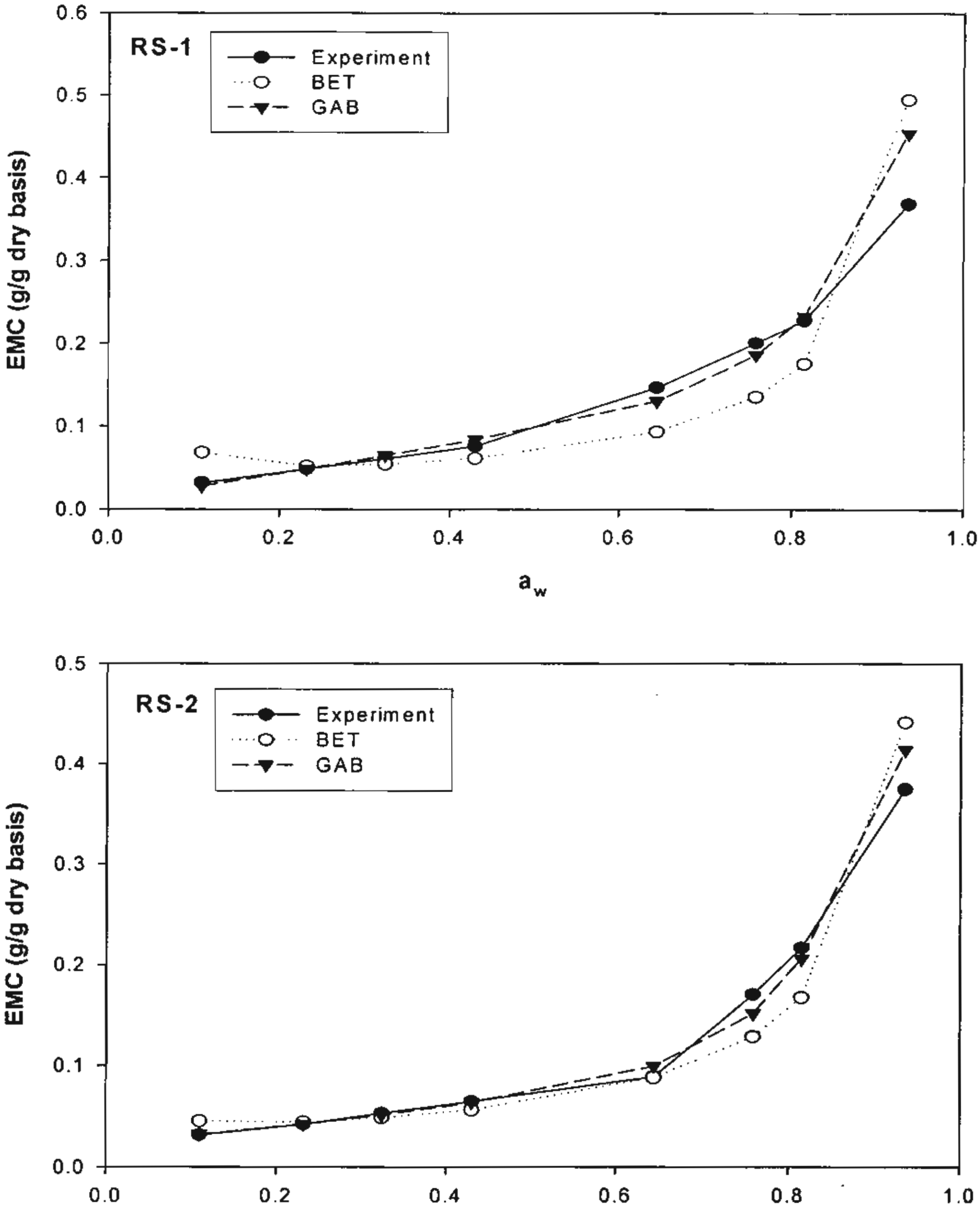
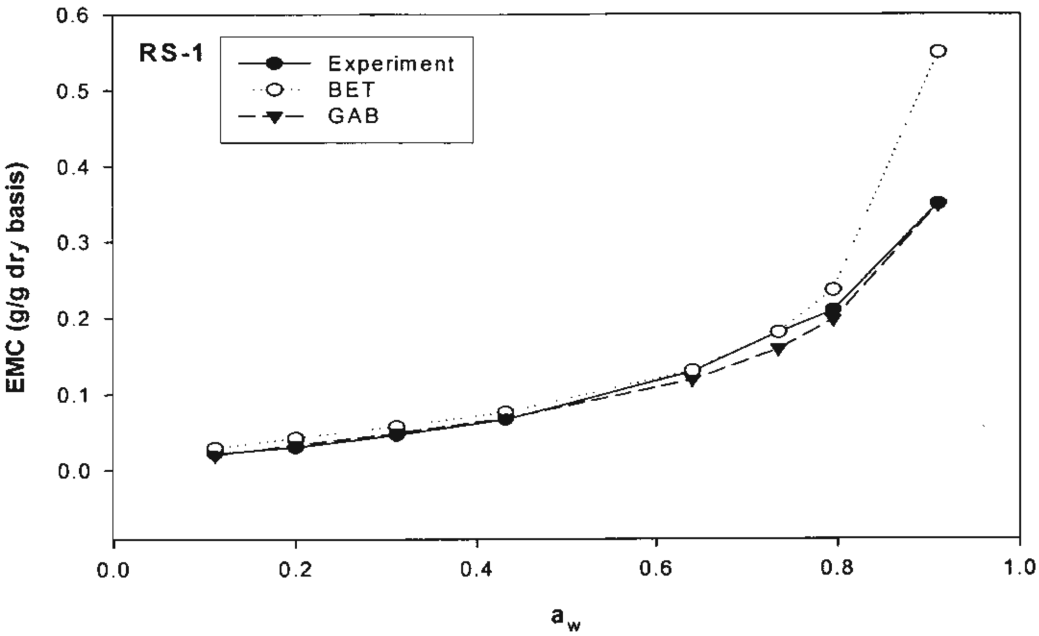


Figure 5.3 Comparison between isotherms of RS-1 and RS-2 from experimental data and from BET and GAB models at 30 °C



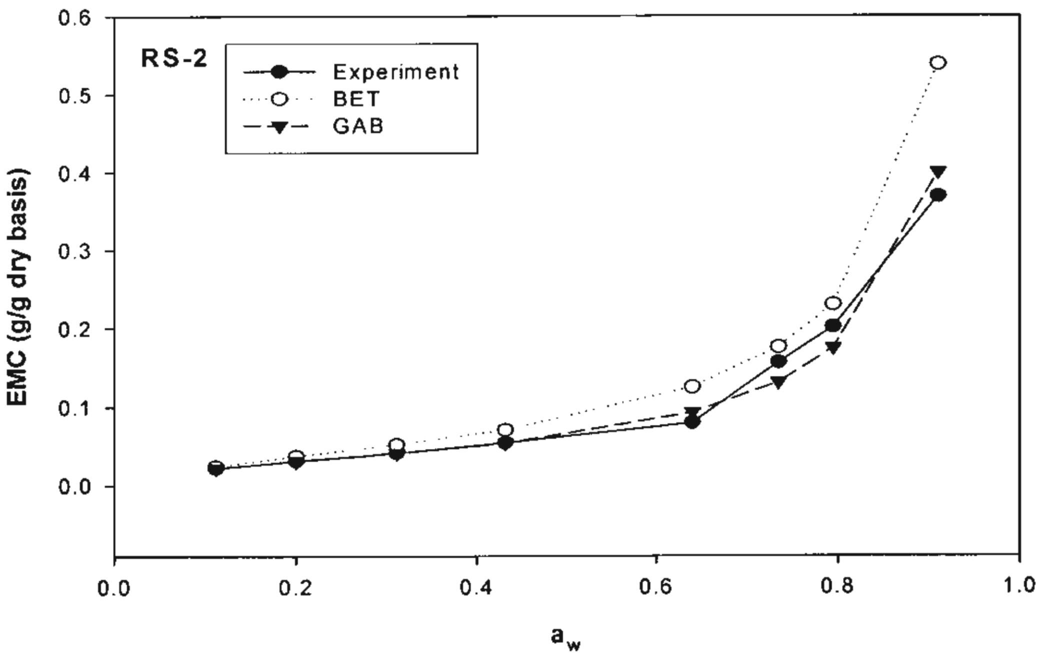


Figure 5.4 Comparison between isotherms of RS-1 and RS-2 from experimental data and from BET and GAB models at 45 °C

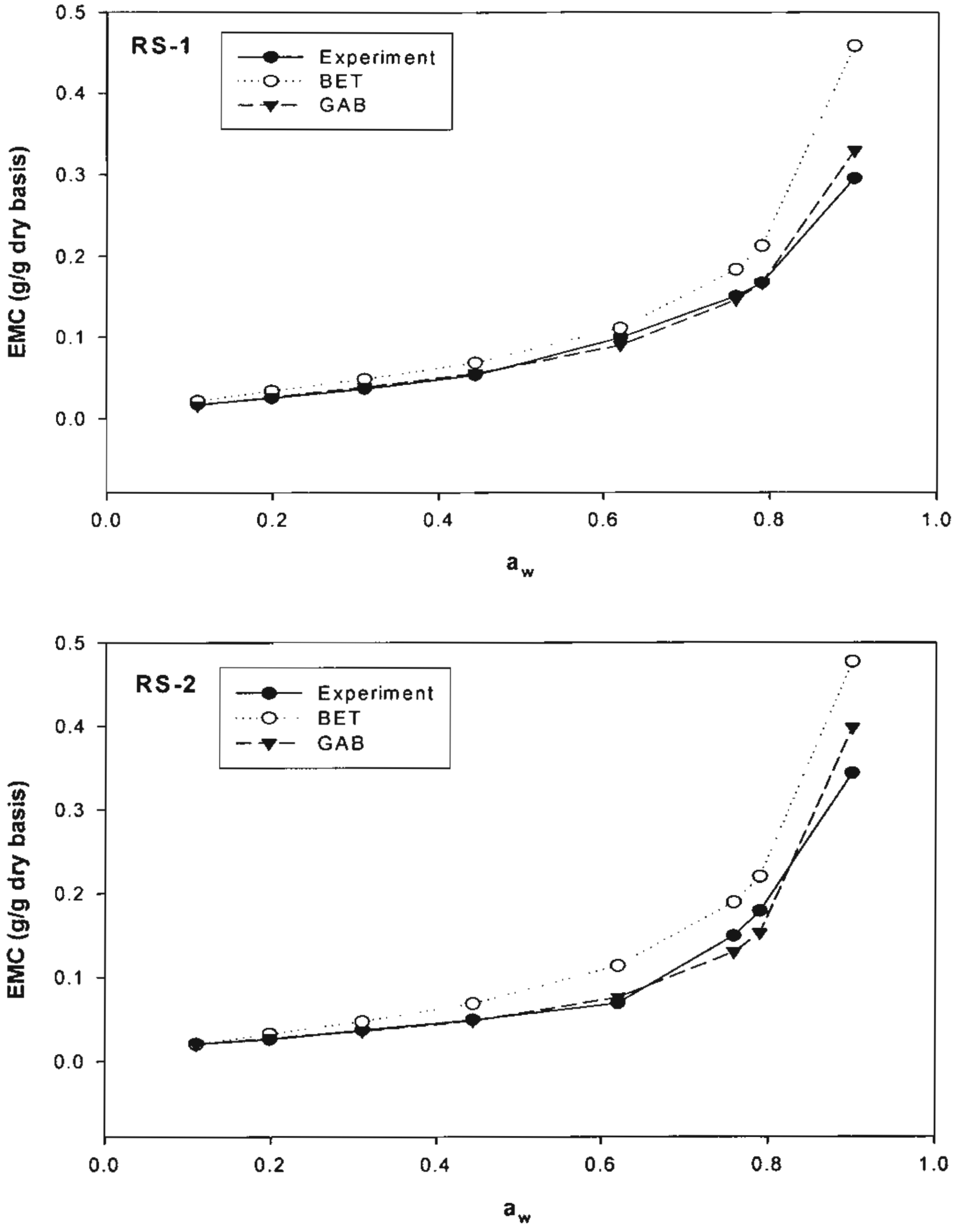


Figure 5.5 Comparison between isotherms of RS-1 and RS-2 from experimental data and from BET and GAB models at 60 °C

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:

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

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

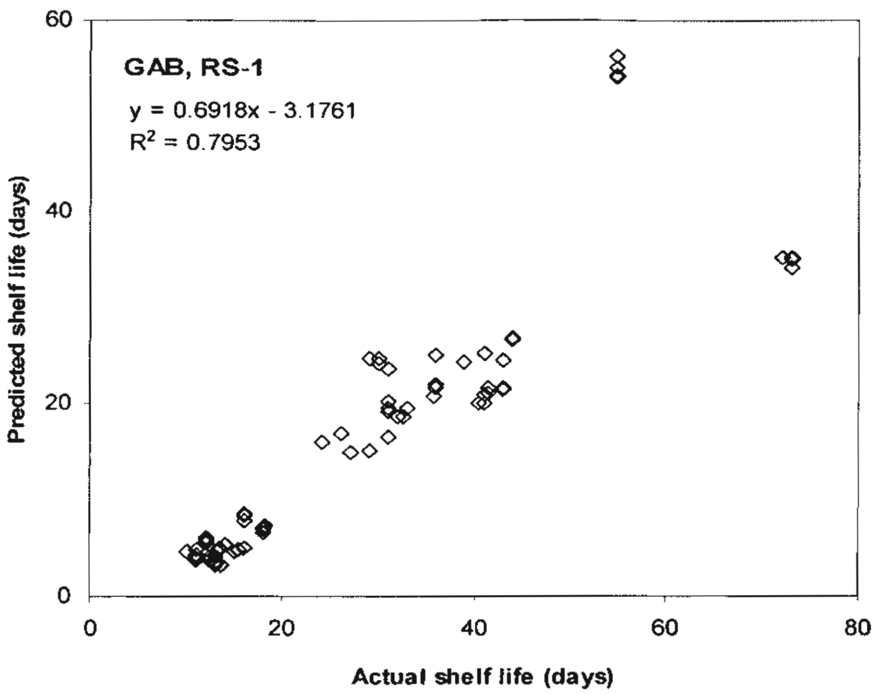


Figure 5.6 The predicted *vs.* actual shelf life of RS-1 using GAB model

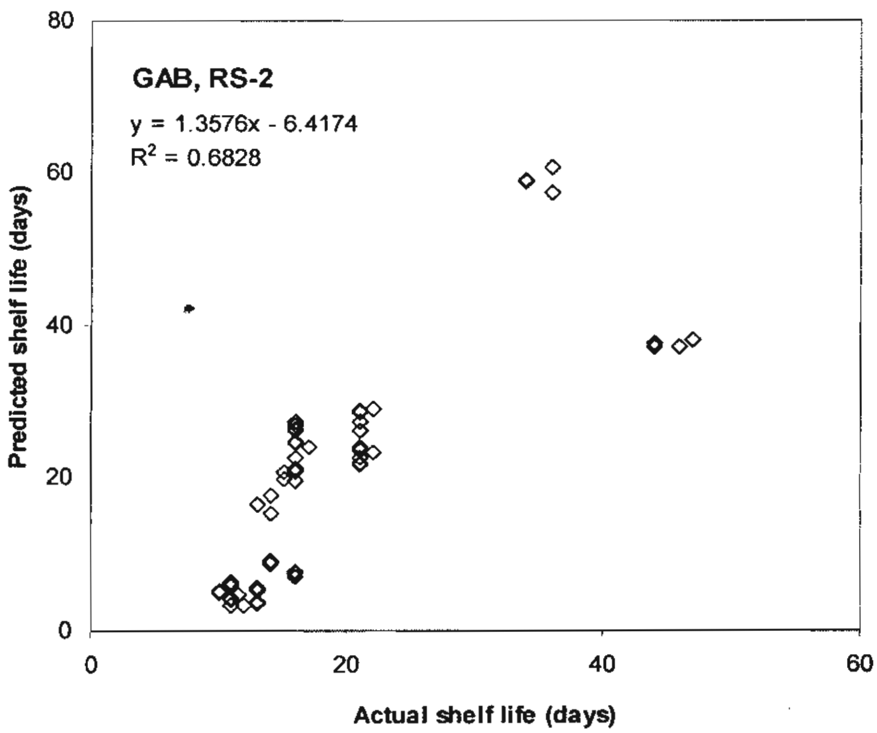


Figure 5.7 The predicted *vs.* actual shelf life of RS-2 using GAB model

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.

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

with v_k being computed as

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

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.

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

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.

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

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

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

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

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

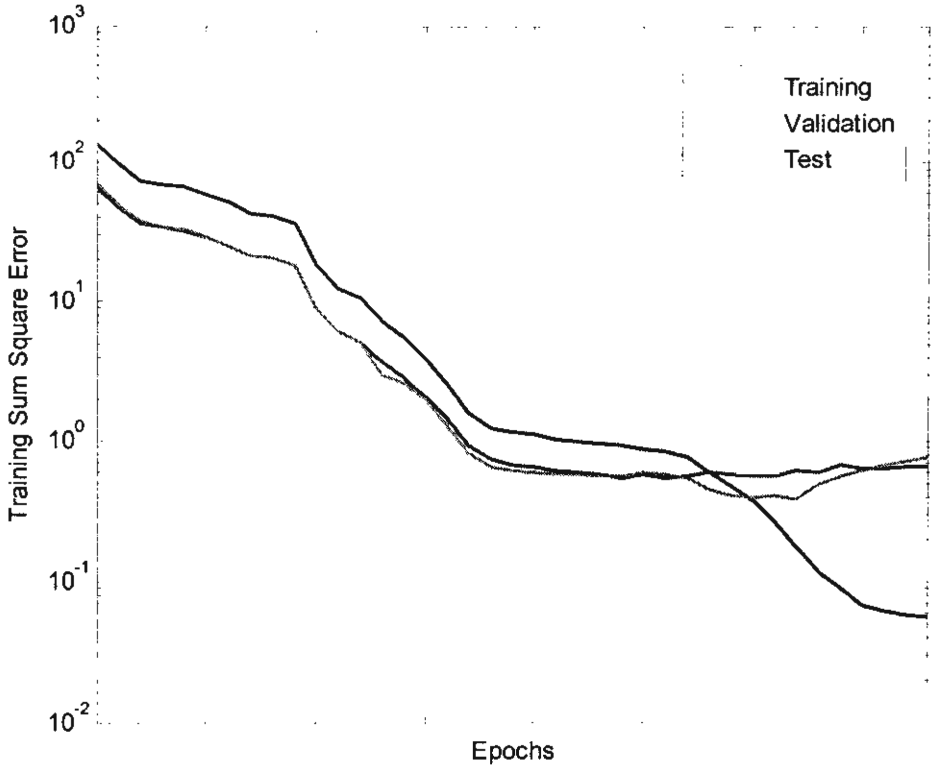


Figure 5.8 Evolution of training, validation and test errors as a function of the number of learning epochs during ANN training

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	40 ± 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

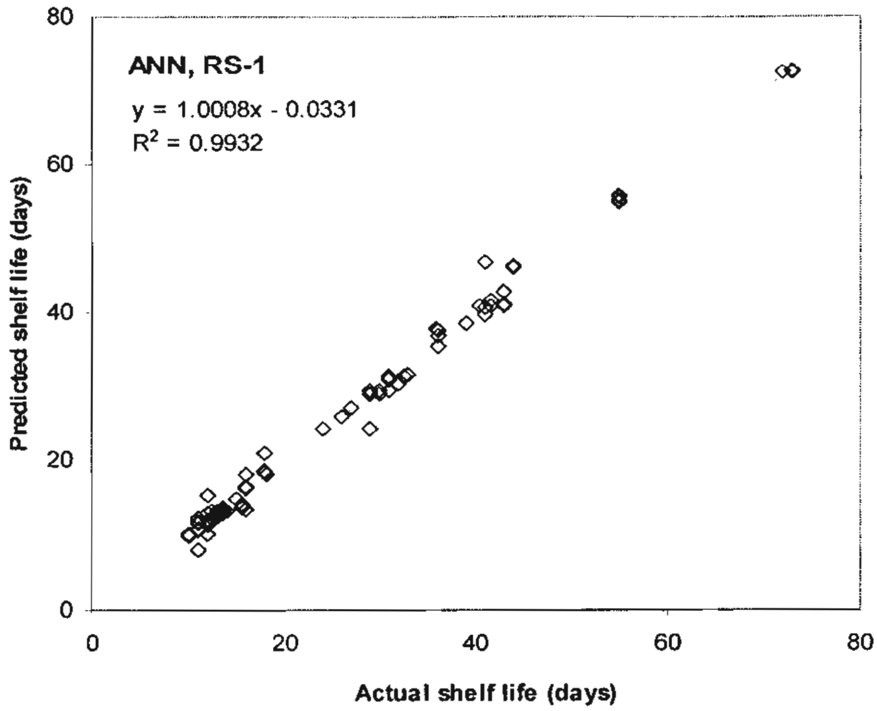


Figure 5.9 The predicted *vs.* actual shelf life of RS-1 using ANN

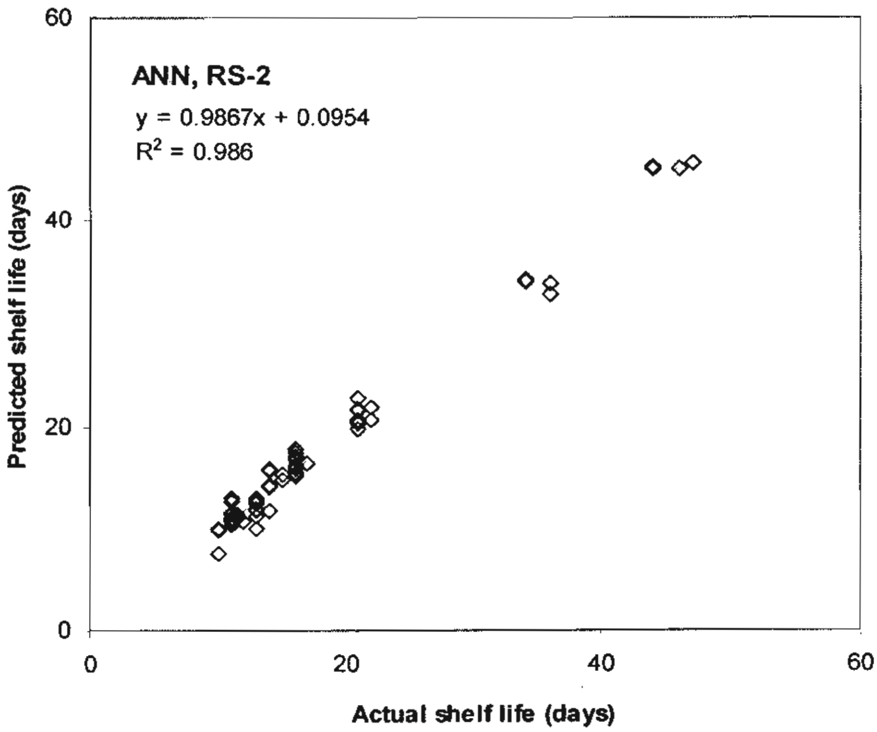


Figure 5.10 The predicted *vs.* actual shelf life of RS-2 using ANN

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.

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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 ($\pm$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:

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

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

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.

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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

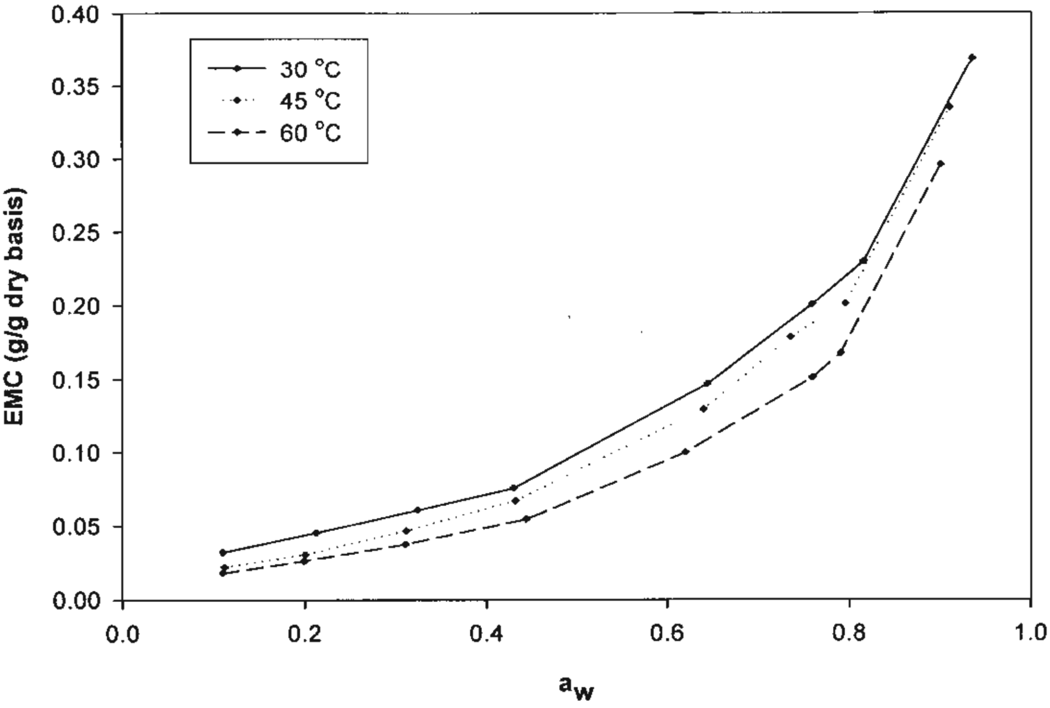


Figure 2

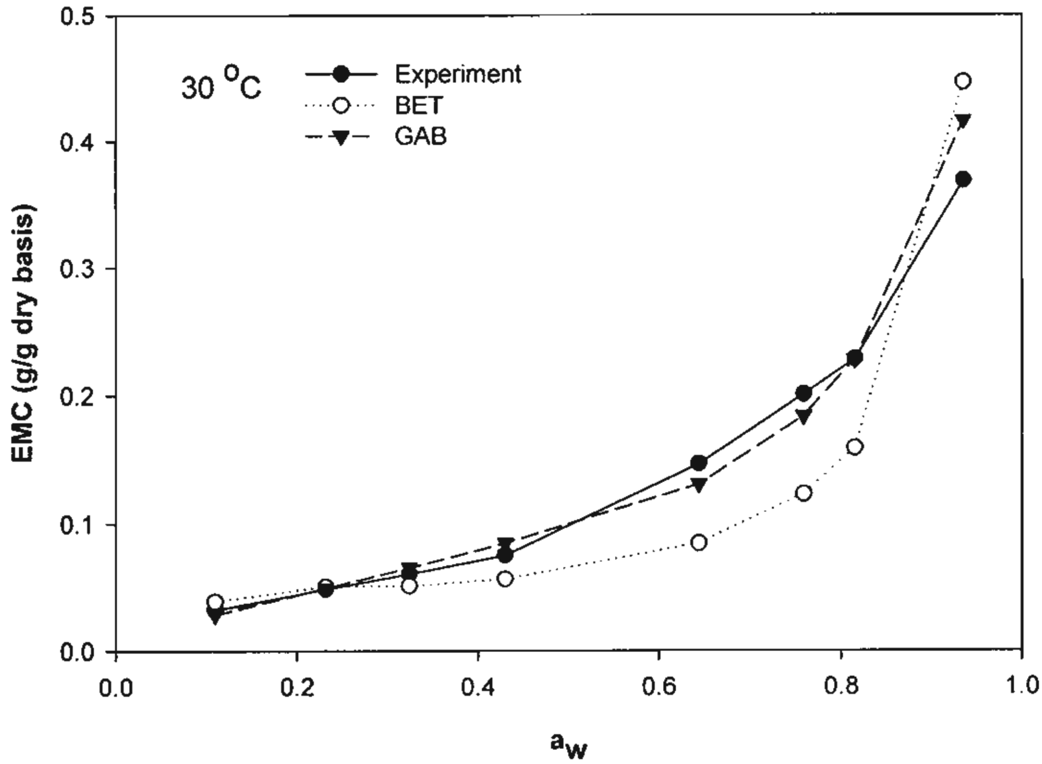
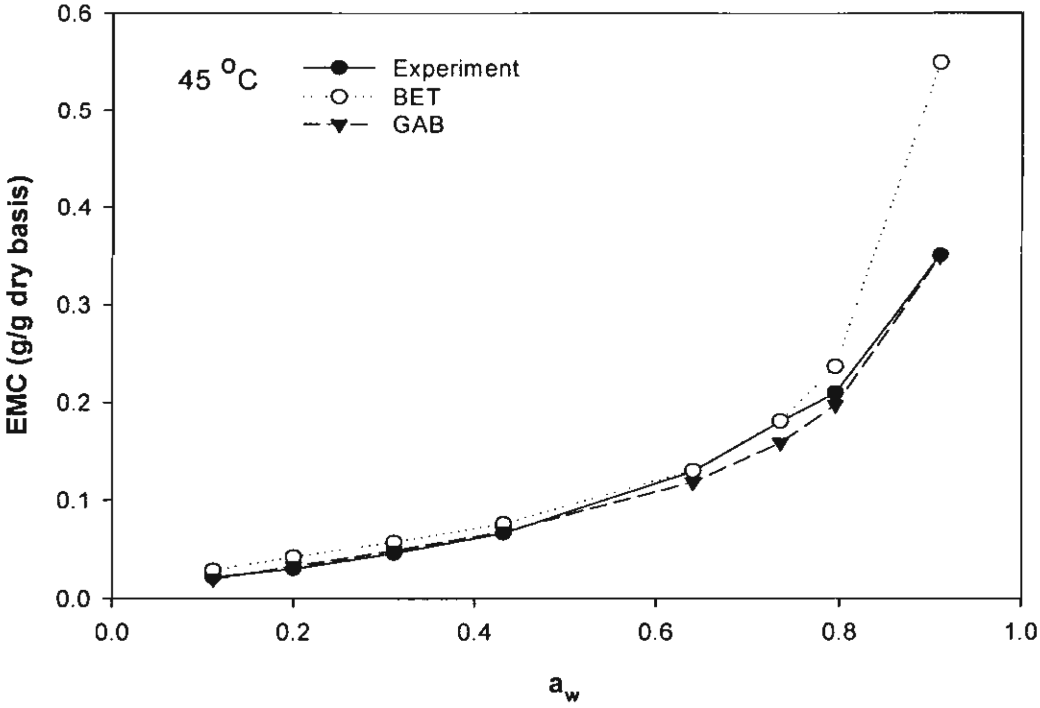
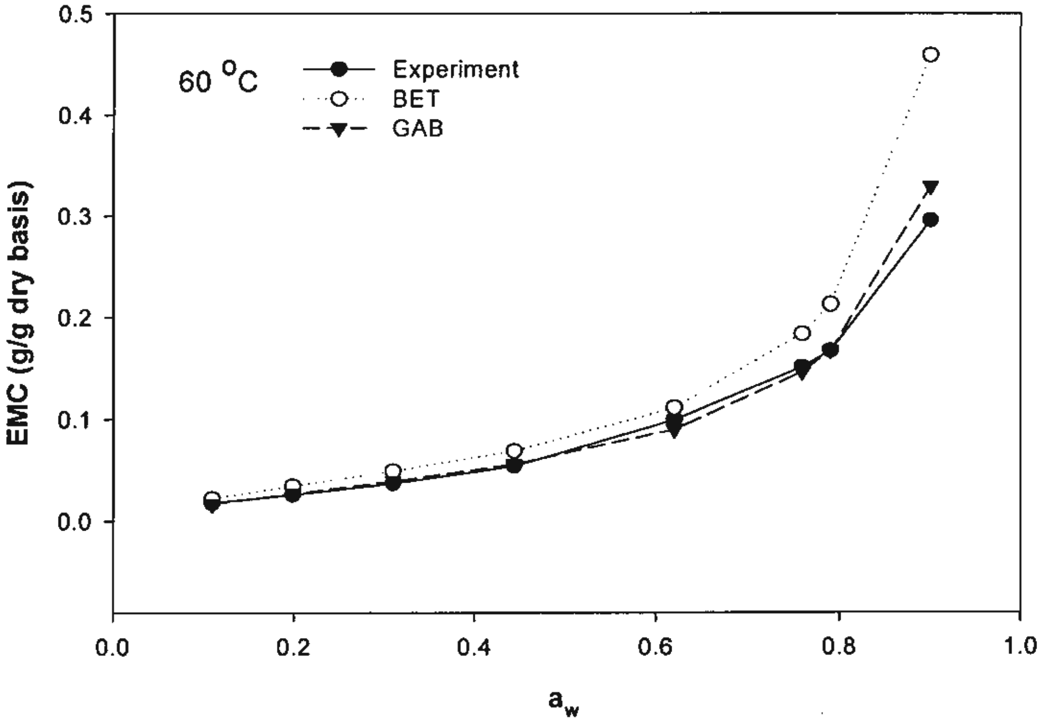


Figure 3



45 °C
Experiment
BET
GAB
EMC (g/g dry basis)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.0
0.2
0.4
0.6
0.8
1.0
a_w

Figure 4



60 °C
Experiment
BET
GAB
EMC (g/g dry basis)
0.0
0.1
0.2
0.3
0.4
0.5
0.0
0.2
0.4
0.6
0.8
1.0
a_w

Figure 5

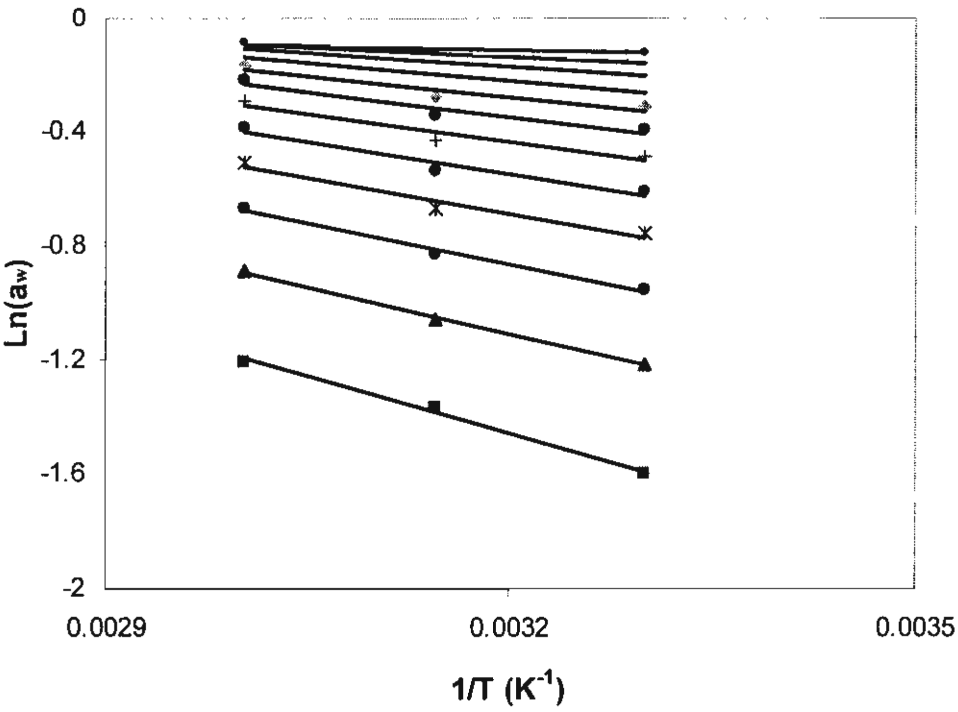
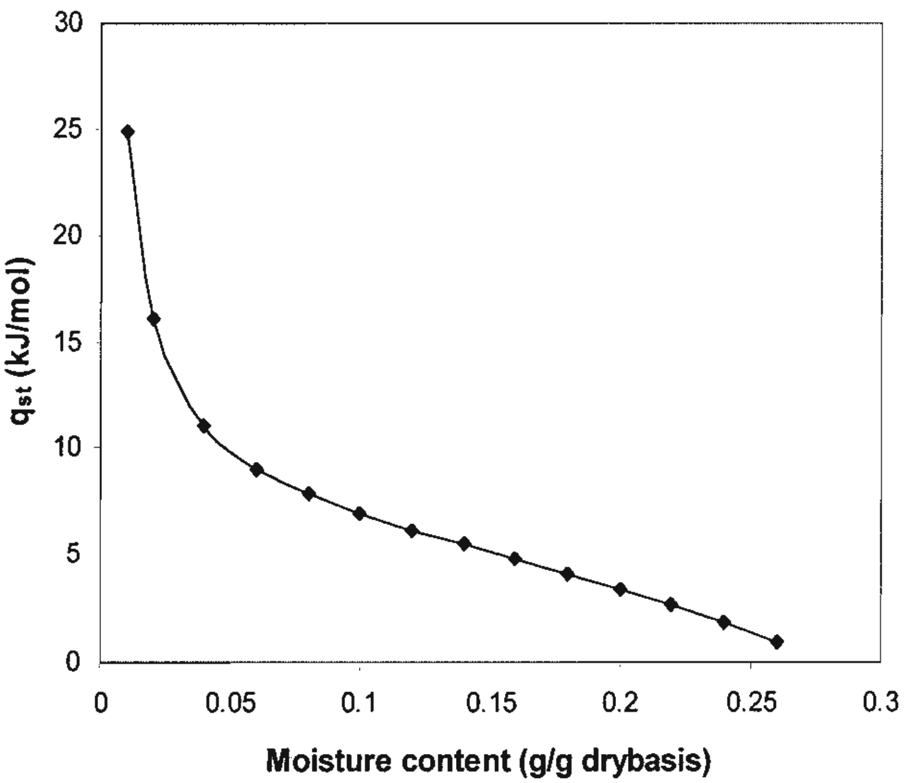


Figure 6



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

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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:

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

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:

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

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:

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

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

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.

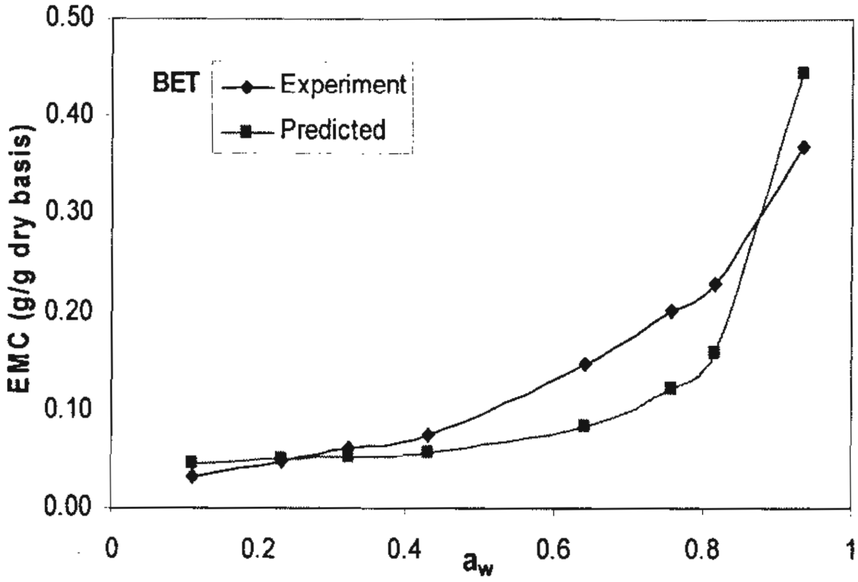

Figure 1 Sorption isotherm of RC at 30 °C using BET model

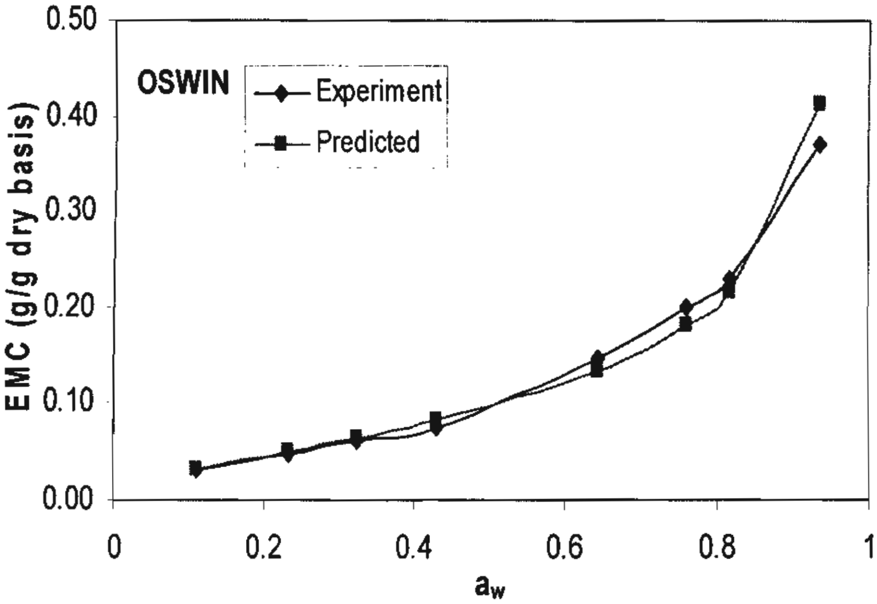

Figure 2 Sorption isotherm of RC at 30 °C using OSWIN model

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.

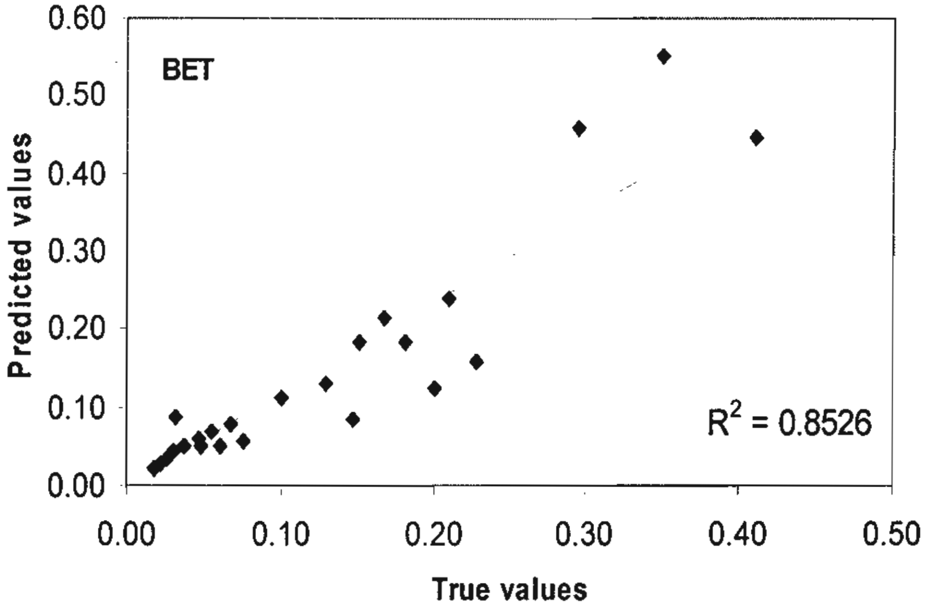

Figure 4 Predicted and experimental EMC of rice snack using BET model

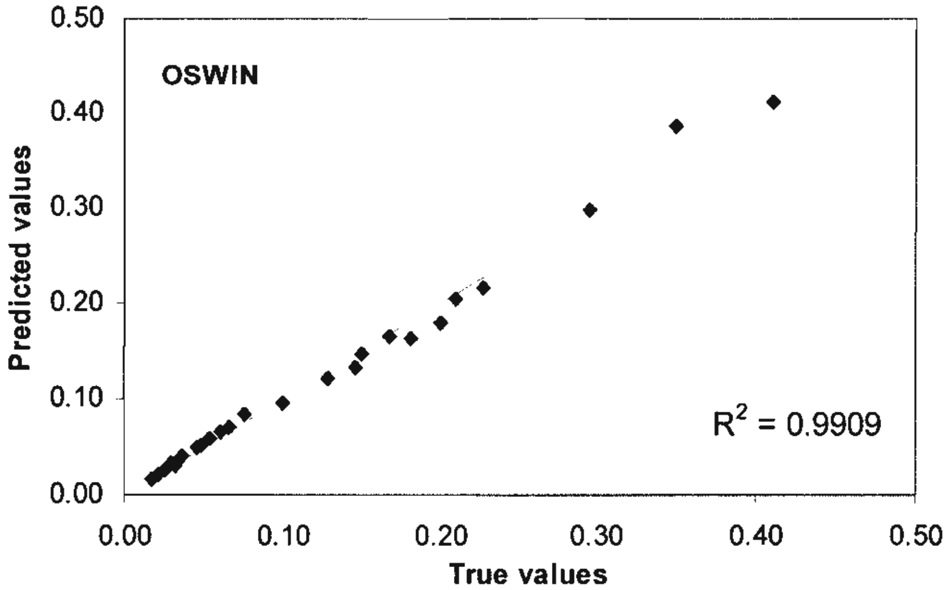

Figure 4 Predicted and experimental EMC of rice snack using OSWIN model

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.

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