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ABSTRACT

MOISTURE SHELF LIFE OF NON-FAT DRY MILK

By

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As new packaging materials become available for non-fat dry milk, there is a need for shelf life simulation to reduce the time and cost needed. In order to perform a simulation, information about product and package characteristics was obtained. GAB equation was employed to describe the moisture sorption isotherm of the product. The barrier properties of packages were described by the permeance of the material since the package is leak proof.

Shelf life simulation consisted of shelf life modeling, model analysis, and model validation. Shelf life modeling was based on mass transfer through the package wall and the GAB equation. From sensitivity analysis of the model, shelf life is most sensitive to the ratio of area to product dry weight and least sensitive to parameter C of GAB equation. Model validation is necessary to ensure the applicability of the model. The shelf life model based on GAB equation is applicable to predict the shelf life of non-fat dry milk packaged in F-flute corrugated board/plastic boxes except for non-fat dry milk package in the poorest barrier package.

Dedicated to my beloved Grandfather,
Mr. Preecha Tanprasert.

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NOMENCLATURES

P/ℓ	permeance
P	permeability coefficient
ℓ	thickness
R	gas constant
T	temperature
RH	relative humidity
E_p	activation energy
$k_1, k_2, \ldots$	constants
WVTR	water vapor transmission rate
a_w	water activity
M	moisture content, dry basis
M_w	moisture content, wet basis
W_d	product dry weight
A	surface area
p_s	saturated water vapor pressure
t	time
M_i	initial moisture content
M_f	final moisture content
V	headspace volume
χ	sensitivity coefficient

INTRODUCTION

Non-fat dry milk, a product with many applications in the food industry, is very sensitive to moisture. Its shelf life and physical and chemical properties depend on its moisture content. Non-fat dry milk requires proper package to maintain its quality and control the uptake of water from the environment. Diverse packaging materials with a range in barrier values have been available for non-fat dry milk. F-flute corrugated board in combination with barrier layer is a new alternative that is of interest due to its strength and barrier properties.

As new materials become available, there is a need to develop expertise to evaluate shelf life of packaged food product in general and dry milk in particular. The experimental testing of shelf life of food products is costly and time consuming especially for the product with long shelf life such as non-fat dry milk. Therefore, shelf life modeling is of great importance for package development and optimization. With the right model and the use of computer, shelf life analysis can be performed rapidly and conveniently.

The shelf life models of moisture sensitive product are based on the mass transfer principles applied to the packaging material and moisture sorption isotherm equation. In order to apply the shelf life model, information about moisture sorption isotherm of a product and barrier characteristic of a package must be obtained. The accuracy of the predicted shelf life depends on the accuracy of the model selected, the accuracy of parameters of the model and the satisfactory of assumptions. Verification is necessary to ensure the validity of the model. Sensitivity analysis of parameters in the model is essential to determine the impact of each parameter in the model on the shelf life value. The objectives of this study were:

A) To determine moisture sorption isotherm of non-fat dry milk.

B) To determine the barrier character of a barrier layer/F-flute corrugated boxes

C) To apply a shelf life model for non-fat dry milk based on moisture sorption isotherm equation that best described its sorption characteristics.

D) To perform sensitivity analysis of the shelf life model.

E) To validate shelf life model at two isothermal storage condition.

CHAPTER 1

LITERATURE REVIEW

Non-fat Dry Milk

Non-fat dry milk is defined by federal law under standard of identity as: the product resulting from the removal of fat and water from milk, and containing the lactose, milk protein, and milk mineral in the same relative portions as the fresh milk from which made. It contains not over 5 percent of moisture by weight. The fat content shall not exceed 1½ percent by weight (USDA, 1999).

Instant non-fat dry milk is non-fat dry milk that has been produced in a manner to substantially improves its dispersing and reconstitution characteristics. Table 1 shows the composition in non-fat dry milk, instant non-fat dry milk, and dry whole milk.

Table 1. Typical compositional range of non-fat dry milk (NFDM) , instant non-fat dry milk (INFDM), and dry whole milk (DWM)

Composition	Percentage		
	NFDM	INFDM	DWM
Protein	34.0 – 37.0	34.0 – 37.0	24.5 – 27.0
Lactose	49.5 – 52.0	49.5 – 54	36.0 –38.5
Fat	0.6 – 1.25	0.6 – 1.25	26.0 – 28.5
Ash	8.2 – 8.6	8.2 – 8.6	5.5 – 6.5
Moisture	3.0 – 4.0	3.5 – 4.5	2.0 – 4.5

Source: American Dairy Product Institute (1998a)

Non-fat dry milk provides advantages of distribution, application and shelf life over fluid milk. Removal of water minimizes the weight and volume resulting in reduction of shipping and storage cost. Furthermore, non-fat dry milk can be stored at ambient temperature but lower than 27°C. It also makes the addition to dry concentrated mixes possible. Due to its minimal fat content, chemical deterioration mechanisms are reduced, thus increasing shelf life (Ogden, 1993).

Since non-fat dry milk is a product of uniform composition with excellent qualities, low handling cost, and consistent supply, it has various applications in the food industry. Table 2 shows application and function of non-fat dry milk. In addition, non-fat dry milk is also found as an ingredient in dairy beverages, custard, gravies, sauces, frozen foods, packaged dry mixes, soups, infant formulas, snack foods, cosmetics (American Dairy Product Inst., 1998a), margarine, salad dressing, and healthy foods (Duxbury, 1992).

Non-fat dry milk is classified as moisture sensitive product because its shelf life depends on its moisture content. The moisture uptake in non-fat dry milk leads to series of physical and chemical changes resulting in reduced quality and consumer acceptance. Since non-fat dry milk must be maintained at very low moisture content there is a large water vapor gradient across the package which requires high moisture barrier package. The low fat content of non-fat dry milk make it more prone to absorb water making it more sensitive to moisture while less sensitive to oxygen. This makes non-fat dry milk highly prone to moisture while not sensitive to oxygen. The critical moisture content of non-fat dry milk is about 10% at room temperature (Thompson, 1997). It has a shelf life of about ½ to 1½ years when kept at the condition below 80°F and 65% RH (American Dairy Products Inst., 1998a).

Table 2. Food product application and function of non-fat dry milk

Application	Function
Reconstituted fluid milk	- Fortifies and standardizes milk composition
Frozen dessert (ice cream, custard, ice milk, sherbet and frozen yogurt	- Increase palatability - Increase food value - Provide economical source of serum solid
Cottage cheese	- Increase yields up to 5%
Yogurt	- Improves texture - Imparts smooth appearance
Bread	- Enlarges loaf volume - Imparts soft and tender texture - Improves crust and crumb color
Bakery products	- Improves water adsorption - Imparts smooth texture - Improves product uniformity
Meat products	- Enhances nutrition - Enhances slicing quality - Minimizes crumbling and shrinkage - Provides excellent binding properties - Provides desirable flavors

Adapted from American Dairy Product Inst., 1998b,c and Duxbury, 1992.

Changes in Non-fat Dry Milk During Storage

During storage, the quality of non-fat dry milk decreases due to series of physical, chemical, and biological changes trigged by an increase of moisture content, for example, lumping or caking, collapsing, Maillard reaction, loss of nutrient and protein solubilization and microbiological deterioration. Browning, oxidation and loss of nutrient occur over wide range of water activity. The gain of moisture above the BET monolayer, which is a water activity corresponding to saturation of all primary sorption sites by one water molecule, increases the rate of these mechanisms (Labuza, 1982). Microbial spoilage and loss of flow properties require minimum water activity. Below certain water activity, the reaction will not take place (Mannheim et al., 1994). Potential changes as a function of moisture content in non-fat dry milk are discussed.

a) Physical changes

The moisture adsorption of non-fat dry milk promotes the formation of interparticle liquid bridges. Further moisture uptake will cause caking, collapse and crystallization of lactose, an amorphous carbohydrate of non-fat dry milk. Caking or clumping reduces flow and leads to poor rehydration and dispersibility. Collapse occurs when a matrix cannot support its own weight resulting in volume reduction and sticking. Lactose crystallization is observed as loss of sorbed water or discontinuity of adsorption isotherm.

Chuy and Labuza (1994) studied the effect of storage condition on physical changes of dairy-based food powders by using surface caking temperature, T_{sc}, and advanced caking temperature, T_{ac}. T_{sc} is a measurement of initial clumping while T_{ac} is a measurement of an advanced stage of collapse. They found that T_{sc} and T_{ac} decreased with increasing moisture content due to the plasticizing effect of water. The effect of storage temperature was random. Lai and Schmidt (1990) studied the lactose crystallization in skim milk powder during two week storage at 20°C. At water activity 0.43 or below, no crystallization was observed. Lactose crystallization occurred after 2.2 days at water activity 0.54. At water activity above 0.54, the crystallization process occurred at the beginning of the sorption process.

b) Nonenzymatic browning

Nonenzymatic browning or Maillard reaction is a predominant deterioration mechanism in dried products and products containing lactose. It is the reaction of reducing sugar and amino group. This reaction results in flavor change, discoloration, nutritive loss, reduced rehydration, and the formation of mutagenic compounds. In non-fat dry milk, Maillard reaction causes the yellowing. Lueng (1987) revealed that at 20°C, the rate of Maillard reaction in skim milk powder increased with increasing water activity in the range of water activity 0.23 to 0.8. At water activity below 0.23, the reaction was detected after a month storage. Tsai et al. (1991) studied the effect of water activity and temperature on nonenzymatic browning in simulated model system of amino acid, glucose, celite and phosphate buffer. The reaction of amino acids can be classified into three types. Type 1 (lysine, histidine, and glycine) showed high rate over broad range of water activity. Type 2 (cysteine and methionine) showed intermediate browning rates and multiple maximum rates. Type 3 (glutamine, valine, and tryptophan) had low rate with single maxima in the water activity range of 0.75 to 0.9. The reaction rate increased as temperature increased from 20 to 33°C, below that, the reaction was retarded. The activation energy was 10 to 35 kcal/mole and Q_{10} was in the range of 1 to 8.

c) Loss of vitamin A

In addition to loss of nutrient due to nonenzymatic browning, loss of vitamin A due to oxidation is important for nutritionally purpose especially in vitamin A fortified food. Arya and Thakur (1990) reported that vitamin A degradation in wheat flour as a function of water activity depended on types of wheat flour. In regular wheat, the rate of degradation was lowest at water activity 0.0 and increased with an increasing water activity while in gluten, starch and enzyme inactivated wheat flour, the rate was highest at water activity of 0.0 and decreased as water activity increases. In microcrystalline cellulose system, the minimum rate was at a_w 0.33 and increased both below and above this water activity.

d) Microbiological spoilage

Microbial deterioration takes place when non-fat dry milk is stored in equilibrium with high relative humidity. The growth of microfungi causes loss of dry matter. Microbial deterioration takes place at water activity over 0.6. Pisecky (1992) stated that, in general, minimum water activity for bacterial and fungi were 0.9 and 0.88-0.80, respectively. The reduction of water activity can inhibit microbial growth by increasing lag phase and decreasing growth rate and maximum level of development of microorganism (Molard et al., 1993).

Packaging for Non-fat Dry Milk

Non-fat dry milk is normally packaged either in bulk container (25 kg) or in package for retail sales. The common package for bulk containers are multiwall Kraft bag with a polyethylene liner, tote bin, and big bag or bag in box (Tokley and GrØnborg, 1995). The retail packages that are currently in used are multi-quart carton with aluminum foil wrap or individual pre-measured envelopes in a cardboard box. Most retail packs contain instant non-fat dry milk (Carpentier and Clark, 1998).

There is an interest in the development of sift-proof retail package using plastic coated or laminated on F-flute corrugated board. The good glue pattern along with the development in glue application system can solve sifting problem. A plastic coating or lamination improves barrier properties, thus, eliminating the need of liner and wrapper but yet retain the desired shelf life.

Factor Affecting Shelf Life of Moisture Sensitive Product

Shelf life can be taken as the length of time that a packaged product will remain in acceptable condition under the specified storage condition (Sacharow, 1986). The acceptance judgement of food product is subjective based on visual inspection followed by organoleptic evaluation after purchase. Factors affecting shelf life of the moisture sensitive product can be classified in two groups: a) factors affecting the product characteristics and b) factors affecting barrier characteristics of a package.

a) Processing and some product compositions influenced the sorption capacity of the moisture sensitive product. For example, drying temperature considerably affected the sorption isotherm of dried beef. The beef dried at higher temperature had lower sorption capacity (Iglesias et al., 1977). The particle size distribution of product had no effect on the isotherm (Iglesias and Chirife, 1982). Fat, which acts as water repellant, reduced sorption capacity. The whole egg powder absorbed less water than albumen (Passy and Mannheim, 1982) and ground sunflower nut meat absorbs less water than its defatted products. Non-protein of defatted sunflower had higher sorption capacity than protein material at high water activity (Mok and Hettiarachchy, 1990). Desugarization did not have any effect on sorption capacity (Passy and Mannheim, 1982).

b) Package integrity had influence on the barrier characteristics of a package. Cardoso and Labuza (1983) reported a large difference between the experimental water vapor permeability of the complete paperboard package with creases and end openings and the calculated result based on permeability of the material measured from the dish method. Labuza (1982) presented the table of water vapor leak through pinholes of packages that pass the leak test at different level. Pires et al. (1988) reported substantial difference in shelf life of oral solid drugs in blister packages and in multiple unit containers. The difference was mainly due to water vapors entering the multiple unit container when the container was open to obtain the dose.

c) Storage condition described by temperature and relative humidity had effect on both product and a barrier property of a package. Wang and Brennan (1991) reported that, at constant temperature, equilibrium moisture content increased with increasing of relative humidity. At specific relative humidity, equilibrium moisture content increased with decreasing of temperature. Sopade and Ajisegiri (1994) reported that the effect of temperature on moisture sorption isotherm was generally more pronounced at lower water activity. Pisecky (1992) stated that temperature had little influence on sorption isotherm of non-fat dry milk above moisture content of 18%.

Water Vapor Transmission Model

Determination of the packaging material permeability coefficient value for every single storage condition is costly, time consuming, and not practical. Therefore, the mathematical model describing the relationship between moisture permeability value and environmental factors becomes useful. It allows the calculation of the permeability value within the range of condition that the model was based on. Four water vapor transmission models for commonly used packaging materials are discussed.

Cardoso and Labuza (1983) described models to predict the permeance of polyethylene and polypropylene as a function of temperature and relative humidity. The models were based on Arrhenius relationship, eqn. 1, with linear relationship of activation energy and relative humidity, eqn. 2, and the permeance pre exponential constant, $(P/\ell)_0$ as a function of relative humidity as eqn 3.

$$\left(\frac{P}{\ell}\right) = \left(\frac{P}{\ell}\right)_0 \exp\left(\frac{E_p}{RT}\right) \qquad (1)$$

$$\left(\frac{P}{\ell}\right)_0 = k_1 + k_2\,(RH) \qquad (2)$$

$$E_p = E_0 + \left(k_3 \times \frac{RH}{100}\right) \qquad (3)$$

where $(P/\ell)_0$ = permeance pre exponential constant, T = absolute temperature, K, and E_0 = activation energy at 0% RH.

Samaniego-Esguera and Robertson (1991) developed a similar model for permeance of LDPE, PET and a laminate at 20-40°C, 55-90 %RH. The model was also based on Arrhenius equation but had different approach to the relationship of permeance pre-exponential constant and relative humidity, eqn. 4, and the relationship of activation energy and relative humidity, eqn. 5. The model is presented in eqn. 6. A good agreement between experimental data and predicted value were obtained.

$$\left(\frac{P}{\ell}\right)_0 = k_1 \exp\left[\frac{k_2}{RH}\right] \quad (4)$$

$$E_p = k_3 + \frac{k_4}{RH} \quad (5)$$

$$\left(\frac{P}{\ell}\right) = \left(k_1 \exp\frac{k_2}{RH}\right)\exp-\left(k_3 + \frac{k_4}{RH}\times\frac{1}{RT}\right) \quad (6)$$

where P/ℓ = permeance, k_1, k_2, k_3, and k_4 = constants, RH = relative humidity, R = gas constant, and T = absolute temperature, K.

Piergiovanni et al (1995) presented the mathematical model for the estimation of water vapor transmission rate of PET, PVC, EVA and LDPE in the range of 1 to 45°C and 11 to 100% RH. They claimed that the effect of temperature on driving force of water vapor was more important than the effect of temperature on the diffusion of water vapor through the material. The author describes the effect of absolute temperature, T, on water vapor pressure by a Clausius Clapeyron's relationship:

$$WVP = WVTR^{*} \exp\left[\frac{\Delta H_{evap}}{R}\left(\frac{1}{T} - \frac{1}{T^{*}}\right)\right] \quad (7)$$

where WVP = water vapor pressure, $WVTR^{*}$ = water vapor transmission rate at temperature T^{*}, and ΔH_{evap} = enthalpy of water evaporation (45.05 KJ/mol at 273 K), and T = absolute temperature

The model based on Clausius Clapeyron's relationship is presented as

$$\mathrm{WVTR}_{\mathrm{new}} = \mathrm{WVTR}_{\mathrm{old}} \exp\left[-5418.6\left(\frac{1}{T_{\mathrm{new}}}-\frac{1}{T_{\mathrm{old}}}\right)\right]\left[\frac{\Delta \mathrm{RH}_{\mathrm{new}}}{\Delta \mathrm{RH}_{\mathrm{old}}}\right] \qquad (8)$$

where subscript "old" refers to the condition of known WVTR and script "new" refers to the condition that the WVTR will be predicted.

The authors reported a good agreement between observed and predicted water vapor transmission rate of PET and LDPE film. The model overestimated water vapor transmission rate of PVC and EVA at low temperature.

Cardoso and Labuza (1983) constructed a model to predict permeability of paperboard box under temperature of 30-45°C. Since its permeability did not follow Arrhenius behavior, they fitted the experimental data by a second-degree polynomial.

$$P = k_1 + k_2T + k_3\mathrm{RH} + k_4T^2 + k_5\mathrm{RH}^2 + k_6\left(\frac{\mathrm{RH}}{T}\right) + k_7\mathrm{RH}.T \qquad (9)$$

Equations for Sorption Isotherm

Moisture sorption isotherm represents the equilibrium relationship between the moisture content and the water activity at constant pressure and temperature. It is a fundamental characteristic necessary for food processing, such as drying and packaging. It provides an easy way to evaluate physical, chemical, and microbiological parameters necessary for processing condition, package design, and shelf life determination (Leiras and Iglesias, 1991). Fitting sorption isotherm data to suitable equation is vital step in order to use sorption isotherm. The major considerations in equation selection are type of food, ease of evaluation, simplicity, and suitability for application over the range of water activity of interest (Sopade and Ajisegiri, 1994).

Kuhn equation (Boquet et al., 1978)

$$M = \frac{k_1}{\ln a_w} + k_2 \tag{10}$$

Mizrahi equation (Boquet et al., 1978)

$$a_w = \frac{k_1 + M}{k_2 + M} \tag{11}$$

Young and Nelson equations (Boquet et al., 1979)

$$M_s = k_1(\theta + \alpha) + k_2\varphi \tag{12}$$

$$M_d = A(\theta + \alpha) + \beta\theta\, a_{w_{max}} \tag{13}$$

$$\text{where } \theta = \frac{a_w}{a_w + (1 - a_w)k_3}$$

$$\varphi = a_w\theta$$

$$\alpha = \frac{k_3 a_w}{k_3 - (k_3 - 1)a_w} + \frac{k_3^{\,2}}{(k_3 - 1)}\ln\left[\frac{k_3 - (k_3 - 1)a_w}{k_3}\right] - (k_3 + 1)\ln(1 - a_w)$$

s refers to adsorption, d refers to desorption, and A, β and E = constants

Chen equation (Boquet et al., 1979)

$$a_w = \exp\left(k_3 + k_1 e^{k_2 M}\right) \tag{14}$$

This equation can be rewritten as

$$M = \frac{1}{k_2}\ln\left(\frac{1}{k_1}(\ln a_w - k_3)\right) \tag{15}$$

Hailwood and Horrobin equation (Boquet et al., 1979)

$$\frac{a_w}{M} = k_1 + k_2 a_w - k_3 a_w{}^2 \tag{16}$$

Oswin equation (Mok and Hettiarachchy, 1990)

$$M = k_1 \left[\frac{a_w}{1 - a_w} \right]^{k_2} \tag{17}$$

Henderson equation (Mok and Hettiarachchy, 1990; Sopade and Ajisegiri, 1994)

$$1 - a_w = \exp\left(k_1 T M^{k_2}\right) \tag{18}$$

This equation can be rearranged as

$$M = \left[\frac{-1}{k_1 T} \ln\left(1 - a_w\right) \right]^{1/k_2} \tag{19}$$

Chung and Pfost equation (Mok and Hettiarachchy, 1990; Sopade and Ajisegiri, 1994)

$$\ln a_w = -\frac{k_1}{RT} \exp(-k_2 M) \tag{20}$$

This equation can be rewritten as

$$M = \frac{\ln\left(\frac{k_1}{RT}\right) - \ln\left(-\ln a_w\right)}{k_2} \tag{21}$$

Chen and Clayton equation (Mok and Hettiarachchy, 1990)

$$a_w = \exp\left(-k_1 T^{k_2} \exp\left(-k_3 T^{k_4} M\right)\right) \tag{22}$$

This equation can be rewritten as

$$M = \frac{\ln k_1 + k_2 \ln T - \ln(-\ln a_w)}{k_3 T^{k_4}} \tag{23}$$

Hasley equation (Sopade and Ajisegiri, 1994)

$$M = \left[\frac{k_1}{T \ln a_w}\right]^{1/k_2} \tag{24}$$

Iglesias and Chirife equation (Mok and Hettiarachchy, 1990)
This model is a modification of Hasley multilayer adsorption equation

$$a_w = \exp(-\exp((k_1 T + k_2)).M^{-k_3}) \tag{25}$$

It can be rewritten as

$$M = \left[\frac{\exp(k_1 T + k_2)}{-\ln a_w}\right]^{1/k_3} \tag{26}$$

Bradley equation (Sopade and Ajisegiri, 1994)

$$\ln a_w = k_1 k_2^M \tag{27}$$

Caurie equation (Sopade and Ajisegiri, 1994)

$$\ln M = k_1 - \frac{100}{k_2 a_w} \tag{28}$$

Brunauer Emmer and Teller (BET) equation

It was developed for localized physical adsorption of inert gases on solid surfaces based on monolayer concept. The first molecule, or monolayer, on site has stronger interaction with the sorbent than following molecules, or multilayer, on the site (Van den Berg, 1983).

$$\frac{M}{W_m} = \frac{C_b k a_w}{(1-a_w)(1-a_w+C_b a_w)} \tag{29}$$

where W_m = monolayer moisture content which is the water content corresponding to the saturation of all primary adsorption site, and C_b = B.E.T constants of adsorption.

BET equation was applicable only up to water activity of 0.5 (Schuchmann et al., 1990). More parameter(s) were added to the equation to extend range of applicable water activity. Van den Berg (1983) had summarized three- and four-parameter equations that were derived from BET equation and evaluated their applicable water activity range. Three-parameter equations substantially extended the applicable water activity range compare to the original two-parameter BET equation.

Guggenheim, Anderson and de Boer (GAB) equation

GAB equation is one of the three-parameter equation derived from BET equation that was found to be as good as or better than most sorption isotherm equations:

$$\frac{M}{W_m} = \frac{Cka_w}{(1-ka_w)(1-ka_w+Cka_w)} \tag{30}$$

where W_m = water content corresponding to saturation of all primary adsorption or monolayer in BET model, C = the Guggenheim constant which can be expressed as a function of temperature as c'exp $[(H_l-H_m)/RT]$, k = a factor correcting properties of the multilayer water molecules with respect to bulk liquid and can be expressed as a function of temperature as k'exp$[(H_l-H_q)/RT]$, H_l = heat of condensation of pure water vapor, H_q = total heat of sorption of the multilayer water molecule, and H_m = total heat of sorption of the first layer on primary sites.

The parameter k describes the energetic state of the average multilayer molecules. Parameter C determines the sigmoid shape and describes the temperature effect on food isotherms over a range of at least 40 degree Celsius (Van den Berg, 1983). The GAB equation can be rewritten in quadratic form as (Schar and Ruegg 1985):

$$\left(\frac{a_w}{M}\right) = \alpha a_w^2 + \beta a_w + \gamma \tag{31}$$

$$\text{where } \alpha = \frac{k}{W_m}\left[\frac{1}{C}-1\right] \tag{32}$$

$$\beta = \frac{1}{W_m}\left[1-\frac{2}{C}\right] \tag{33}$$

$$\gamma = \frac{1}{W_m Ck} \tag{34}$$

Bizot (1991) claimed that GAB was the best model for moisture sorption isotherm of food and had been adopted by European cooperation in the field of scientific and technical research subgroup on water activity.

Schuchmann et al. (1990) wrote GAB equation in general form as:

$$M = \frac{C_1 a_w}{(1+C_2 a_w)(C_3 - a_w)} \tag{35}$$

where $C_1 = CkW_m$, $C_2 = C\text{-}k$, and $C_3 = 1/k$. The attempt to extend the prediction capability up to the water activity of 0.98-0.99 was made by replacing a_w in eqn. 35 with either $\ln[1/(1-a_w)]$ or $a_w/(1-a_w)$. The log transformation yielded better fit. The constant C_1 described the sorptive capacity at low water activity, the constant C_2 was a rough measurement of shoulder, and the constant C_3 was a measurement of steepness at high water activity region but none of them had kinetic significant.

Boquet et al. (1978, 1979) evaluated the capability of two- and three- parameter sorption isotherm equations in describing water sorption isotherm of various food products. They concluded that the use of third parameter did not necessarily improve the goodness of fit over the two-parameter equation. For milk products, the most suitable equation was Hailwood and Horrobin equation, which is mathematically equivalent to GAB equation. They suggested that this equation was versatile and easy to handle mathematically.

Lamaruo et al. (1985a, 1985b) compared the capability of Hasley, Oswin, Iglesias and Chirife, and GAB equation for products including fruits, vegetables, meat products, milk, coffee, tea, nuts, oilseeds, spices and starchy foods. GAB equation gave a better fit over wide range of water activity for most sigmoid shape isotherm.

Mok and Hettiarachchy (1990) compared percent root mean square of four sorption isotherm equations containing a parameter accounting for temperature effect. Chen-Clayton equation gave the best fit for sorption isotherm of ground sunflower nutmeat and its product.

Wang and Brennan (1991) reported that GAB and Oswin equation gave the best fit to the moisture sorption isotherm data of potatoes in water activity range of 0 up to 0.88 while BET equation gave the best fit only for water activity range of 0.05 to 0.40.

Sopade and Ajisegiri (1994) studied the sorption isotherm for maize and sorghum. Henderson model gave the best fit either when temperature effect was excluded or included.

Several researchers used general mathematical model to describe sorption isotherm. Lazarides (1990) reported that the sorption data of Basturma, an intermediate moisture meat product, can be well-described with eqn. 36 for both desorption and adsorption isotherm.

$$M = k_1 e^{k_2 a_w} \qquad (36)$$

Mok and Hettiarachchy (1990) used cubic polynomial equation to describe sigmoid isotherm at the specific temperature.

$$M = k_1 + k_2 a_w + k_3 a_w^2 + k_4 a_w^3 \qquad (37)$$

They reported that percent root mean square of cubic polynomial equation was comparable to GAB equation but significantly less than Oswin equation.

Sharma and Nath (1991) studied the sorption isotherm of dehydrated rings of onion which was J-type and found that eqn. 38 gave a highest correlation coefficient

$$M = k_1 a_w^{k_1} \qquad (38)$$

Peleg (1993) used semi-empirical double power law four-parameter to fit sigmoid moisture sorption isotherm:

$$M = k_1 a_w^{k_2} + k_3 a_w^{k_4} \qquad (39)$$

This equation had the same or better fit than GAB equation for agar-agar, carageenan, gelatin, pectin, wheat bran, raisins, casein, potato starch, dextrin, and coffee. Furthermore, this equation is not based on the assumption of the existence of well-defined monolayer.

<u>Evaluation the goodness of fit</u>

The goodness of fit is an important tool to evaluate the capacity of sorption isotherm equation to describe the experimental data. It measures the deviation of the calculated isotherm from the experimental data. Several methods to evaluate the goodness of fit have been proposed.

a) Sum of squares of the residuals, S (Schar and Ruegg, 1985)

$$S = \sum_{i=1}^{n}(M_{exp} - M_{calc})^2 \tag{40}$$

b) Variance, V (Pisecky, 1992)

$$V = \sum_{i=1}^{n}\frac{(M_{calc} - M_{exp})^2}{n-1} \tag{41}$$

c) Mean relative percentage deviation in modulus, PD (Boquet et al., 1979; Wang and Brennan, 1991)

$$PD = \frac{100}{n}\sum_{i=1}^{n}\left[\frac{|M_{exp} - M_{calc}|}{M_{exp}}\right] \tag{42}$$

d) Percent root mean square, PRMS (Schar and Ruegg, 1985)

$$PRMS = \sqrt{\frac{\sum_{i=1}^{n}\left(\frac{M_{exp} - M_{calc}}{M_{exp}}\right)^2}{n}} \times 100 \tag{43}$$

where M_{exp} is experimental moisture content, M_{calc} is calculated moisture content, and n is number of observations.

PRMS and PD take into account the number of observations and they yield the relative deviation to the experimental data. S and V yield the absolute deviation from experimental data and only V takes into account the number of observations. All of these methods can be employed to compare the goodness of fit for the same experimental data. Only PRMS and PD can be used to compare the goodness of fit from the different experimental data.

The acceptable limit of deviation from experimental data can be established based on the experimental error. Lerias and Iglesias (1991) presented errors of 9% at low water activity and 2-3 % at high water activity. Since the reproducibility of sorption isotherm was slightly dependent on the type of product, they set the acceptable limit at 9% deviation.

Shelf Life Modeling of Moisture Sensitive Product

The complete experimental testing of shelf life is costly and time consuming. It might not be even possible in some situations. Therefore, shelf life simulation becomes necessary for package design and optimization. Gyeszly (1980) stated several other reasons to use shelf life simulation: the uneconomy of over- or under packaging, the possibility of establishing shelf life to packaging cost relationship, and the necessity of short development time due to the competitive nature of the industry. Reliable shelf life models are of prime important for shelf life simulation.

Many researchers have developed mathematical models and computer programs to calculate moisture gain, predict shelf life, and optimize the package for moisture sensitive product. Most models were basically based on the steady state mass transfer as expressed by the permeability coefficient, P. It is assumed that all the resistance to moisture transport is in the film and so there is no internal resistance. All the moisture permeated into the package are absorbed by the product immediately. The schematic of the steady state mass transfer in product-package-environment system is illustrated in Figure 1.

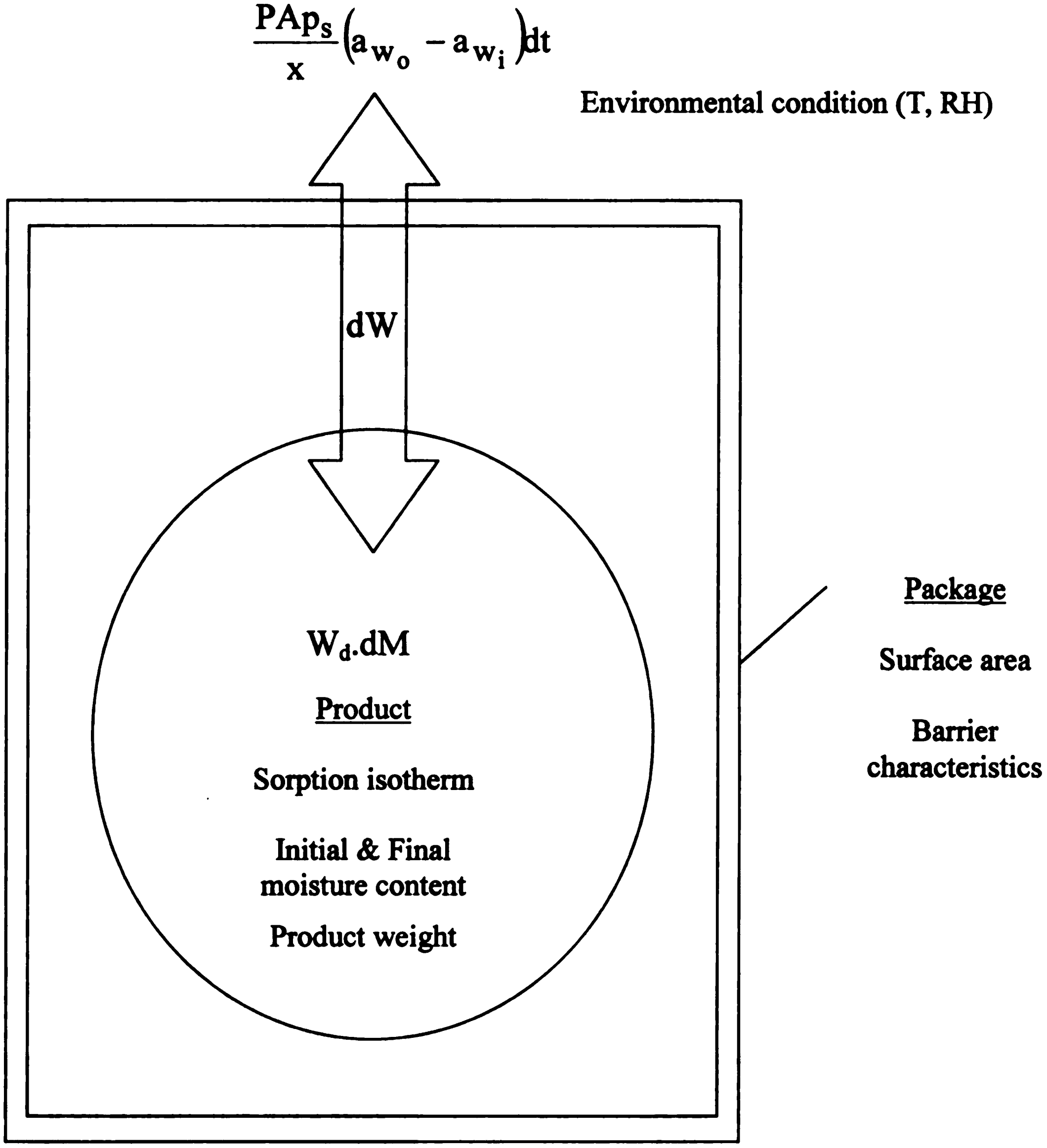

Figure 1. The steady state mass transfer in product-package-environment system

The change in the amount of water in a product is equal to the amount of water permeated into a package in a given time,

$$W_d dM = \frac{PAp_s}{\ell}(a_{wo} - a_{wi})dt \tag{44}$$

$$\int_0^t dt = \frac{W_d \ell}{PAp_s}\int_{M_i}^{M_t} \frac{dM}{(a_{wo} - a_{wi})} \tag{45}$$

where dM is a change in the amount of water in the product or the amount of water permeated into the package in time dt, a_{wo} is water activity outside the package, and a_{wi} is water activity inside the package which relates to moisture content of the product by the sorption isotherm equations. Various isotherm equations can be employed.

Iglesias et al. (1977) studied the moisture gain of dried beef as a function of time based on the integration of eqn. 45 using three different moisture sorption isotherm equations including straight line (eqn. 46), BET equation (eqn. 47), and Hasley equation.

$$t = \frac{\ell W_d b}{PAp_s} \ln \frac{M_e - M_{ini}}{M_e - M_t} \tag{46}$$

where b is slope of straight line portion of sorption isotherm

$$dt = \frac{\ell W_d}{PA}\left[\left(\frac{1}{p_s}\frac{dp}{(1-(p/p_s))^2}\right)+\left(\frac{1}{p_s}\frac{(C_b-1)dp}{(1+(C_b-1)(p/p_s))^2}\right)\right]\frac{W_m}{p_{out}-p} \tag{47}$$

where C_b and W_m are constants for BET equations.

The model based on straight line gave significant error while analysis based on both BET and Hasley equation gave good agreement with experimental data when narrow moisture content interval (4-9%) was considered. For wider moisture content range (4-13%), Hasley equation-based analysis gave a better prediction of moisture change. In 1979, they developed computer program for prediction of moisture transfer in the mixture of packaged dried food based on the application of BET equation and concept of additivity of isotherm.

Clifford et al (1977) predicted internal relative humidity of three types of cereal as a function of time, $RH_i(t)$, by using the concept of steady state mass transfer and taking water vapor in the headspace into account as presented in eqn. 48 and 49. The authors found that the difference between calculated and experimental data was less than 10% except one type of cereal in the package with the poorest barrier property.

$$RH_i(t) = RH_e - RH_i(t=0)^{-\alpha t} \tag{48}$$

$$\alpha = \frac{P \frac{A}{\ell} \frac{p_s}{100}}{\left(18 \frac{V}{RT} \frac{p_s}{100}\right) + \frac{bW_d}{100}} \tag{49}$$

where $RH_i(t)$ is relative humidity inside the package at time t, RH_e is equilibrium relative humidity which is equal to the storage relative humidity, $RH_i(t=0)$ is initial relative humidity inside the package, V is headspace volume, and b is the slope of straight line portion of moisture sorption isotherm.

Cardoso and Labuza (1983) used a computer iterative technique based on the steady state mass transfer and linear isotherm (eqn. 46) to predict moisture gain of packaged pasta subjected to the sine wave of temperature and relative humidity. Good predictions were obtained for pasta packaged in laminated polypropylene bags. The technique failed to give a good prediction for pasta packaged in paperboard boxes because the assumption of all resistance to moisture transfer is in the package was not satisfied for this type of package.

Chuzel and Zakhia (1991) used eqn. 46 to calculate the potential storage time of gari under three isothermal storage conditions. The equilibrium moisture content, M_e, of product when exposed to atmosphere outside the package was calculated by iteration from the GAB equation that used to describe isotherm at the storage temperature.

Mannheim et al. (1994) stated that the eqn. 46 is valid only for hydrophobic packaging material. For hydrophilic material, the effect of different driving force must be taken into account. The authors described model based on the assumption of second order polynomial relationship between the permeability value and the driving force but no experimental validation was performed.

$$t = \int_{M_{ini}}^{M_{fin}} \frac{\ell W_d}{A P p_s \left(a_{w_e} - a_w(M,T)\right)^2} \qquad (50)$$

Diosady et al. (1996) developed shelf life model of canola meal based on the mass transfer equation and the assumption that moisture sorption isotherm was described by GAB equation. The model was valid only when C is large so that $4W_mC >> 2W_mC^2$.

$$t = \frac{1}{(\beta + C)\phi}\left[M_f - M_i + \frac{2W_mC}{(\beta + C)}\ln\left(\frac{(\beta + C)M_{fin} - 2W_mC}{(\beta + C)M_{ini} - 2W_mC}\right)\right] \qquad (51)$$

where

$$C = c'\exp\left[\frac{(H_l - H_m)}{RT}\right] \qquad (52)$$

$$k = k'\exp\left[\frac{(H_l - H_n)}{RT}\right] \qquad (53)$$

$$\phi = \frac{P}{\ell}\frac{p_s A 100}{2k(1 - C)W_d} \qquad (54)$$

$$\beta = \left(\frac{W_m}{M_e}\right)C - \sqrt{\left[\left(2 + \left(\frac{W_m}{M_e}\right)C - C\right)^2 - 4 + 4C\right]} \qquad (55)$$

$$M_e = \frac{W_m C k a_w}{(1 - k a_w)(1 - k a_w + C k a_w)} \qquad (56)$$

The model is adequate to describe moisture gain as a function of time of canola meal packaged in Propafilm C and Melinex 813 for temperature lower than 40°C.

Alves et al. (1996) applied mathematical model as shown in eqn. 45 to predict shelf life of cream cracker biscuit using linear, Hasley and GAB equation to describe the product sorption isotherm. Eqn. 45 gave the good prediction up to the product moisture content of 11% regardless of the isotherm equation. At higher moisture content only GAB and Hasley equations yielded the good prediction.

Rudolph (1986) suggested a simple method to determine shelf life and optimize the packaging of moisture sensitive food by plotting a graph of $\alpha = (WVTR)At/W_d$ versus M, where Q is package transmission rate and t_L is shelf life. If the initial moisture content is given, the origin of the graph will change from (0,0) to (M_{ini}, Qat_{ini}/W_d). It was claimed that this model could also be applied to non- reactive gases and vapors other than moisture. Dock et al. (1998) validated Rudolph's method and reported that, for pretzel, the method was valid only at some temperatures.

Kim et al. (1998) developed a model and a computer program to estimate the unsteady state moisture transfer through blister package using finite difference method. The model is based on diffusion coefficient of water in the product and the packaging material and the solubility of water and the packaging material. The shelf life value of a circular plate shaped product obtained from this model agreed well with the value obtained from the analytical solution for the case that the diffusion coefficient of the product is significantly lower than the diffusion coefficient of the packaging material.

Model Analysis

Any mathematical model can be evaluated by using the so-called sensitivity analysis (Beck and Arnold, 1977). A sensitivity analysis indicates the magnitude of the change in the dependent variable due to the alteration in the values of the parameters. To perform a sensitivity analysis, we must calculate the sensitivity coefficient which are the first derivative of model with respect to each parameter in the model.

$$\chi = \frac{\partial \eta}{\partial \beta} \tag{57}$$

where $\eta = \eta(x, t, \beta)$, x and t are independent variables, and β is a parameter

A sensitivity coefficient provides information about the linearity of parameters. If all sensitivity coefficients are not functions of the parameters, the model is linear in terms of its parameters. If the sensitivity coefficients over the range of the observations are not linearly dependent, parameters of the model can be estimated. For parameter, the linear dependence occurs when eqn. 58 holds for all i observations and not all C_j values equal to zero.

$$C_1 \frac{\partial \eta_{ii}}{\partial \beta_1} + C_2 \frac{\partial \eta_i}{\partial \beta_2} + \ldots\ldots + C_p \frac{\partial \eta_i}{\partial \beta_p} = 0 \tag{58}$$

Liu et al (1997) analyzed the sensitivity for hygrostress crack formation in cylindrical food during drying. They evaluated the trend of time, moisture ratio, average temperature, and crack formation as a function of initial moisture content, relative humidity and temperature of dried air, convective surface, mass and heat transfer coefficients, initial cylindrical diameter, and ratio of assumed and reference moisture diffusivity. For the effects of relative humidity and temperature of dry air on temperature at crack formation were further examined by constructing three-dimensional plot of Biot number, food moisture concentration at surface, and surface temperature.

CHAPTER 2

MATERIALS AND METHODS

Product-Package System

Non-fat dry milk

Instant non-fat dry milk fortified with vitamin A and D was obtained from Stone container Corp (Chicago, IL). Its ingredients were non-fat dry milk, vitamin A palmitate, and vitamin D. Instant non-fat dry milk composed of carbohydrate (52%), protein (35%), sodium (0.5%), cholesterol (less than 0.02%), calcium, and vitamin D, A, and C as stated on the label of the package.

Package

Six types of packaging material were supplied by Stone Container, Corp. (Chicago, IL). Materials were conditioned at 72°F, 50% RH for 72 hours prior testing. The description of each material is presented in Table 3. The two most suitable packaging materials were chosen to construct boxes. Boxes were closed by two different glue patterns, identified as Bellow, and full overlap, FOL, as shown in Figure 2 and 3, respectively. There were two sizes of boxes as described in Table 4.

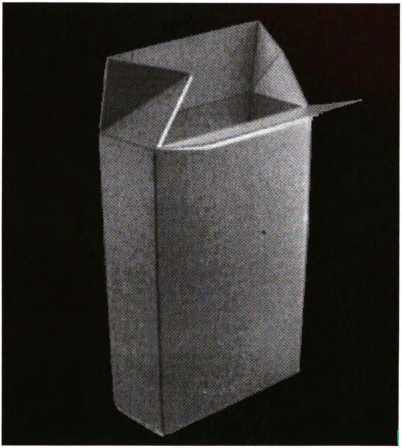

Figure 2. Bellow style box

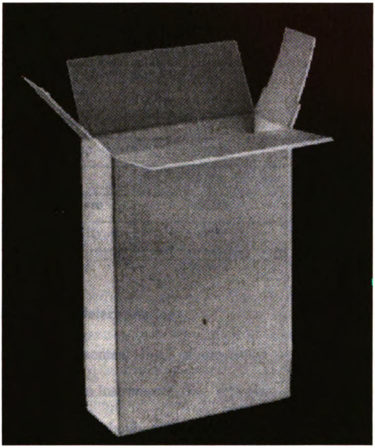

Figure 3. FOL style box

Table 3. Description of packaging material

Type	Description
A	AA coated F-flute corrugated board
B	B coated F-flute corrugated board
C	BB coated F-flute corrugated board
D	Single-face polyliner F-flute corrugated board
E	Double-face polyliner F-flute corrugated board
Control	Paperboard

Table 4. Package description

Character	Large	Small
Dimension	32.5 x 21.5 x 8.7 cm	25 x 17 x 6 cm
Surface area, cm^2	2315	1354
Product capacity, g	350	290

Initial Moisture Content Determination

The initial moisture content (IMC) of non-fat dry milk was determined by Karl Fischer Titration (Brinkmann Instruments, Inc., Westbury, NY). Half a gram of the sample were transferred to a weighing spoon and placed into a titration beaker containing fresh solution of methanol. The sample was homogenized by a Brinkmann apparatus for 40 seconds. Then, water molecules in the sample were titrated with Hydranal Composite 5 (Aldrich Chemical Company, Inc., Milwaukee, WI) consisting of Diethylene glycol monoethyl ether, imidazole, sulfur dioxide, iodine, and hydriodic acid. The moisture content was reported on percent wet basis, M_w. The percent moisture content (dry basis), M, was calculated as

$$M = \frac{M_w}{1 - M_w} \tag{59}$$

Moisture Sorption Isotherm Determination

Moisture sorption isotherms were determined gravimetrically by exposing a sample of non-fat dry milk of known weight and initial moisture content to humid air in a closed container. The equilibrium moisture content of the sample were evaluated in three series of nine relative humidity values ranging from 8% to 95% RH. Each series were maintained at a different constant temperature of 20, 30 and 40°C. The equilibrium moisture content, expressed as dry basis, was calculated based on moisture gain of a sample at equilibrium.

The relative humidity value in the container was obtained by placing in 500 ml crystal bowls selected saturated salt solution. The containers were a 3.5-gallon plastic bucket tightly-closed. The saturated salt solutions were prepared from analytical pure salts and distilled water. Salts employed and their corresponding measured relative humidity values are listed in Table 5. The relative humidity in each bucket was monitored by humidity sensor (Hygrodynamics, Inc., Silver Spring, MD) which was mounted to the lid of each bucket. From relative humidity, water activity can be calculated by

$$a_w = \frac{RH}{100} \tag{60}$$

Approximately 2 grams of non-fat dry milk were weighed into a petridish with diameter of 5.5 cm. Three replicates and two controls (empty petridish) were used at each condition of temperature and relative humidity. At predetermined time intervals, lidded petridishes were weighed on AE 160 Mettler Analytical Balance. The procedure was repeated until a constant weight was obtained. The equilibrium moisture content (dry basis), M, was calculated by eqn. 62.

Table 5. Salt solutions and their corresponding relative humidities at 20, 30 and 40°C

Saturated salt solutions	Relative humidity at			Source of salt
	20°C	30°C	40°C	
Lithium chloride	8.4	8.9	9.2	Aldrich Chemical Company, Inc., WI
Potassium acetate	23.1	23.2	23.8	J.T. Baker, NJ
Magnesium chloride	34.0	34.2	34.3	J.T. Baker, NJ
Potassium carbonate	47.2	46.6	45.6	Mallinckrodt Baker, Inc., KY
Potassium nitrite	50.4	48.7	47.6	EM Science, NJ
Sodium nitrite	64.9	63.6	62.7	Columbus Chemical Industries, Inc., WI
Sodium chloride	75.6	75.9	79.6	J.T. Baker, NJ
Ammonium sulfate	81.3	81.5	77.5	Columbus Chemical Industries, Inc., WI
Potassium nitrate	94.5	93.5	91.3	EM Science, NJ

$$M = \left[\frac{W_e(M_i + 1)}{W_i} - 1\right] \times 100 \qquad (61)$$

where M = equilibrium moisture content, % dry basis

M_i = initial moisture content, % dry basis

W_e = weight at equilibrium, g

W_i = initial weight, g

GAB, Oswin, Henderson, and cubic polynomial equations were employed to fit the experimental moisture sorption isotherm. Parameters in each equation were estimated as the following:

GAB equation

$$\frac{M}{W_m} = \frac{Cka_w}{(1-ka_w)(1-ka_w+Cka_w)} \tag{62}$$

In order to estimate parameters, the equation was transformed into a quadratic form as

$$\frac{a_w}{M} = \alpha a_w{}^2 + \beta a_w + \gamma \tag{63}$$

$$\text{where } \alpha = \frac{k}{W_m}\left(\frac{1}{C}-1\right) = \frac{1}{W_m C}(1-C)$$

$$\beta = \frac{1}{W_m}\left(1-\frac{2}{C}\right) = \frac{1}{W_m C}(C-2)$$

$$\gamma = \frac{1}{W_m Ck}$$

The quadratic regression was performed by Microsoft Excel 97-SR1. GAB constants C, W_m, and k were calculated by eqn. 64, 65, and 66, respectively. The detail of obtaining those equations are presented in Appendix A.

$$C = \frac{\theta \pm \sqrt{\theta^2 - 4\theta}}{2} \tag{64}$$

$$\text{where } \theta = 4 + \frac{\beta^2}{(-\alpha)\gamma}$$

$$W_m = \frac{1}{\beta C}(C-2) \tag{65}$$

$$k = \frac{1}{W_m Ck} \tag{66}$$

Oswin Equation

$$M = k_1\left[\frac{a_w}{1-a_w}\right]^{k_2} \tag{67}$$

Parameter A_0 and B_0 were estimated by non-linear regression performed by STATPRO, a statistical software. The first derivatives with respect to each parameter were required to be entered into the program

$$\frac{\partial M}{\partial k_1} = \left[\frac{a_w}{1-a_w}\right]^{k_2} \tag{68}$$

$$\frac{\partial M}{\partial k_2} = k_1\left[\left(\frac{a_w}{1-a_w}\right)^{k_2}\ln\left(\frac{a_w}{1-a_w}\right)\right] \tag{69}$$

Henderson Equation

$$1-a_w = \exp\left(k_1 M^{k_2}\right) \tag{70}$$

"ln (1-a_w)/T" was considered as dependent variable, y, and "M" was considered as an independent variable, x. Non-linear regression was performed by STATPRO to estimate parameters. The first derivatives with respect to each parameter needed to be entered are

$$\frac{\partial y}{\partial k_1} = M^{k_2} \tag{71}$$

$$\frac{\partial y}{\partial k_2} = k_1 M^{k_2}\ln M \tag{72}$$

Cubic Polynomial Equation

$$M = k_1 a_w^3 + k_2 a_w^2 + k_3 a_w + D_c \tag{73}$$

The polynomial regression was performed by Microsoft Excel 97-SR1

The goodness of fit for each isotherm equation was evaluated based on the minimum value of percent root mean square, PRMS.

$$PRMS = \sqrt{\frac{\sum_{i=1}^{N}\left(\frac{M_{exp} - M_{calc}}{M_{exp}}\right)}{N}} \times 100 \tag{74}$$

where M_{exp} = experimental moisture content, % dry basis, M_{calc} = calculated moisture content, % dry basis, and N = number of data point

Standard deviations of parameters in the equation that best-described the experimental moisture sorption isotherms were determined for further use in the error analysis of shelf life calculation. For GAB equation, since its parameters were estimated using transformed equation, the standard deviations were determined using Gauss' Law of Error Propagation which stated that an error of final results derives from the error in each number used to get that results. The equation employed for calculation of standard deviation of GAB constants are presented in Appendix A.

Determination of Water Vapor Transmission of Packaging Material

The dish method in ASTM E96-93, Standard Test Methods for Water Transmission of Materials, was employed to determine water vapor transmission rate, WVTR, and permeance, P/ℓ, of the packaging material (flat and unscored). Six types of packaging materials, A, B, C, D, E, and control, were tested in four replicates at 40°C, 75% RH. Each aluminum dish was cleaned thoroughly and approximately 20 grams of desiccant (8 mesh anhydrous calcium sulfate) was added to cover the bottom of the dish. A specimen was cut into circle with diameter of 8.25 cm and sealed to the mouth of the test dish with the hot paraffin wax.

The inner side of actual package was placed toward desiccant in order to simulate water vapor flow direction. Dish sets were weighed in a AE 160 Mettler Analytical balance and placed in an environmental chamber at controlled humidity. Then they were reweighed at predetermined intervals. One extra sample of each type of packaging material was mounted to an aluminum dish containing no desiccant and tested in the same manner as other samples. This was done to compensate the error from moisture sorption of test material. The water vapor transmission rate and permeance were calculated based on the slope of graph of weight gain as a function of time using eqn. 76 and 77.

$$\mathrm{WVTR} = \frac{\mathrm{SL}}{\mathrm{A}} \tag{75}$$

$$\frac{\mathrm{P}}{\ell} = \frac{\mathrm{WVTR}}{\Delta \mathrm{p}} \tag{76}$$

where SL = slope of the weight gain versus time graph, g/day, $\mathrm{A} = 0.5346\ \mathrm{m}^2$, p_{in} = partial pressure inside the package, mmHg, and $\mathrm{p}_{\mathrm{out}}$ = partial pressure outside the package, mmHg

Two packaging materials with the lowest permeance values were selected for the additional testing at 25°C and 30°C, 75% RH.

Evaluation of Package Integrity

The moisture gain of FOL and Bellow style boxes were experimentally determined in accordance with the ASTM D895-79, Test Method for Water Vapor Permeability of Packages. Packages were filled with approximately 454 grams of desiccant (8 mesh anhydrous calcium sulfate) and sealed by using ITW Dynatec Adhesive Application System (Glenview, IL). At each end and side of package, extra adhesive was applied to ensure the sift proof. The sealed package was weighed and placed in the environmental chamber at 40°C, 75% RH. In order to eliminate the effect of moisture sorption of packaging material and fluctuation of storage environment, one package for each glue pattern without desiccant was used as a control. Control packages were sealed and tested with the same manner as test packages. The control and test packages were reweighed at predetermined intervals always with the same sequence. The experimental total moisture gain was determined and compared to the calculated moisture gain obtained as

$$\text{Moisture gain} = (P/\ell)\cdot A\cdot \Delta p\cdot t \tag{77}$$

The box style with better barrier characteristics were constructed using material A and were tested at the same manner to ensure the package integrity of package made from material A.

Model Validation

The two most suitable package based on the previous experiment was chosen for shelf life validation experiment. Boxes filled with non-fat dry milk were closed in the same manner as in the experiment to evaluate package integrity. Boxes were weighed and placed in the environmental chamber and reweighed every day. Two storage conditions including 40°C, 83% RH and 25°C, 67% RH were employed. Controls (empty boxes) were tested along with other samples. The experimental design is described in Table 6.

Table 6. Experimental design for model validation experiment

Condition	Material	Size
40°C, 75% RH	A	Small
	A	Large
	E	Small
25°C, 75% RH	A	Small
	A	Large
	E	Small

CHAPTER 3

PRODUCT AND PACKAGE CHARACTERISTICS

Initial Moisture Content

Initial moisture content of non-fat dry milk determined by Karl Fischer was 4.86 ± 0.04 % (dry basis). The experimental data are presented in Table 7.

Table 7. Initial moisture content of non-fat dry milk

Replicate	Moisture content, % (dry basis)
1	4.86
2	4.79
3	4.84
4	4.92
5	4.86
6	4.85
7	4.91
Average	4.86
Standard deviation	0.04

Moisture Sorption Isotherm

The equilibrium moisture content on a dry basis was determined at 20, 30 and 40°C, for each value of relative humidity. The experimental values at all temperatures are presented in Table 8.

Table 8. Experimental moisture sorption isotherm for non-fat dry milk at 20, 30 and 40°C

20°C		30°C		40°C	
RH	M, % (dry basis)	RH	M, % (dry basis)	RH	M, % (dry basis)
0.0	0.00 ± 0.00	0.0	0.00 ± 0.00	0.0	0.00 ± 0.00
8.4	4.23 ± 0.01	8.9	3.88 ± 0.03	9.2	3.67 ± 0.02
23.1	4.84 ± 0.02	23.2	4.58 ± 0.03	23.8	4.44 ± 0.02
34.0	6.04 ± 0.03	34.2	6.09 ± 0.03	34.3	5.90 ± 0.08
47.3	8.97 ± 0.07	46.6	6.54 ± 0.04	45.6	6.00 ± 0.02
50.4	8.03 ± 0.01	48.7	7.13 ± 0.02	47.8	6.43 ± 0.01
64.9	11.58 ± 0.03	63.6	11.59 ± 0.02	62.8	9.61 ± 0.01
75.6	14.35 ± 0.02	75.9	14.01 ± 0.03	77.5	13.68 ± 0.01
81.3	16.96 ± 0.07	81.5	16.51 ± 0.01	79.6	16.42 ± 0.02
94.5	38.45 ± 0.51	93.5	33.48 ± 0.06	91.3	27.3 ± 0.04

As indicated in Chapter 1, several equations were available to describe the experimental data of moisture sorption isotherm. In this work, GAB, Oswin, Henderson, and cubic polynomial equations were employed to fit the experimental moisture sorption data of non-fat dry milk. Equations and their percent root mean square, PRMS, are presented in Table 9, 10, 11, and 12, respectively.

As seen from Table 9 to 12, the GAB equation showed the best fit since it produced the lowest percent root mean square for the experimental sorption isotherm of non-fat dry milk at all temperatures. The result agreed with the one reported by Boquet et al. (1979). The authors claimed that Hailwood and Horrobin equation, or transformed

Table 9. GAB equation describing moisture sorption isotherm of non-fat dry milk

Temperature, °C	GAB equation	PRMS
20	$M = \dfrac{4.25a_w}{(1-0.93a_w)(1-0.93a_w+96.24a_w)}$	7.03
30	$M = \dfrac{4.67a_w}{(1-0.95a_w)(1-0.95a_w+118.45a_w)}$	6.10
40	$M = \dfrac{3.35a_w}{(1-0.96a_w)(1-0.96a_w+91.64a_w)}$	7.78

Table 10. Oswin equation describing moisture sorption isotherm of non-fat dry milk

Temperature, °C	Oswin Equation	PRMS
20	$M = 0.0813\left(\dfrac{a_w}{1-a_w}\right)^{0.56}$	17.44
30	$M = 0.0785\left(\dfrac{a_w}{1-a_w}\right)^{0.55}$	15.37
40	$M = 0.0744\left(\dfrac{a_w}{1-a_w}\right)^{0.56}$	13.83

Table 11. Henderson equation describing moisture sorption isotherm of non-fat dry milk

Temperature, °C	Henderson equation	PRMS
20	$M = -\left(\dfrac{\ln(1-a_w)}{0.33T}\right)^{0.96}$	39.99
30		26.01
40	T is temperature, °C	32.47

* Since Henderson model includes the effect of temperature, only one equation is presented for the three temperatures.

Table 12. Cubic polynomial model describing moisture sorption isotherm of non-fat dry milk

Temperature, °C	Cubic polynomial equation	PRMS
20	$M=1.64a_w^3-1.82a_w^2+0.65a_w-0.0045$	19.76
30	$M=1.40a_w^3-1.50a_w^2+0.54a_w-0.0019$	13.66
40	$M=1.11a_w^3-1.15a_w^2+0.43a_w-0.0009$	7.23

GAB equation, gave the best fit for the isotherm of dairy product. The values of experimental and calculated (with GAB equation) moisture sorption isotherm of non-fat dry milk at 20, 30, and 40°C are presented in Appendix A and the plots are presented in Figure 4, 5, and 6, respectively. The GAB constants and their standard deviation for all temperatures are presented in Table 13.

Table 13. GAB constants and their standard deviation at 20, 30, and 40°C

Temperature, °C	C	s_c	k	s_k	W_m, g/g	S_{Wm}, g/g
20	103.55	0.05	0.93	0.11	0.0441	0.0057
30	124.63	0.03	0.95	0.10	0.0394	0.0046
40	95.46	0.06	0.96	0.11	0.0366	0.0044

Parameter C changed significantly when temperature changes but had no pattern. The similar result was observed in the adsorption isotherm of potato in the temperature range of 40 to 70°C (Wang and Brennan, 1991) and the desorption isotherm of maize in the temperature range of 20 to 40°C (Sopade and Ajisegiri, 1994). This error would only contribute to the very low region of water activity (0.01 to 0.04) and will not have much impact on the shelf life prediction. The error of parameter C is discussed and the correction is proposed in Appendix C.

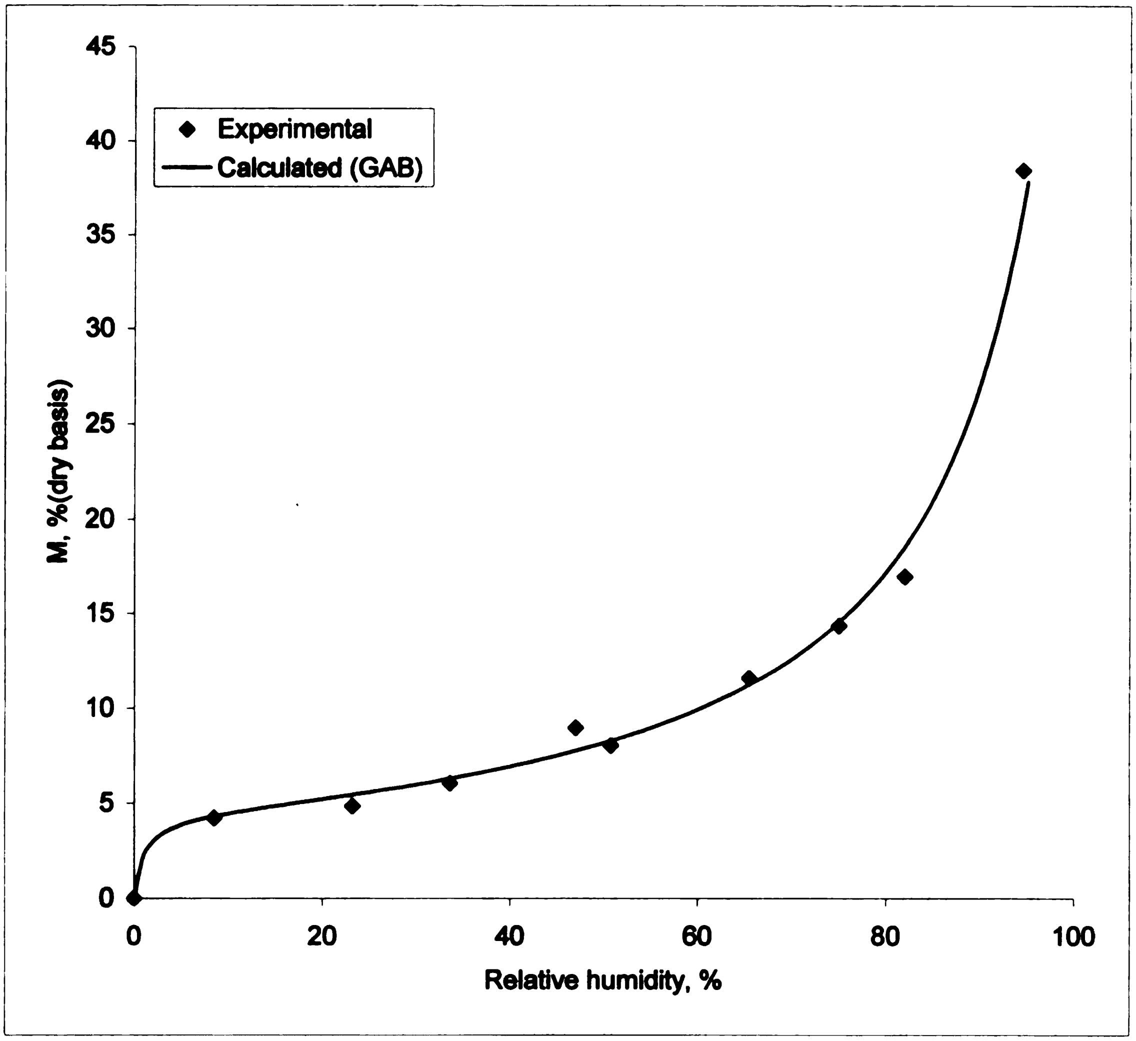

Figure 4. Experimental and calculated (with GAB) moisture sorption isotherm of non-fat dry milk at 20°C

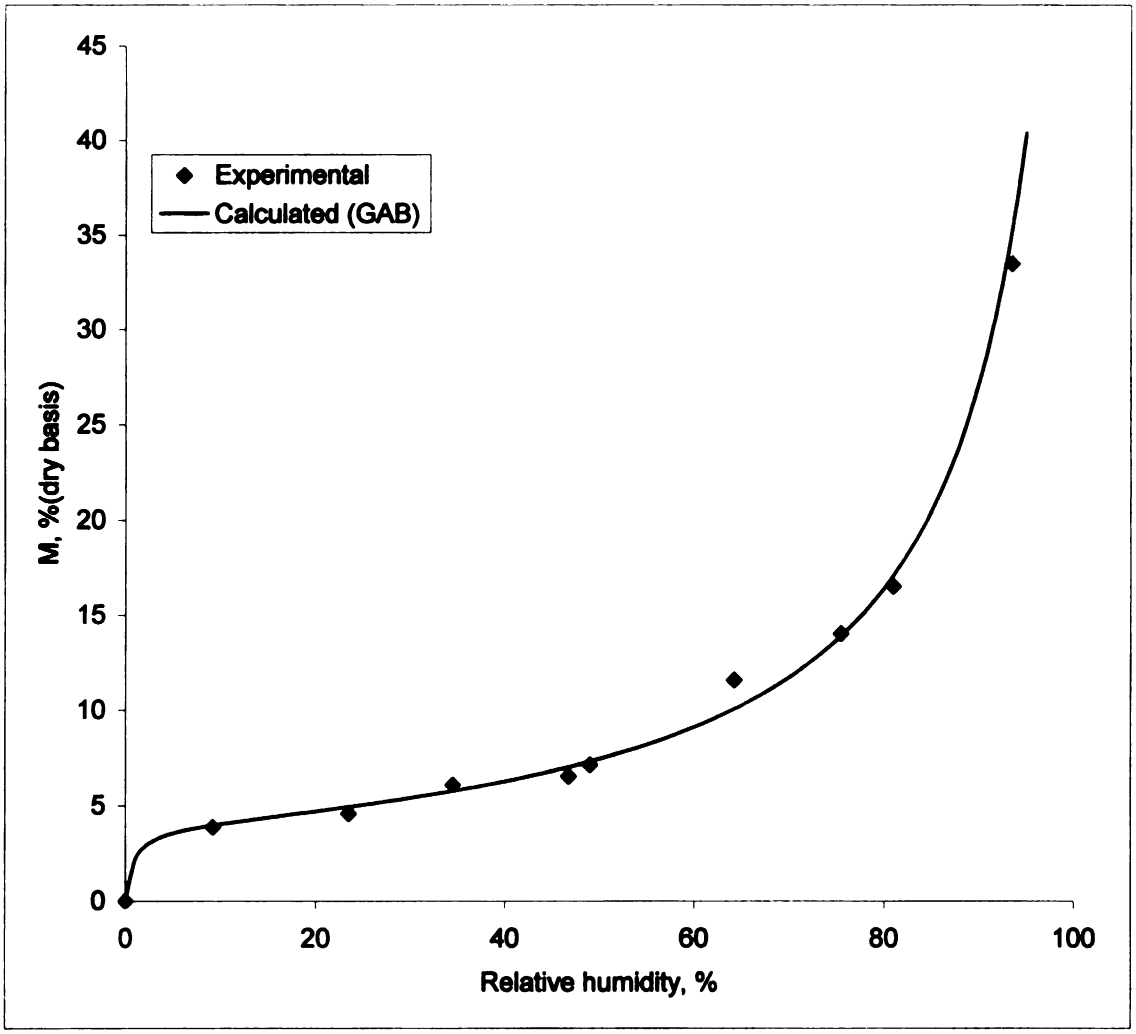

Figure 5. Experimental and calculated (with GAB equation) moisture sorption isotherm of non-fat dry milk at 30°C

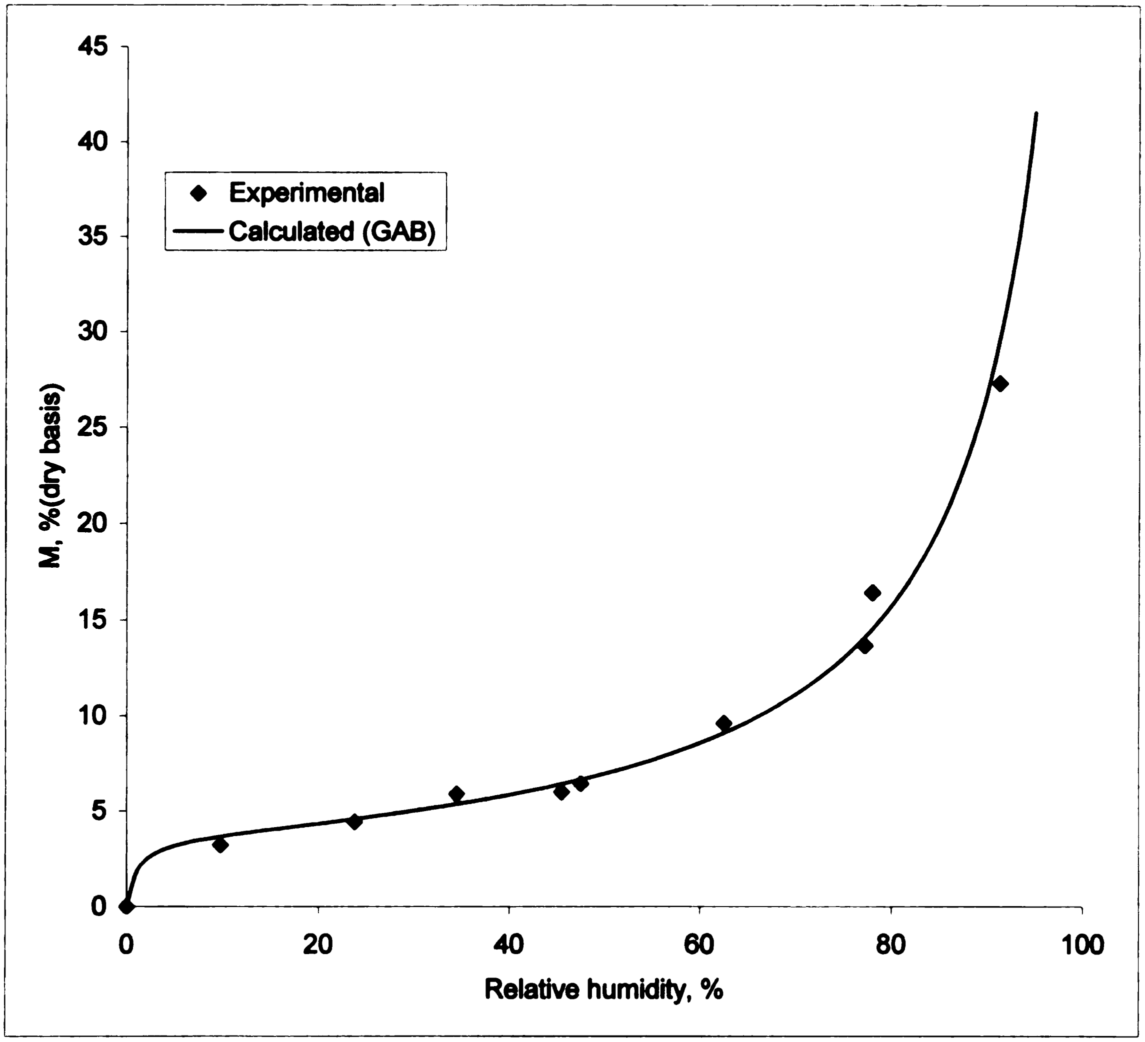

Figure 6. Experimental and calculated (with GAB equation) moisture sorption isotherm of non-fat dry milk at 40°C

As seen in Table 13, parameter k slightly increased with increasing temperature. The relationship between parameter k and temperature, T, was described by an Arrhenius equation (Van den Berg, 1983)

$$k = k'\exp\left[\frac{(H_l - H_q)}{RT}\right] \tag{78}$$

where H_l is heat of condensation of pure water, H_q is total heat of sorption of the multilayer, and k' = pre-exponential k constant.

From this study, $(H_l - H_q)$ was – 0.29 kCal/mol ($r^2 = 0.9697$). Since the heat of condensation of pure water in the range of experimental temperature was approximately 10.4 kCal/mol (Lide and Frederikse, 1996), total heat of sorption of the multilayer was found to be approximately 10.6 kCal/mol.

Parameter k indicate the property of bulk liquid. If k = 1, multilayers will have the property of bulk liquid (Diosady et al., 1996). The parameter k of non-fat dry milk indicated that multilayer water in non-fat dry milk had properties between monolayer and bulk liquid but closer to the bulk liquid and had trend toward behaving more like bulk liquid as temperature increases.

The monolayer moisture content, W_m, depends on the number of adsorption sites which in principle are constant and therefore independent of temperature. However, the monolayer moisture content of non-fat dry milk decreased with increasing temperature from 0.0441 g/g at 20°C to 0.0366 g/g at 40°C. Similar result was reported for moisture adsorption and desorption isotherms of maize, sorghum, and millet (Sopade and Ajisegiri, 1994). The result could be explained by the reduction of sorption sites due to physicochemical changes induced by an increasing of temperature. The temperature dependency of W_m was expressed by Arrhenius relationship.

$$W_m = (W_m)' \exp\left(-\frac{E_a}{RT}\right) \tag{79}$$

where W_m' is pre-exponential W_m, and E_a is monolayer binding energy

In this study, monolayer binding energy for non-fat dry milk in the temperature range of 20 to 40°C was –1.70 kCal/mole ($r^2 = 0.9898$).

Since the shelf life model validation was performed at 40°C and 25°C, the information on the moisture sorption isotherm at 25°C was necessary. Lagrange interpolation method, as shown in eqn. 80, was employed to obtain those information based on isotherm at 20, 30, and 40°C.

$$M_x = \frac{(T_x - T_2)(T_x - T_3)}{(T_1 - T_2)(T_1 - T_3)}M_1 + \frac{(T_x - T_1)(T_x - T_3)}{(T_2 - T_1)(T_2 - T_3)}M_2 + \frac{(T_x - T_1)(T_x - T_2)}{(T_3 - T_1)(T_3 - T_2)}M_3 \tag{80}$$

where M_x = % equilibrium moisture content (dry basis) at T_x = 25°C, M_1 = % equilibrium moisture content (dry basis) at T_1 = 20°C, M_2 = % equilibrium moisture content (dry basis) at T_2 = 30°C, and M_3 = % equilibrium moisture content (dry basis) at T_3 = 40°C

The GAB constants at 25°C were found to be C = 120.16 ±0.05, W_m = 0.0419 ± 0.0049 or 4.19 ± 0.49 %, and k = 0.94 ± 0.11. The moisture sorption isotherm of 20, 25, 30, and 40°C are presented in Figure 7.

Equilibrium moisture content increased with increasing temperature at constant relative humidity (Figure 7). The effect of temperature was more pronounced in the intermediate relative humidity range (20-80%). The upper limit of 80% corresponds to 17-19% moisture content (dry basis). At relative humidity higher than 80%, all isotherms tended to collapse into one line. This agreed with Pisecky (1992) who reported the

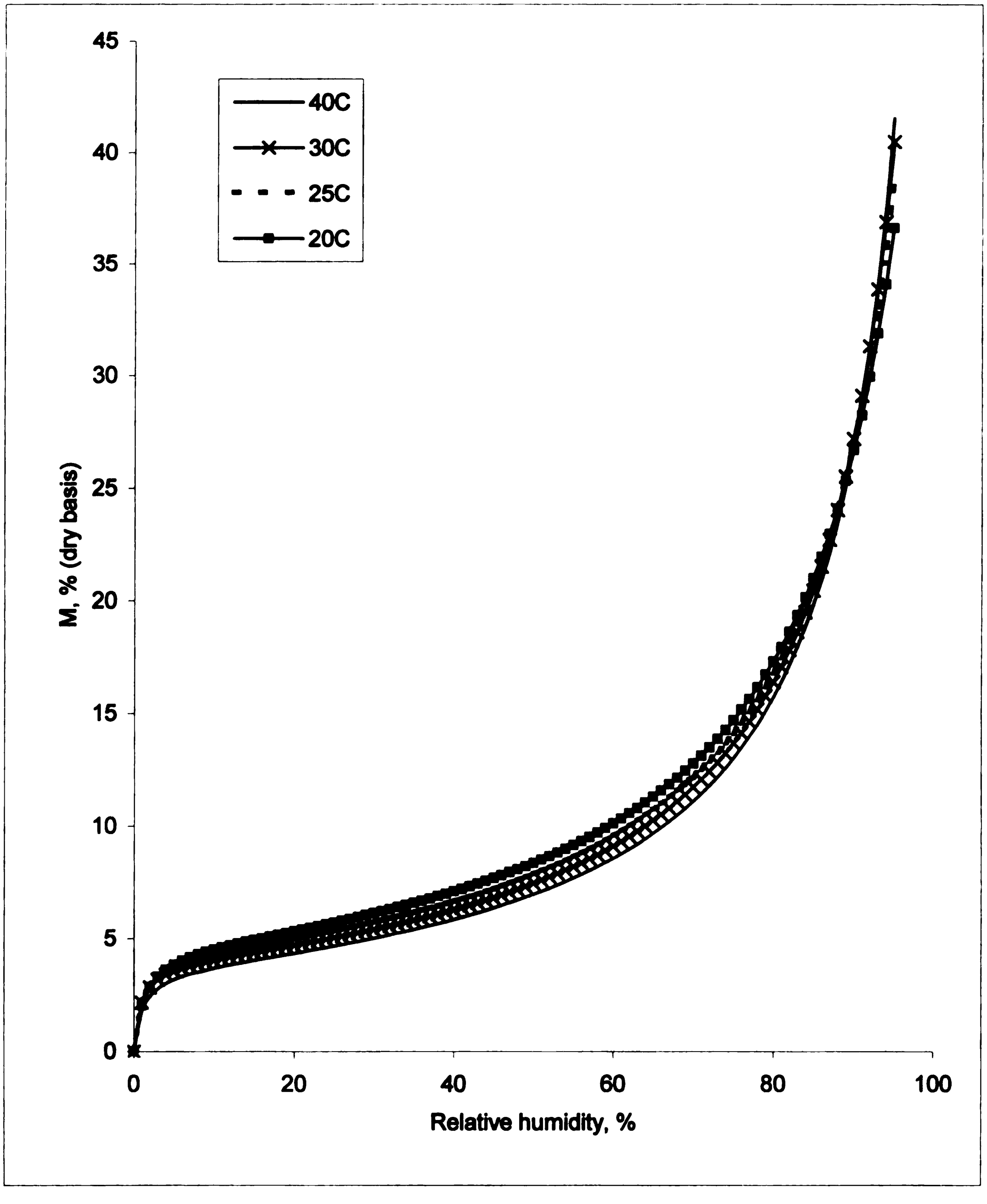

Figure 7. Calculated moisture sorption isotherm of non-fat dry milk at 20, 25, 30 and 40°C

intersection of isotherm at relative humidity of 60% which corresponds to 18% moisture content (dry basis).

GAB Equation Analysis

Sensitivity coefficient, χ, of each GAB parameters were determined and plot against the independent variables, a_w. The sensitivity coefficients of parameter C, k, and W_m are presented in eqn. 81, 82, and 83, respectively.

$$\chi_C = \frac{\partial M}{\partial C} = \frac{W_m k a_w}{(1 - k a_w + C k a_w)^2} \tag{81}$$

$$\chi_k = \frac{\partial M}{\partial k} = \frac{C k a_w}{\left[(1 - k a_w)(1 - k a_w + C k a_w)\right]^2}\left[(c+1)k^2 a_w^2 + 1\right] \tag{82}$$

$$\chi_{W_m} = \frac{\partial M}{\partial W_m} = \frac{C k a_w}{(1 - k a_w)(1 - k a_w + C k a_w)} \tag{83}$$

As seen in eqn. 81, 82, and 83, χ_C was a function of a_w, C, k, and W_m; χ_k was a function of a_w, C, k and W_m; and χ_{Wm} was a function of a_w, C, and k. The equation was not linear in term of its parameters. Sensitivity coefficients of each parameter at 20, 30, and 40°C were plotted against water activity as shown in Figure 8, 9, and 10.

The plot of χ_C against water activity in Figure 8 indicates that the moisture content was very sensitive to parameter C at low water activity region (0-0.04 a_w) and the sensitivity is greater at 20°C. The sensitivity to parameter C was about the same at 20 and 40°C. In higher water activity, the sensitivity of moisture to C for all temperatures were minute. However, from Figure 8 to 10, the sensitivity of the equilibrium moisture content to parameter C was much smaller than those to W_m and k.

The graph of χ_k versus water activity in Figure 9 indicates that parameter k had little or no effect below water activity of 0.8. Above that, sharp rise, indicating the increase in sensitivity of moisture content to k, was noticed. This agreed with the fact that k is the property of multilayer water because k did not have any effect at low water activity range which is monolayer. The sensitivity of equilibrium moisture content to parameter k was the least at 20°C and the most at 40°C. The impact of error due to an error from parameter k was expected to be larger at high water activity especially at high temperature.

The graph of χ_{W_m} versus water activity in Figure 8 indicated that the equilibrium moisture content in the range of high water activity (0.8-1 a_w) was very sensitive to parameter W_m. The sensitivity was the greatest at 40°C and least at 20°C. At low water activity region, the sensitivity of equilibrium moisture content to parameter W_m were small and not significantly different for all temperature. The impact of error due to an error in parameter W_m was expected to be large at high water activity especially at high temperature.

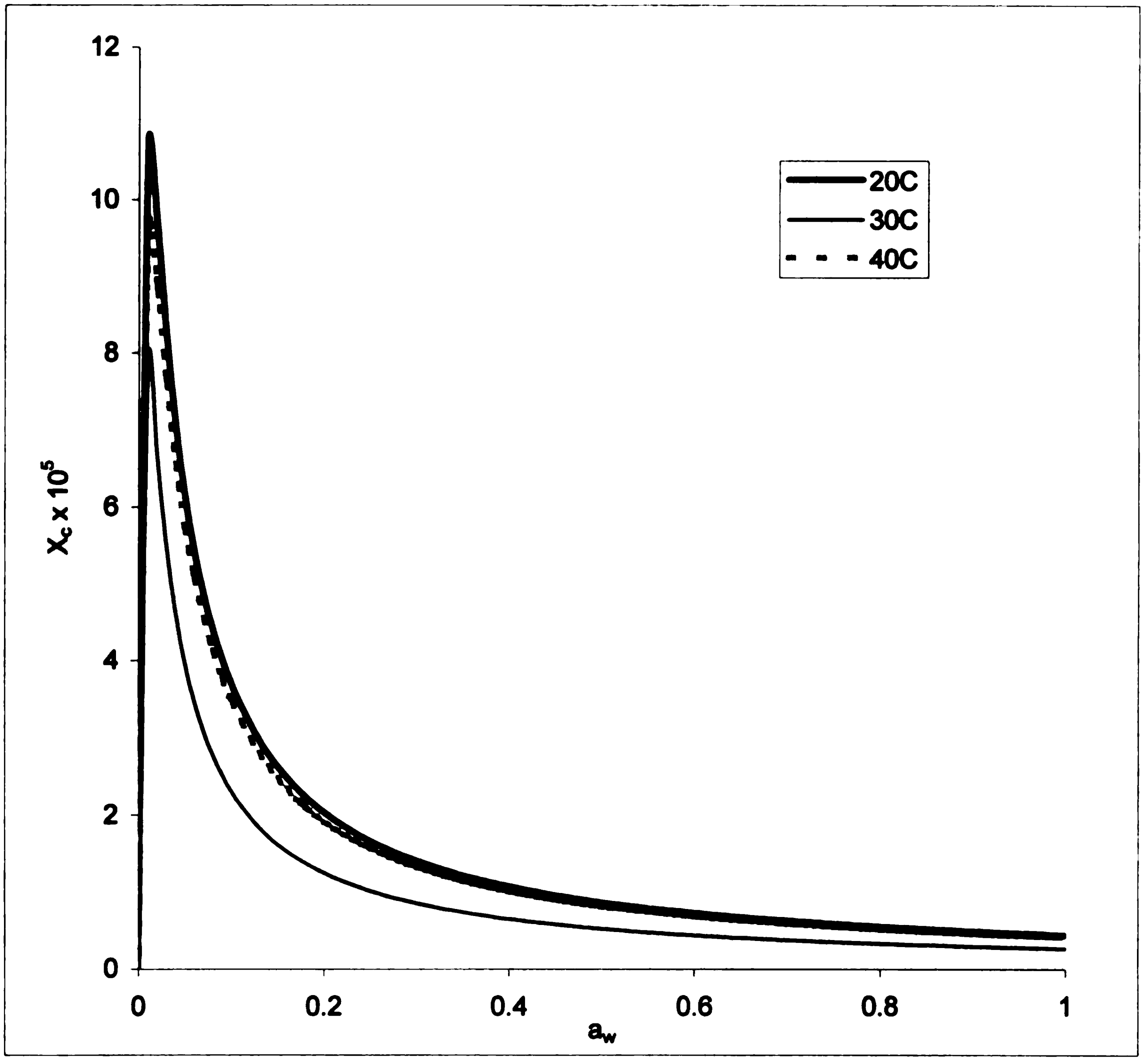

Figure 8. Plot of sensitivity coefficient of parameter C as a function of water activity

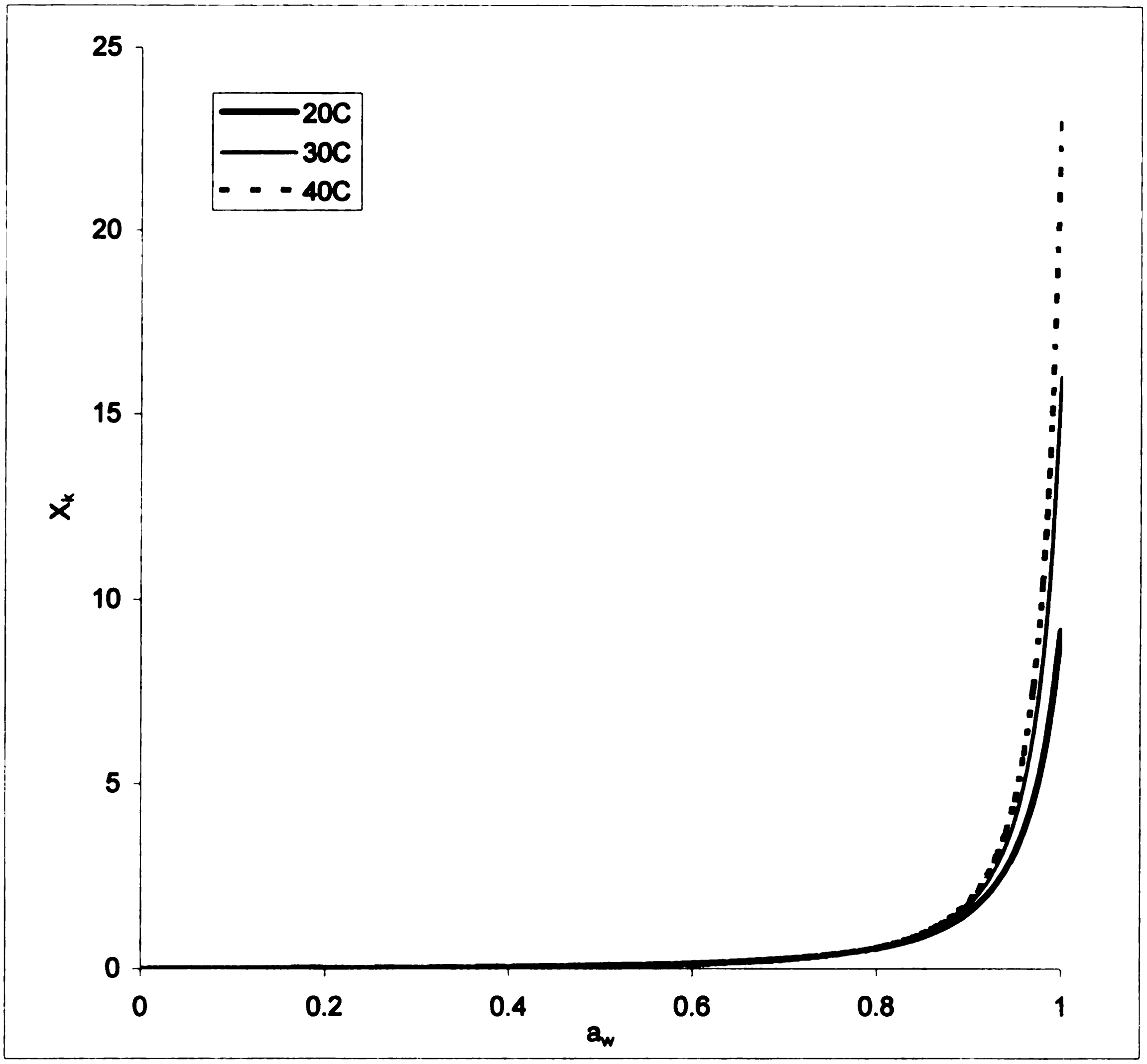

Figure 9. Plot of sensitivity coefficient of parameter k as a function of water activity

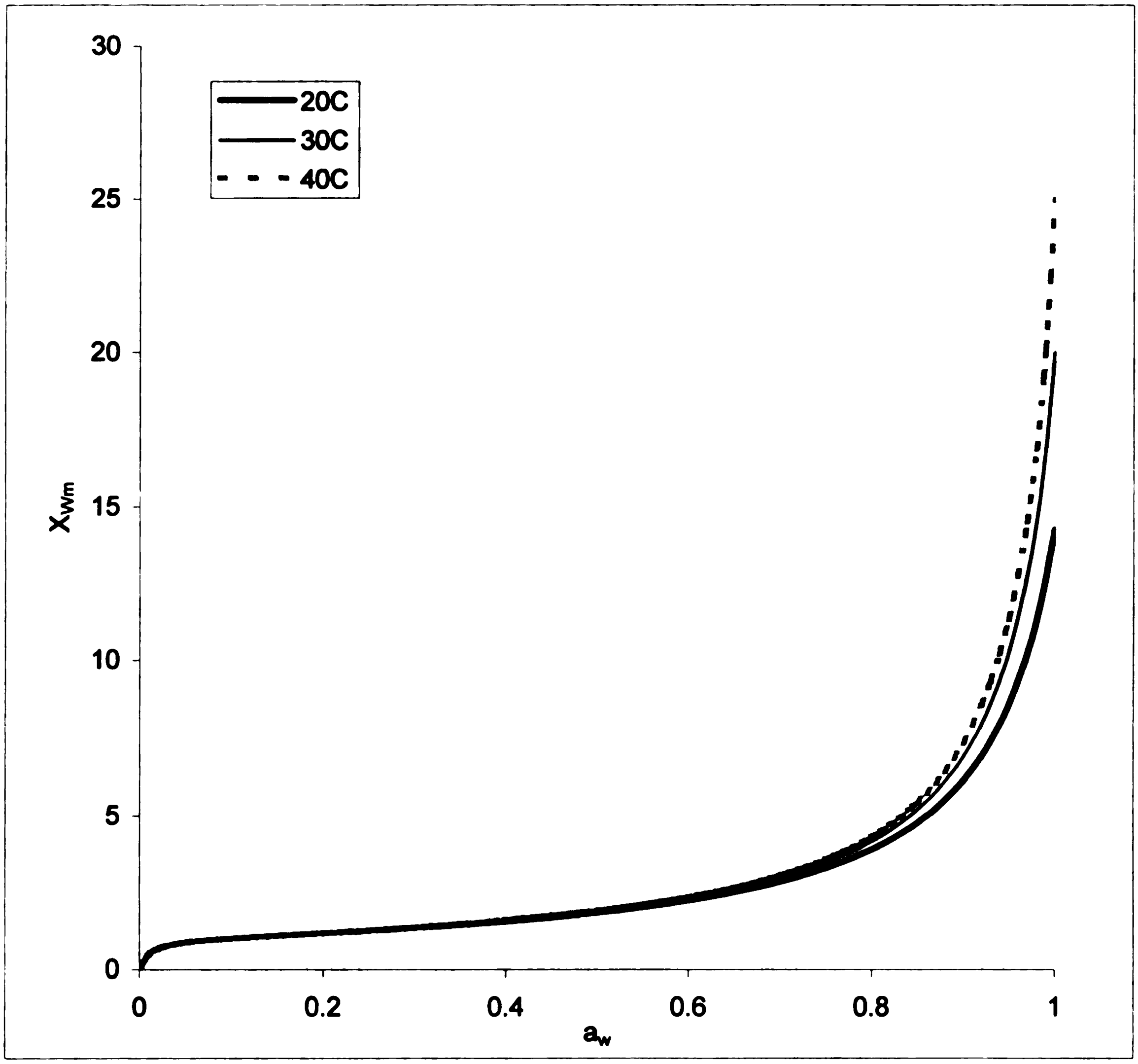

Figure 10. Plot of sensitivity coefficient of parameter W_m as a function of water activity

Water Vapor Transmission of Packaging Material

Permeance of six packaging materials were determined at approximately 40°C, 75% RH. The averages of permeance of packaging materials are presented in Figure 11. The data were analyzed by Minitab Release 11.12. Analysis of variance showed that all the data were significantly different at 95% confident level. Then a Fisher Least Significant Difference was employed for multiple comparison. Control material was excluded from the multiple comparison test due to its extremely high permeance. The statistical analysis indicated that permeance of all materials were significantly different at confident level of 95%. Packaging material type A and E had the lowest permeance or highest barrier properties. Therefore, they were chosen for the additional testing at 30°C, 75% RH and 25°C, 67% RH. The averages of permeance of all materials at all conditions are presented in Table 14. The experimental values of WVTR and permeance are presented in Appendix D.

Table 14. Permeances of packaging materials at 25, 30, and 40°C

Material	25°C		30°C		40°C	
	RH, %	P/ℓ^*	RH, %	P/ℓ^*	RH, %	P/ℓ^*
A	67 ± 0	1.8 ± 0.2	75 ± 1	1.6 ± 0.1	73 ± 3	1.2 ± 0.3
B	-	-	-	-	73 ± 3	1.7 ± 0.4
C	-	-	-	-	74 ± 3	2.4 ± 0.2
D	-	-	-	-	74 ± 3	4.2 ± 0.3
E	67 ± 0	0.44 ± 0.07	75 ± 1	0.46 ± 0.1	74 ± 3	0.49 ± 0.06
Control	-	-	-	-	75 ± 3	55 ± 1.3

$^*P/\ell$ is permeance, g/(m^2.day.mmHg)

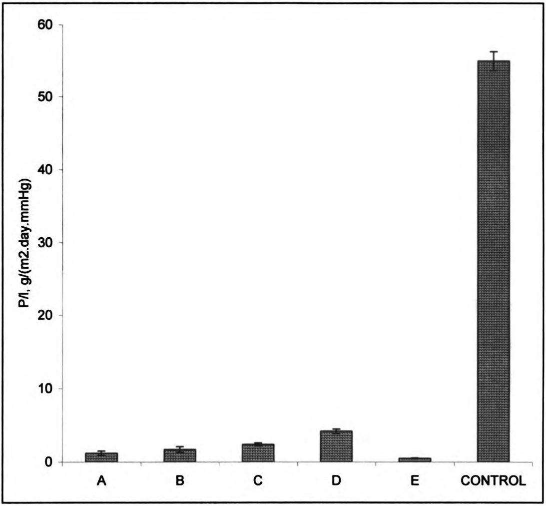

Figure 11. Permeances of packaging materials at 40°C, 75% RH

Permeance of material A increased with decreasing temperature, which indicated that permeance as a function of temperature did not follow Arrhenius equation. Based on analysis of variance and Fisher Least Significant Difference, at 95% confident level, although the permeance of material A at 25 was lower than at 30°C, they were not significantly different but both of them were significantly different from the permeance at 40°C. The permeance of material was plotted against the temperature as in Figure 12. Quadratic regression was performed by Microsoft Excel 97-SR1 to obtain the equation describing the effect of temperature on the permeance of material A in the range of 25 to 40°C as

$$(P/\ell) = -0.004T^2 + 0.3T - 3.8 \qquad (84)$$

where T = temperature, °C, and (P/ℓ) = permeance, $g/(m^2.day.mmHg)$

Permeance of material E increased with increasing of temperature, following Arrhenius equation. Analysis of variance and Fisher Least Significance Difference at 95% confidence indicated no significant difference in Permeance of material E in the temperature range of 25 to 40°C. Arrhenius plot was constructed, as in Figure 13, and Arrhenius equation was obtained from the linear regression of Arrhenius plot.

$$\log\left(\frac{P}{\ell}\right) = -\frac{294.93}{T} + 1.4351 \qquad (85)$$

where T is temperature, K and (P/ℓ) = permeance, $g/(m^2.day.mmHg)$

The activation energy was calculated using eqn. 86 and was found to be 0.97 KCal/mol. Low activation energy supported the result of little or no temperature effect.

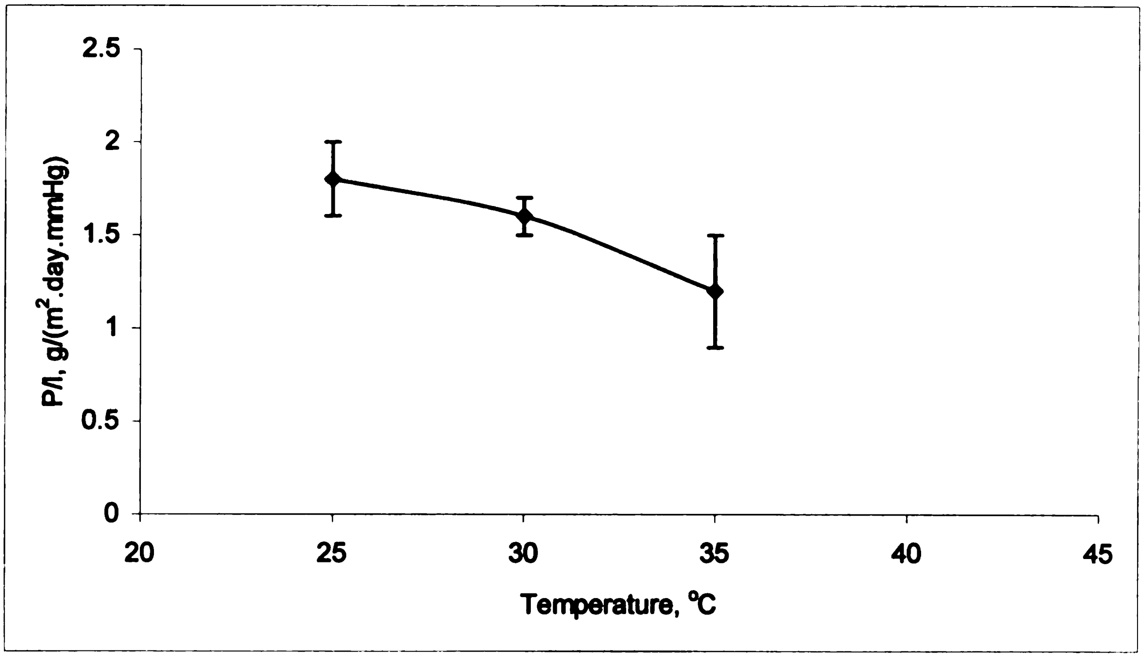

Figure 12. Permeance of material A as a function of temperature

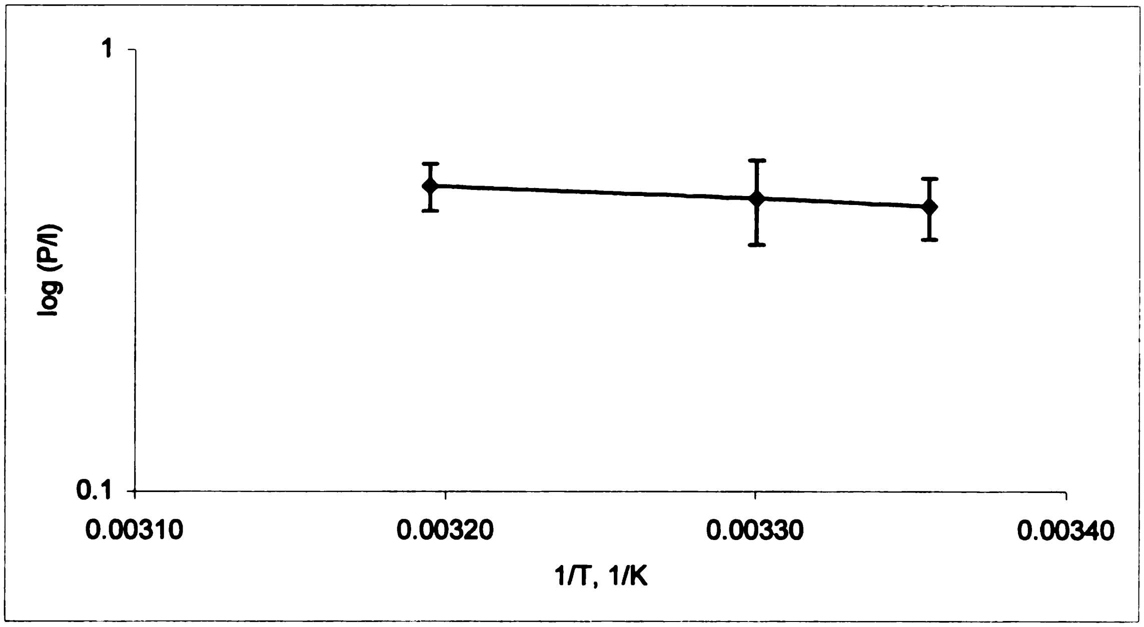

Figure 13. Arrhenius plot of material E

$$E_a = -\frac{s \times 2.3 \times R}{1000} \qquad (86)$$

where E_a is activation energy, KCal/mol, s is slope of Arrhenius plot obtained by linear regression, and R is gas constant, 1.987 KCal/mol.

Cardoso and Labuza (1983) reported non-Arrhenius behavior in permeability of paperboard. They provided an explanation of such behavior by assuming a reduction of mean pore size of paperboard at high temperature, resulting in decreasing diffusion rate because diffusion rate is partly proportional to the pore radius. The effect of diffusion was greater than the effect of solubility, which increases with increasing temperature. Since material A and E consist of F-flute corrugated board, this concept should be applicable to both materials but it is only applicable to material A.

The cross sectional area of material A and E were magnified by optical microscope with the magnification of 37.5 to examine their structure and provide potential explanation on their barrier property as a function of temperature. The structure of material A and E are presented in Figure 14 and 15, respectively. Both materials consisted of three layers from outside to inside the package: paper liner, corrugated paper, and paper and plastic liner. Two outer layer of both materials were same. The plastic layer in the inner liner of material A was difficult to locate from Figure 14 but with the visual and tearing inspection, the plastic layer was the innermost layer. As seen in Figure 15, it was obvious that the plastic layer of material E was incorporated in the middle of the inner liner.

The difference in the inner liner should be accounted for the difference in the barrier property as a function of temperature. In material A, the plastic and the paper layers acted as two separate layers. The paper layers, which faces high relative humidity

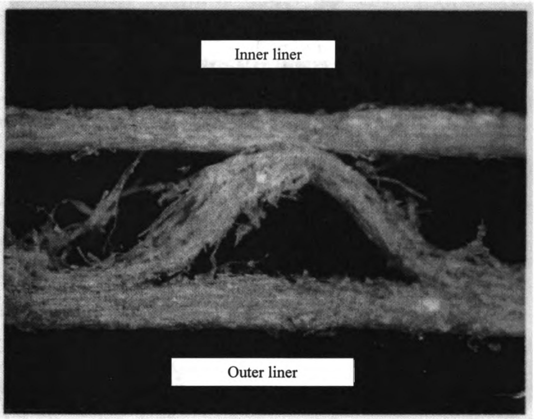

Figure 14. Cross sectional area of material A

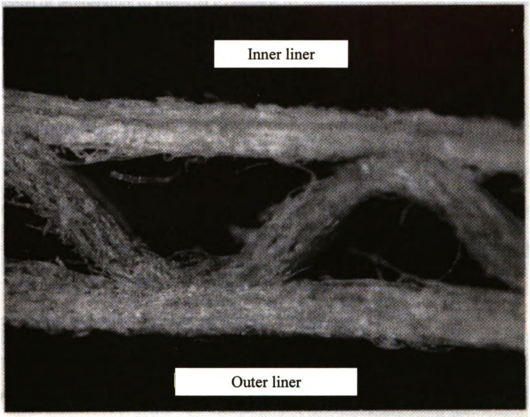

Figure 15. Cross sectional area of material E

environment, limited the amount of moisture exposed to the plastic barrier layer. Thus, permeability of the paper layer affected the driving force across the plastic layer. As temperature increased, permeability of the paper layer as well as the driving force decreased. Unlike material A, the plastic molecule in material E which disperse into voids between fibers restricted the change of pore size. Therefore, the permeability as a function of temperature of material E depends on the behavior of plastic which follows Arrhenius equation.

Package Integrity

Weight gain of small size FOL and Bellow style boxes made with material E and filled with desiccant was monitored as a function of time at 40°C, 74±1% RH to compare the performance of each style. The experimental moisture gain was then compared with the calculated moisture gain to evaluate package integrity in each box style. The experimental and calculated data are presented in Table 15.

The calculated and experimental weight gain of FOL and Bellow style boxes were plotted as a function of time as shown in Figure 16. The calculated data was represented by a band instead of a single line because it had incorporated an error in relative humidity fluctuation (1.4%) and the uncertainty in permeance (12.2%). The performance of Bellow style boxes were not significantly different from the performance of FOL style boxes.

Weight gain of large size bellow style boxes made from material A was monitored as a function of time. The experimental data was compared to calculated data in Table 16. Graphical comparison is presented in Figure 17. The calculated bar incorporating the error of relative humidity fluctuation (4.1%) and the uncertainty in permeance (25%).

After about 10 days for packages made from material E and 3 days for packages made from material A, the experimental data deviated from the calculated data. It was due to the moisture building up inside the package after desiccant were saturated. This made Δp in eqn. 77 variable and no longer equal to pressure outside the package.

Table 15. Experimental and calculated weight gain of Bellow and FOL style boxes made with material E and filled with desiccant at 40°C, 74±1 %RH

Time, day	Weight gain, g		
	Bellow	FOL	Calculated
0.0	0.00	0.00	0.00
1.0	2.31	2.41	2.72
2.0	5.16	5.15	5.43
3.0	8.00	7.90	8.15
4.0	10.88	10.68	10.86
5.0	13.69	13.48	13.58
6.0	16.46	16.20	16.30
7.0	19.22	18.93	19.01
8.0	21.94	21.63	21.73
9.0	24.54	24.18	24.45
10.0	27.13	26.72	27.16
11.0	29.43	29.11	29.88
12.1	31.74	31.47	32.82
13.0	33.27	33.00	35.31
14.0	34.80	34.43	38.03
15.0	36.16	35.85	40.74
16.0	37.60	37.26	43.46
17.0	38.92	38.56	46.18
18.0	40.08	39.75	48.89
19.0	41.17	40.83	51.61
20.0	42.20	41.87	54.32

Table 16. Experimental and calculated weight gain of material of Bellow style boxes made with material A and filled with desiccant at 40°C, 73±2% RH

Time, day	Weight gain, g	
	Experimental	Calculated
0.0	0.00	0.00
0.8	9.34	8.41
1.8	20.04	19.63
2.3	26.00	25.24
2.8	30.88	31.09
3.3	35.41	36.46
3.8	38.96	42.07
4.3	41.66	47.68
4.8	44.76	53.29
5.8	50.89	64.51
6.8	57.29	75.73

Since, for both packaging materials, experimental data was within the calculated bar, it can be concluded that the package was leak-proof. Water vapor permeated into the package only through the package wall. Therefore, permeance of package can be calculated from permeance of packaging material.

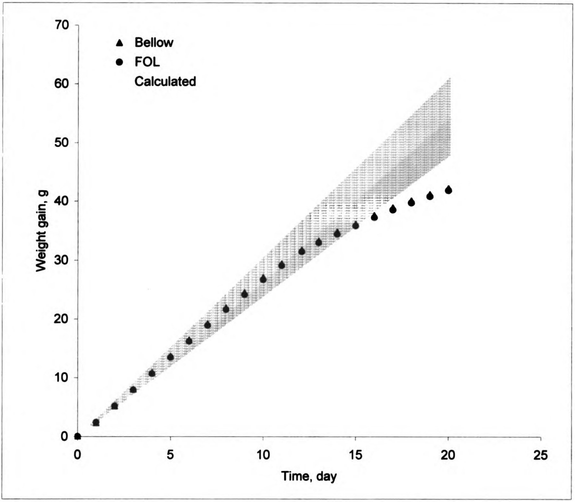

Figure 16. Experimental and calculated weight gain of material E boxes filled with desiccant at 40°C, 74±1 %RH.

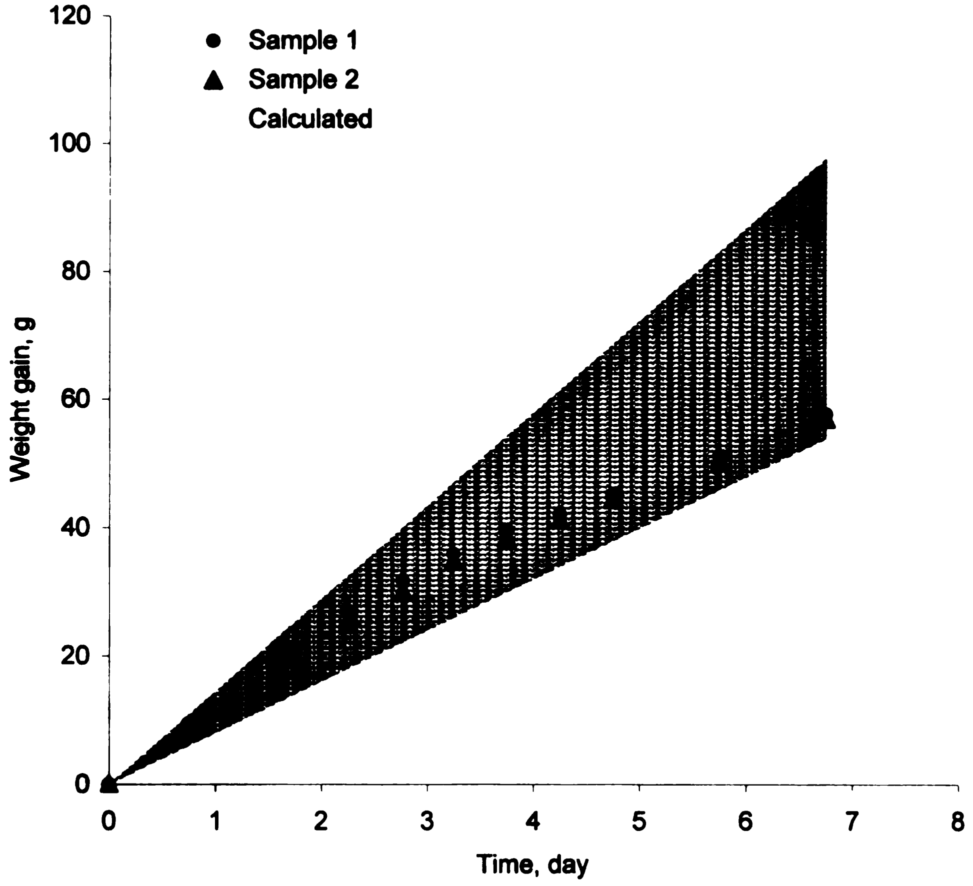

Figure 17. Experimental and calculated weight gain of small Bellow style boxes (material A) at 40°C, 73±2 %RH

CHAPTER 4

SHELF LIFE SIMULATION

Shelf life simulation consisted of shelf life modeling, model analysis, and model validation. All calculations performed in this chapter were based on the data obtained from Chapter 3.

Shelf Life Modeling

GAB equation was the best equation to fit the moisture sorption isotherm of non-fat dry milk. Therefore, the shelf life model was developed based on the mass balance of water permeated into the package and the amount of water sorbed by non-fat dry milk and GAB equation.

Assumptions for the shelf life modeling were:

1. The moisture permeated into the package is calculated based on permeance of packaging material because the package has no discontinuities.
2. All the moisture permeated into the package is absorbed by the product and distributed to the whole product. Therefore, the quantity of permeant in the headspace is negligible.
3. The equilibrium between product and headspace can be achieved within a short period of time.

4. The water activity inside the package is a function of moisture content of the product expressed by GAB equation.

The shelf life model for non-fat dry milk was developed as follow (Diosady et al. 1996):

Water permeated into the package is given by

$$dW = \frac{P}{\ell} \cdot A \cdot \Delta p \cdot dt \tag{87}$$

and the water sorbed by the product is

$$dW = W_d \frac{dM}{100} \tag{88}$$

Substituting eqn. 87 into eqn. 88, gives

$$\frac{P}{\ell} A \, \Delta p \, dt = W_d \frac{dM}{100} \tag{89}$$

$$\frac{P}{\ell} A \, \Delta p \int_0^t dt = \frac{W_d}{100} \int_{M_i}^{M_f} dM \tag{90}$$

The value of $\Delta p = p_o - p_i$ is the difference in partial water vapor pressure across the package wall being p_o the outside value and p_i the inside value. The partial pressure inside the package is a function of moisture content. In order to integrate eqn. 90, Δp need to be expressed as $p_o - p_i(M)$ and eqn. 90 can be rewritten as

$$\frac{P}{\ell} A \, \Delta p \int_0^t dt = \frac{W_d}{100} \int_{M_i}^{M_f} \frac{dM}{p_o - p_i(M)} \tag{91}$$

Partial pressure outside the package, p_o, is a function of relative humidity and saturated water vapor pressure as

$$p_o = p_s \frac{RH_o}{100} \tag{92}$$

Water activity in the package headspace directly relates to moisture content of non-fat dry milk by GAB equation. GAB equation (eqn. 62) can be rewritten in the form of water activity as a function of moisture content as follows:

$$\frac{W_m \cdot C \cdot k \cdot a_w}{M} = 1 - ka_w + Cka_w - ka_w + k^2a_w^2 + Ck^2a_w^2 \tag{93}$$

$$k^2(1-C)a_w^2 + k\left(C\left(1-\frac{W_m}{M}\right)-2\right)a_w + 1 = 0 \tag{94}$$

Since eqn. 94 is in quadratic form, there are two solutions. Only the positive solution will be used and can be rewritten as

$$a_w = \frac{2+\left(\frac{W_m}{M}-1\right)C-\sqrt{\left(2+\left(\frac{W_m}{M}-1\right)C\right)^2-4+4C}}{2k(1-C)} \tag{95}$$

Therefore, the value of $p_i = p_s.a_w$ can be expressed as a function of M as

$$p_i = p_s\frac{2+\left(\frac{W_m}{M}-1\right)C-\sqrt{\left(2+\left(\frac{W_m}{M}-1\right)C\right)^2-4+4C}}{2k(1-C)} \tag{96}$$

Substituting eqn. 92 and 96 into eqn. 91

$$100\left(\frac{P}{\ell}\right)\cdot\frac{A\cdot p_s}{W_d}\int_0^t dt = \int_{M_i}^{M_f}\frac{dM}{\left(\frac{RH}{100}\right)-\left[\frac{2+\left(\frac{W_m}{M}-1\right)C-\sqrt{\left(2+\left(\frac{W_m}{M}-1\right)C\right)^2-4+4C}}{2k(1-C)}\right]} \tag{97}$$

$$100\left(\frac{P}{\ell}\right)\cdot\frac{A\cdot p_s}{W_d}\,\frac{1}{2k(1-C)}\int_0^t dt \;=$$

$$\int_{M_i}^{M_f}\frac{dM}{\left(2k(1-C)\left(\frac{RH}{100}\right)\right)-2-\left(\frac{W_m}{M}\right)C+C+\sqrt{\left(\frac{W_m}{M}\right)(4C-2C^2)+\left(\frac{W_m}{M}\right)^2C^2+C^2}} \qquad (98)$$

Assign

$$\alpha \;=\; 100\left(\frac{P}{\ell}\right)\cdot\frac{A\cdot p_s}{W_d}\,\frac{1}{2k(1-C)} \qquad (99)$$

$$\beta \;=\; \left[2k(1-C)\cdot\left(\frac{RH}{100}\right)\right]-2+C \qquad (100)$$

Then, eqn. 97 can be rewritten as

$$\alpha t \;=\; \int_{M_i}^{M_f}\frac{dM}{\beta-\left(\frac{W_m}{M}\right)C+\sqrt{\left(\frac{W_m}{M}\right)(4C-2C^2)+\left(\frac{W_m}{M}\right)^2C^2+C^2}} \qquad (101)$$

If C value is much larger than 2, 4C will be much smaller than $2C^2$ and can be neglected. In this study, the minimum C value is about 95, which make $(-2C^2)$ differ from $(4C-2C^2)$ for approximately 2%. Therefore, 4C can be disregarded and eqn. 101 can be rewritten as

$$\alpha t \;=\; \int_{M_i}^{M_f}\frac{dM}{\beta-\left(\frac{W_m}{M}\right)C+C\sqrt{\left(\frac{W_m}{M}\right)^2-2\left(\frac{W_m}{M}\right)+1}} \qquad (102)$$

Since $\left(\frac{W_m}{M}\right)^2-2\left(\frac{W_m}{M}\right)+1 \;=\; \left[1-\left(\frac{W_m}{M}\right)\right]^2$, eqn. 102 can be rewritten as

$$\alpha t \;=\; \int_{M_i}^{M_f}\frac{dM}{\beta-\left(\frac{W_m}{M}\right)C+C\sqrt{\left[1-\left(\frac{W_m}{M}\right)\right]^2}} \qquad (103)$$

$$\alpha t = \int_{M_i}^{M_f} \frac{M dM}{M(\beta + C) - 2W_m C} \tag{104}$$

Making a change variable, $U = M(\beta+C)-2W_mC$, and $dU/dM = \beta+C$. Eqn. 104 can be rewritten as

$$\alpha t = \int_{M_i(\beta+C)-2W_mC}^{M_f(\beta+C)-2W_mC} \frac{U + 2W_m C}{(\beta + C)} \frac{dU}{(\beta + C)} \frac{1}{U}$$

(105)

$$\alpha t = \frac{1}{(\beta + C)^2} \left[U + 2W_m C(\ln U) \right] \Bigg|_{M_i(\beta+C)-2W_mC}^{M_f(\beta+C)-2W_mC} \tag{106}$$

$$\alpha t = \frac{1}{(\beta + C)^2} \left[(\beta + C)(M_f - M_i) - 2W_m C \ln \frac{(M_f(\beta + C) - 2W_m C)}{(M_i(\beta + C) - 2W_m C)} \right] \tag{107}$$

Assign $$\theta = \beta + C = (1 - C)\left[\left(2k\left(\frac{RH}{100} \right) \right) - 2 \right] \tag{108}$$

Substituting eqn. 108 into eqn. 107

$$t = \frac{1}{\alpha\theta} \left[M_f - M_i - \frac{2W_m C}{\theta} \ln \frac{(M_f\theta - 2W_m C)}{(M_i\theta - 2W_m C)} \right] \tag{109}$$

where $$\alpha = 100\left(\frac{P}{\ell} \right) \cdot \frac{A \cdot p_s}{W_d} \cdot \frac{1}{2k(1 - C)}$$

$$\theta = (1 - C) \cdot \left[\left(2k\left(\frac{RH}{100} \right) \right) - 2 \right]$$

Shelf life model at 40 °C and 25 °C

The shelf life model of packaged non-fat dry milk at a specific condition was developed based on the shelf life model and the results from Chapter 3. Parameters employed in shelf life modeling of non-fat dry milk packaged in small and large size Bellow style packages made from material A and E and stored at two storage condition are presented in Table 17.

Table 17. Parameters used for shelf life modeling of packaged non-fat dry milk at two storage conditions

Parameter	Condition					
	HiAS	HiAL	HiES	LoAS	LoAL	LoES
Temperature, °C	40	40	40	25	25	25
RH, %	83	83	83	67	67	67
Packaging material	A	A	E	A	A	E
Package size	Small	large	small	small	large	small
C	95.4	95.4	95.4	120.16	120.16	120.16
K	0.96	0.96	0.96	0.94	0.94	0.94
W_m, % dry basis	3.66	3.66	3.66	4.19	4.19	4.19
p_s, mmHg	55.324	55.324	55.324	23.756	23.756	23.756
M_i, % dry basis	4.86	4.86	4.86	4.86	4.86	4.86
A, m^2	0.1354	0.2315	0.1354	0.1354	0.2315	0.1354
W_d, g	273.56	333.96	276.72	276.88	334.09	277.07
P/ℓ, g/(m^2.day.mmHg)	1.2	1.2	0.49	1.8	1.8	0.44

Hi is high storage temperature and relative humidity,
Lo is low storage temperature and relative humidity,
A is package made from material A,
E is package made from material E,
S is small package, and
L is large package

Shelf life models at each specific condition are:

HiAS (High temperature and relative humidity, small package made from material A)

$$t = -\frac{1}{0.70}\cdot\left[M_f - 4.86 + 18.20\cdot\ln\left(\frac{38.39M_f - 698.77}{-512.19}\right)\right] \qquad (110)$$

HiAL (High temperature and relative humidity, large package made from material A)

$$t = -\frac{1}{0.97}\cdot\left[M_f - 4.86 + 18.20\cdot\ln\left(\frac{38.39M_f - 698.77}{-512.19}\right)\right] \tag{111}$$

HiES (High temperature and relative humidity, small package made from material E)

$$t = -\frac{1}{0.28}\cdot\left[M_f - 4.86 + 18.20\cdot\ln\left(\frac{38.39M_f - 698.77}{-512.19}\right)\right] \tag{112}$$

LoAS (Low temperature and relative humidity, small package made from material A)

$$t = -\frac{1}{0.82}\cdot\left[M_f - 4.86 + 11.43\cdot\ln\left(\frac{88.23M_f - 1006.94}{-578.14}\right)\right] \tag{113}$$

LoAL (Low temperature and relative humidity, large package made from material A)

$$t = -\frac{1}{1.16}\cdot\left[M_f - 4.86 + 11.43\cdot\ln\left(\frac{88.23M_f - 1006.94}{-578.14}\right)\right] \tag{114}$$

LoES (Low temperature and relative humidity, small package made from material E)

$$t = -\frac{1}{0.20}\cdot\left[M_f - 4.86 + 11.43\cdot\ln\left(\frac{88.23M_f - 1006.94}{-578.14}\right)\right] \tag{115}$$

Shelf Life Model Analysis

In the shelf life model based on GAB equation, nine parameters are needed to calculate shelf life based on the final equilibrium moisture content. The parameters can be classified into three groups: parameters describing product characteristics, parameters describing package characteristics, and parameters describing storage conditions. Parameters describing product characteristics include GAB constants (C, W_m, and k) and M_i. Parameters describing package characteristics include A, W_d, and P/ℓ. Parameters describing storage condition include RH and p_s. Temperature is included in the shelf life model through saturated water vapor pressure, p_s, sorption isotherm, and permeance or permeability of package. In packaging design and optimization, it is necessary to learn how each parameter in the model influences the global outcome of the model. One way to understand the impact of each parameter on the independent variable t or shelf life is by performing the sensitivity analysis of the model.

Sensitivity coefficient, χ, allows the evaluation of the sensitivity of the model to each parameter. The plus or minus sign of the sensitivity coefficient indicates whether the change in the parameter will shorten or lengthen the shelf life. The shelf life will be longer when the parameter which has positive sensitivity coefficient increases or when the parameter whose sensitivity coefficient is negative decreases. The absolute value indicates the magnitude of the impact. When the parameter with higher absolute value of sensitivity coefficient changes, the shelf life will be altered more than when the parameter with a lower value of sensitivity coefficient changes.

The sensitivity of coefficient of each parameter are presented in Appendix E. From the sensitivity coefficient, it can be said that the shelf life model was not linear in its parameter because a sensitivity coefficient of one parameter was a function of other parameters. To analyze the sensitivity of one parameter, the value of other parameters must be assigned. Sensitivity coefficients were calculated at the certain combination of factors. The factors were described by assigned values which are divided into I: storage condition, II: permeance, and III: size of package. The calculation was performed at 8 factor combinations based on full 2^3 factorial design. The calculation of $\chi_{(P/\ell)}$ and $\chi_{A/Wd}$ were performed at 4 factor combinations based on 2^2 factorial design (I and III) and (I and II), respectively. The description of parameter in each group and its assigned values are presented in Table 18. Table 19 summarize the value of sensitivity coefficient at each condition. The values and the plot of sensitivity coefficient as a function of the parameter are presented in Appendix E. The example of the plot of parameter C against its sensitivity coefficients are presented in Figure 18.

Table 18. Conditions used in sensitivity coefficient calculation.

Condition	Storage condition		Permeance		Size of package	
	High S_H	Low S_L	High R_H	Low R_L	High P_S	Low P_L
Description	40°C, 83% RH	25°C, 67% RH	High permeance	Low permeance	Small	Large
C	95.46	120.16	-	-	-	-
K	0.96	0.94	-	-	-	-
W_m, % dry basis	3.66	4.19	-	-	-	-
p_s, mmHg	55.324	23.756	-	-	-	-
RH, %	83	67	-	-	-	-
P/ℓ^*	-	-	1.8	0.44	-	-
A, m^2	-	-	-	-	0.1354	0.2315
W_d, g	-	-	-	-	275	333
M_i, % dry basis	4.86	4.86	-	-	-	-
M_f, % dry basis	17.82	11.26	-	-	-	-

* g/(m^2.day.mmHg)

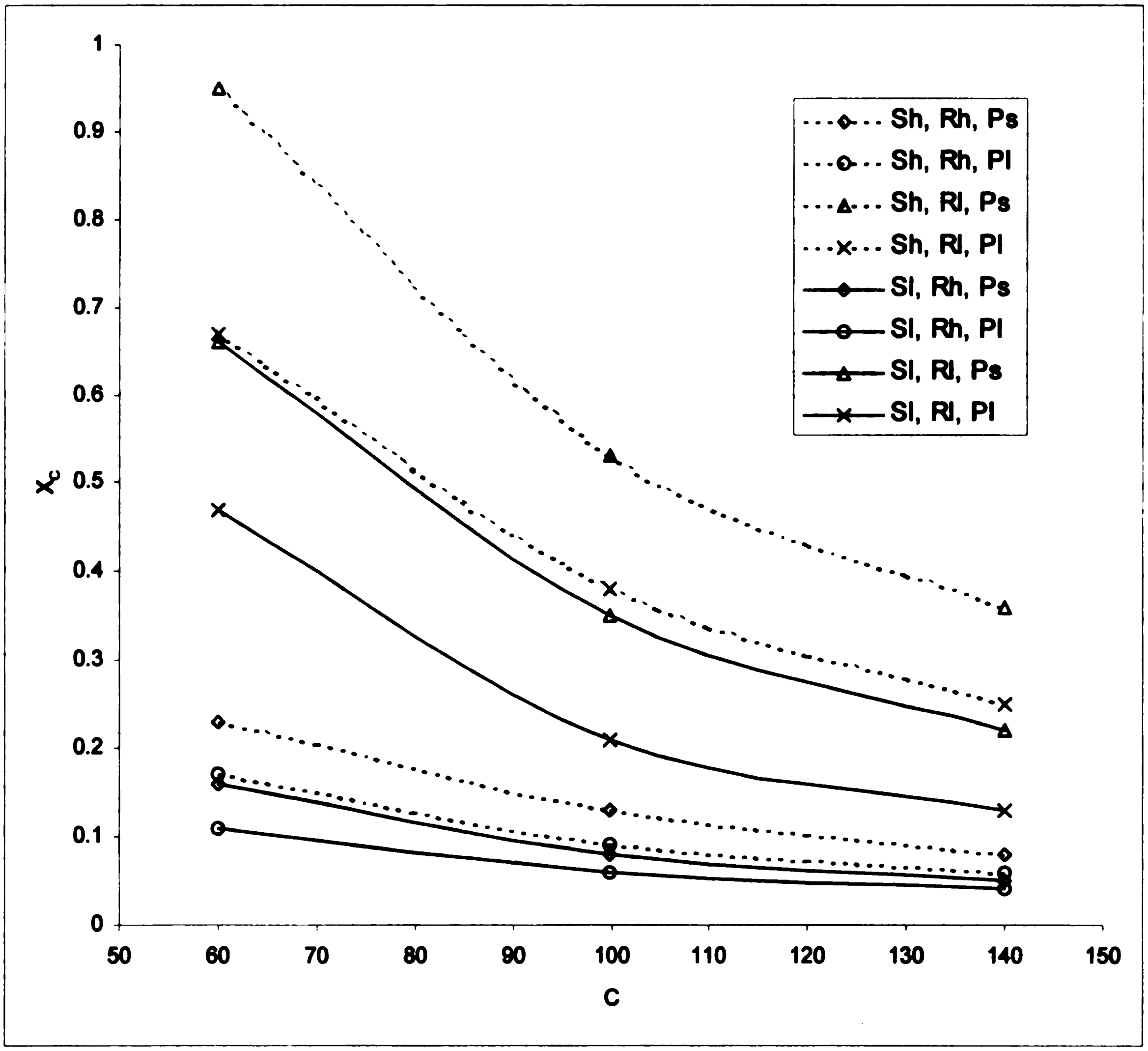

Figure 18. The plot of χ_C as a function of C at different factor combinations

Table 19. Sensitivity coefficients of parameters in shelf life model

		S_H, R_H, P_S	S_H, R_H, P_L	S_H, R_L, P_S	S_H, R_L, P_L	S_L, R_H, P_S	S_L, R_H, P_L	S_L, R_L, P_S	S_L, R_L, P_L
χ_C^{*}	Min	0.08	0.06	0.36	0.25	0.05	0.04	0.22	0.13
	Max	0.23	0.17	0.95	0.67	0.16	0.11	0.66	0.47
χ_{Wm}^{**}	Min	-11	-8	-45	-32	-9	-7	-39	27
	Max	-990	-701	-4048	-2868	-150	-141	-610	432
χ_k^{*}	Min	-238	-169	-974	-690	-127	-90	-520	368
	Max	-4818	-3412	-19700	-13900	-1373	-970	-5615	3978
χ_{Mi}^{**}	Min	-0.19	-0.13	-0.78	-0.56	-0.43	-0.3	-1.7	1.2
	Max	-0.37	-0.26	-1.5	-1.06	-0.94	-0.66	-3.8	2.7
χ_{Wd}^{***}		0.21	0.12	0.86	0.5	0.16	0.09	0.67	0.38
χ_A^{*}	Min	-372	-158	-1520	-644	-283	-120	-1160	492
	Max	-591	-205	-2417	-837.3	-451	-156	-1845	639
$\chi_{A/Wd}^{*}$	Min	-0.06		-0.02		-0.004		-0.02	
$x10^7$	Max	-2.84		-11.6		-2.16		-8.86	
χ_{ps}^{*}	Min	-0.4	-0.3	-1.5	-1.1	-0.1	-0.1	-0.5	0.3
	Max	-38	-27	-154	-109	-12	-8	-48	34
χ_{RH}^{**}	Min	-2.9	-2	-11.7	-8.3	-5.7	-4	-23	16
	Max	-68	-481	-2778	-197	-456	-322.8	-1864.8	1320
χ_R^{*}	Min	S_H, P_S	-29	S_H, P_L	-20	S_L, P_S	-22	S_L, P_L	-16
	Max		-649		-460		-495		-350

* Sensitivity coefficients decrease with increasing parameter

** Sensitivity coefficients increase with increasing parameter

*** Sensitivity coefficients are independent of magnitude of parameter

From the sensitivity analysis, parameters had either positive or negative values of sensitivity coefficient. Parameters with negative value of sensitivity coefficient include k, W_m, M_i, A, A/W_d, P/ℓ, p_s, and RH. As these parameters increase, shelf life of non-fat dry milk decreases. Parameters with positive value of sensitivity coefficient included C, M_f, and W_d. As these parameters increase, shelf life of non-fat dry milk increases. This means that the shelf life can be increased by either reduction of parameter k or W_m of GAB equation, increasing parameter C, lowering initial moisture content (M_i), reduction of surface area of package (A), reduce the ratio of surface area to product weight, filling mo

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more product in each package (W_d), using packaging material with better barrier property (P/ℓ), or store the product at lower temperature and relative humidity (p_s and RH).

The impact of each parameter on the shelf life were compared by comparing the absolute value of the sensitivity coefficient. When consider each single parameter, k had the highest sensitivity coefficient which infer that parameter k had the highest impact on the shelf life, then W_m, A, M_f, RH, P/ℓ, p_s and M_i, in this order. The impact of parameter C and W_d on shelf life was minute. The reduction of parameter k could significantly increase shelf life while the increasing of parameter C may insignificantly or may not increase the shelf life. Change in product dry weight may not seem to be significant when consider only the value of χ_{W_d} but it does has high impact on shelf life because it will change the ratio of surface area and product dry weight which had higher sensitivity coefficient than χ_k.

The change in any parameter for NFDM packaged in small box made from low permeance package altered shelf life more than the change in the same parameter for other boxes. When consider the same type of package, the shelf life model was more sensitive to the change of W_m, M_i, and RH when the product was stored at low temperature and relative humidity (or low temperature in case of parameter RH) than at high temperature and relative humidity. The model was more sensitive to the change of C, k, M_f, A, P/ℓ, W_d, p_s, and A/W_d when non-fat dry milk was stored at high temperature and relative humidity (or high relative humidity in case of p_s) than at low temperature and relative humidity.

The impact of parameter on the shelf life changed as the parameter increased or decreased except for W_d that its sensitivity coefficient at the certain factor combination was independent of the change in product weight. When GAB constants (C, W_m, and k), saturated water vapor pressure, p_s, surface area, A, and permeance, P/ℓ, increased, they had less impact on shelf life. The impact of initial moisture content and relative humidity increased as the parameter increased.

Model Validation

The validation of the shelf life model was conducted with boxes of two sizes at two isothermal storage conditions. The predicted moisture content was calculated using shelf life models presented in eqn. 110 to 115. The experimental and predicted moisture content of the packaged milk powder as a function of time at 40°C and 25°C are presented in Table 20 and 21, respectively. Iteration method performed by computer software, namely Mathematica, was employed to determine the value of moisture content as a function of time.

Figure 19 to 24 show the graph of predicted and experimental moisture content as a function of time. Predicted values are presented as a band incorporating uncertainties of the parameters. The uncertainties of parameters are presented in Appendix E. The predicted band was constructed using x-axis error bar to describe error in the independent variable t. The width of the band was equal to the percent error of each specific package at certain storage condition. Percent errors were calculated based on Gauss' Law of Error Propagation. All parameters and M_f value must be specified in order to calculate the percent error. Therefore, values of percent error were calculated at certain values of variable M_f and are presented in Appendix F. The average of the percent error of central M_f values were chosen to represent the error bar and are presented in Table 22.

Total error for certain type of package and storage condition at each value of final moisture content consists of uncertainties from GAB constants, initial moisture content, product dry weight, permeance of packaging material, relative humidity, and saturated water vapor pressure. Graphs of error contributed from each parameter relative to the total percent error at each specific storage condition are presented in Appendix F. The contribution of an uncertainty of each parameter to the total error related to the sensitivity coefficient of that parameter and the magnitude of its uncertainty. The error was mainly from P/ℓ, W_m, M_i, and k. The error due to M_i was significant only when M_f was close to M_i. The error from W_m and P/ℓ were higher when M_f was close to M_i and became less as M_f is closer to equilibrium moisture content of that particular storage condition. The error due to parameter k increased as M_f was approaching equilibrium moisture content. At 40°C, the error due to relative humidity was more significant than at 25°C and equally contributes to the total error for all M_f values.

As seen in Figure 19 to 21, the experimental moisture contents of non-fat dry milk as a function of time were within the predicted band upto 16% moisture content (dry basis) or 0.8 a_w where the growth of microorganism was observed outside boxes. The decreasing of moisture content of non-fat dry milk in boxes made from material A was not because of the loss of moisture but the loss of dry mass due to the growth of microorganism. The shelf life model based on GAB equation was applicable to predict the moisture content of non-fat dry milk at this condition regardless of permeance of packaging material but the model was unusable when there is a growth of microorganism.

Table 20. Experimental and predicted moisture content as a function of time of non-fat dry milk in three different packages stored at 40°C, 83% RH

Time, day	Moisture content, % (dry basis)					
	Material A-small		Material A-large		Material E-small	
	Experimental	Calculated	Experimental	Calculated	Experimental	Calculated
0.0	4.86 ± 0.00	4.86	4.86 ± 0.00	4.86	4.86 ± 0.00	4.86
0.8	6.03 ± 0.11	6.05	6.10 ± 0.07	6.44	5.10 ± 0.03	5.39
2.3	8.01 ± 0.22	7.72	8.32 ± 0.13	8.49	6.02 ± 0.03	6.26
2.8	8.49 ± 0.24	8.17	8.94 ± 0.16	9.00	6.27 ± 0.02	6.52
3.8	9.43 ± 0.32	8.94	9.93 ± 0.18	9.88	6.71 ± 0.11	6.99
4.3	9.79 ± 0.35	9.28	10.27 ± 0.17	10.27	6.88 ± 0.11	7.21
5.8	10.89 ± 0.37	10.16	11.40 ± 0.19	11.25	7.37 ± 0.12	7.80
6.8	11.52 ± 0.39	10.67	12.01 ± 0.28	11.79	7.70 ± 0.11	8.15
8.8	12.87 ± 0.41	11.54	13.32 ± 0.19	12.70	8.35 ± 0.11	8.79
9.7	13.32 ± 0.40	11.82	13.79 ± 0.17	13.00	8.63 ± 0.11	9.00
12.7	14.07 ± 0.34	12.78	14.43 ± 0.20	13.98	9.33 ± 0.13	9.78
14.8	14.12 ± 0.29	13.37	14.39 ± 0.19	14.55	9.78 ± 0.13	10.28
16.8	14.60 ± 0.27	13.83	14.85 ± 0.18	14.98	10.13 ± 0.14	10.68
17.8	14.94 ± 0.28	14.03	15.20 ± 0.21	15.17	10.34 ± 0.14	10.87
20.8	15.86 ± 0.29	14.57	16.11 ± 0.22	15.66	10.90 ± 0.14	11.39
21.8	16.32 ± 0.26	14.73	16.55 ± 0.22	15.80	11.26 ± 0.14	11.55
23.8	16.41 ± 0.22	15.02	16.58 ± 0.20	16.06	11.53 ± 0.15	11.86
24.8	16.51 ± 0.21	15.16	16.65 ± 0.21	16.17	11.68 ± 0.15	12.00
26.8	16.64 ± 0.18	15.41	16.72 ± 0.23	16.38	11.95 ± 0.14	12.27
27.8	16.70 ± 0.17	15.52	16.78 ± 0.23	16.47	12.05 ± 0.15	12.40
29.8	16.95 ± 0.17	15.74	17.09 ± 0.23	16.65	12.32 ± 0.15	12.65
31.8	17.16 ± 0.15	15.93	17.28 ± 0.24	16.80	12.54 ± 0.15	12.88
34.8	17.95 ± 0.20	16.18	18.16 ± 0.26	16.99	13.05 ± 0.14	13.20
42.8	18.41 ± 1.03	16.71	18.10 ± 0.99	17.37	14.01 ± 0.16	13.94
48.7	16.12 ± 1.58	16.99	15.31 ± 2.59	17.55	14.57 ± 0.18	14.38
51.8	15.00 ± 1.70	17.12	14.20 ± 3.32	17.63	14.75 ± 0.18	14.60
54.8	12.34 ± 1.68	17.20	11.69 ± 4.85	17.69	15.10 ± 0.18	14.79
56.8					15.26 ± 0.18	14.91
61.8					15.64 ± 0.18	15.19
65.8					15.91 ± 0.19	15.39
67.8					16.06 ± 0.19	15.66
73.8					16.51 ± 0.17	15.82

Table 21. Experimental and predicted moisture content as a function of time of non-fat dry milk in three different packages stored at 25°C, 67% RH

Time, day	Moisture Content, % dry basis					
	Material A-small		Material A-large		Material E-small	
	Experimental	Calculated	Experimental	Calculated	Experimental	Calculated
0.0	4.86 ± 0.00	4.86	4.86 ± 0.00	4.86	4.86 ± 0.00	4.86
0.8	5.22 ± 0.00	5.59	5.40 ± 0.04	5.84	4.97 ± 0.01	5.05
1.7	5.67 ± 0.05	6.17	6.13 ± 0.13	6.57	5.10 ± 0.02	5.23
2.7	6.10 ± 0.06	6.79	6.89 ± 0.16	7.31	5.26 ± 0.02	5.46
3.8	6.69 ± 0.12	7.42	7.66 ± 0.21	8.02	5.44 ± 0.04	5.73
4.7	7.02 ± 0.11	7.73	8.14 ± 0.17	8.36	5.57 ± 0.04	5.87
5.7	7.45 ± 0.17	8.09	8.70 ± 0.20	8.75	5.73 ± 0.05	6.05
6.7	8.21 ± 0.21	8.41	9.48 ± 0.15	9.07	6.03 ± 0.06	6.23
7.7	8.75 ± 0.49	8.69	9.65 ± 0.09	9.35	6.20 ± 0.07	6.39
8.7	8.92 ± 0.25	8.93	9.78 ± 0.08	9.59	6.35 ± 0.07	6.54
9.7	9.22 ± 0.23	9.15	9.86 ± 0.06	9.79	6.48 ± 0.08	6.69
10.8	9.49 ± 0.15	9.39	9.90 ± 0.07	10.01	6.57 ± 0.14	6.89
11.7	9.65 ± 0.10	9.51	9.94 ± 0.04	10.13	6.74 ± 0.09	6.96
12.7	9.77 ± 0.10	9.67	10.00 ± 0.03	10.27	6.87 ± 0.09	7.08
13.7	9.86 ± 0.09	9.81	10.04 ± 0.01	10.39	6.99 ± 0.10	7.20
14.7	9.95 ± 0.11	9.94	10.07 ± 0.02	10.50	7.11 ± 0.11	7.32
16.7	10.14 ± 0.11	10.16	10.19 ± 0.04	10.68	7.36 ± 0.12	7.53
18.7	10.30 ± 0.11	10.35	10.25 ± 0.01	10.82	7.61 ± 0.13	7.73
19.8	10.45 ± 0.12	10.45	10.37 ± 0.04	10.89	7.83 ± 0.14	7.85
21.8	10.58 ± 0.13	10.59	10.48 ± 0.07	10.99	8.04 ± 0.14	8.02
23.7	10.67 ± 0.11	10.69	10.54 ± 0.07	11.06	8.27 ± 0.15	8.17
27.7	10.88 ± 0.10	10.88	10.66 ± 0.04	11.18	8.67 ± 0.17	8.47
29.7	10.98 ± 0.10	10.96	10.69 ± 0.02	11.22	8.83 ± 0.14	8.60
31.7	11.11 ± 0.09	11.02	10.74 ± 0.01	11.26	8.99 ± 0.11	8.73
34.7	11.12 ± 0.04	11.10	10.74 ± 0.03	11.30	9.06 ± 0.12	8.90
37.8	11.23 ± 0.05	11.17	10.77 ± 0.03	11.33	9.19 ± 0.11	9.08
39.8	11.27 ± 0.05	11.20	10.84 ± 0.03	11.35	9.21 ± 0.17	9.18
44.8	11.31 ± 0.04	11.26	10.78 ± 0.07	11.37	9.38 ± 0.12	9.41
46.8	11.31 ± 0.01	11.28	10.77 ± 0.03	11.38	9.42 ± 0.12	9.49
48.8	11.30 ± 0.02	11.30	10.79 ± 0.04	11.39	9.47 ± 0.13	9.57
54.8	11.32 ± 0.00	11.34	11.01 ± 0.02	11.40	9.63 ± 0.13	9.79
56.8	11.30 ± 0.01	11.35	11.02 ± 0.01	11.40	9.70 ± 0.12	9.85

Table 22. Percent error employed in construction of x-axis error bar

Condition	Error, %
HiAS	38
HiAL	37
HiES	33
LoAS	30
LoAL	30
LoES	33

As seen in Figure 22 and 24, the experimental moisture contents of non-fat dry milk in small box made from material A and E were within the predicted band. As seen from Figure 23, the experimental moisture contents of non-fat dry milk in large box made from material A were within the predicted band up to moisture content of 10%. Beyond this point, the model over predicted the moisture content. This could results from the violation of assumption of equilibrium between product and headspace can be achieved within a short period of time. This assumption could be satisfied only when the diffusion coefficient of water in the product is higher than the diffusion coefficient of water in the packaging material. Large box made from material A had the highest permeation rate because of high permeance value of material A and its large surface area.

With the shelf life model based on GAB model, shelf life values of non-fat dry milk in different package at each storage conditions were calculated based on critical moisture content of 10% and are presented in Table 23. Shelf life of non-fat dry milk in the large box made from material A was not calculated since the model was not applicable.

Table 23. Calculated shelf life of non-fat dry milk by the shelf life model based on GAB equation

Package description		Calculated shelf life, day	
Material	Size	40°C, 83% RH	25°C, 67% RH
A	Small	5.3	15
A	Large	3.8	-
E	Small	13.2	61.5
E	Large	7.7	36

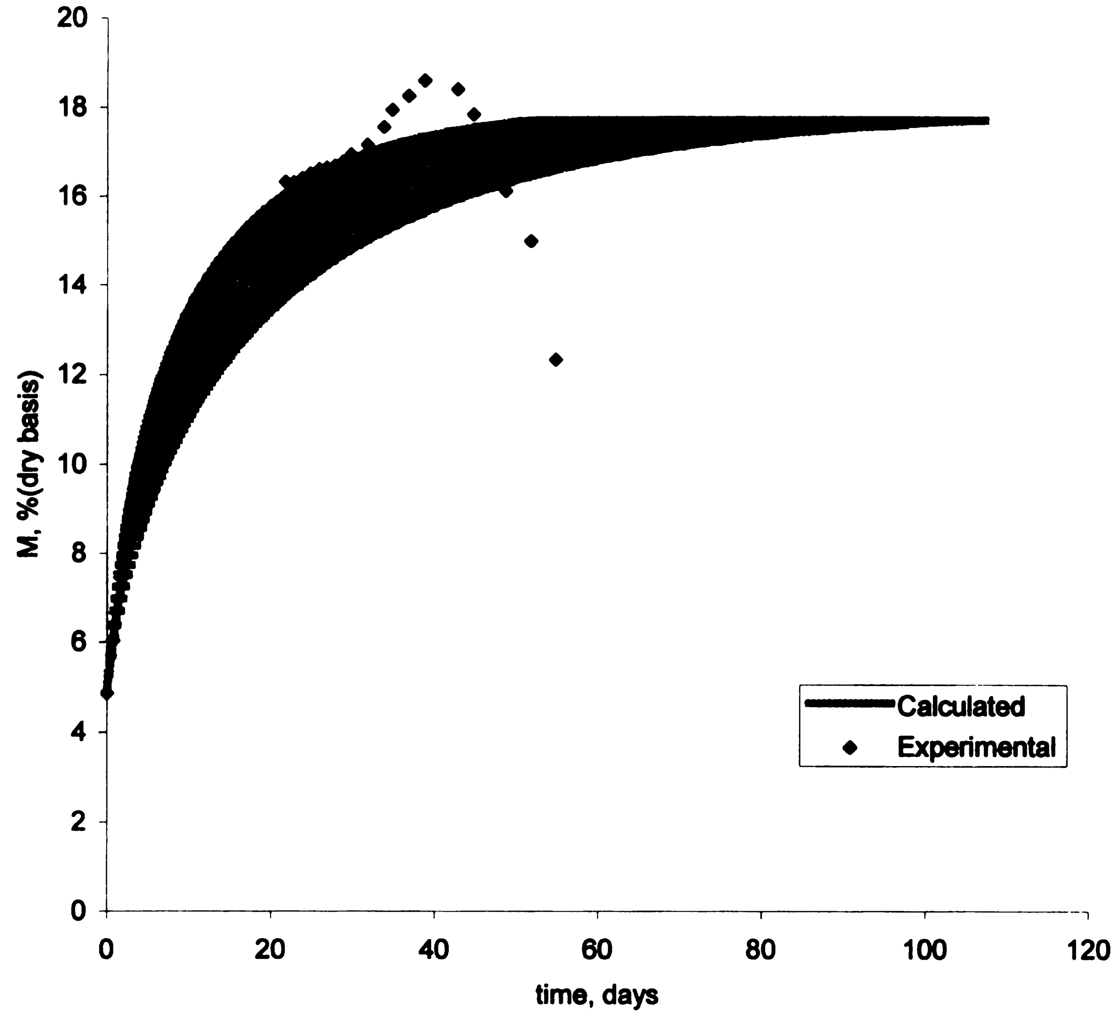

Figure 19. Predicted and experimental moisture content as a function of time of non-fat dry milk in small boxes made from material A and stored at 40°C, 83% RH (HiAS)

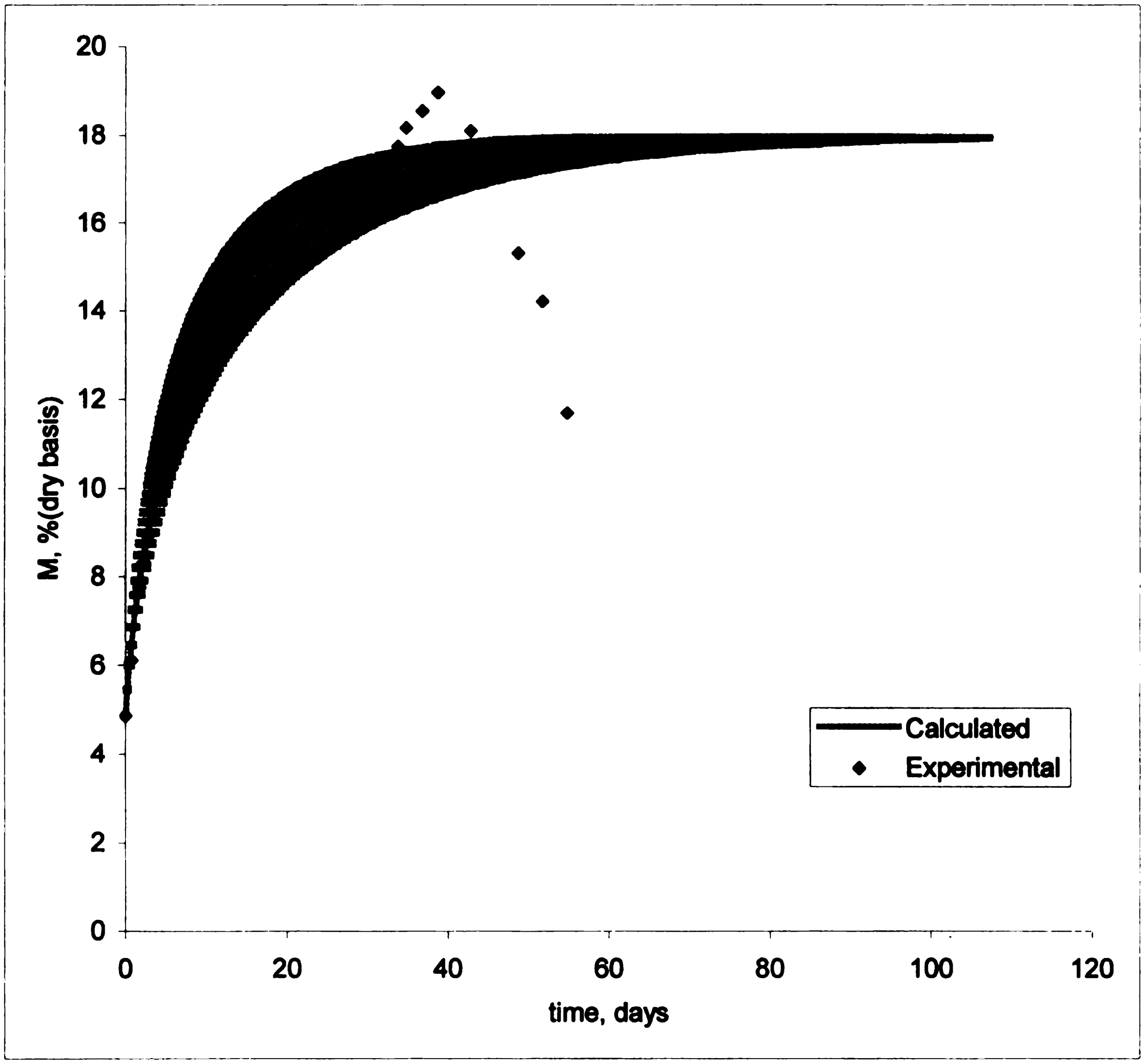

Figure 20. Predicted and experimental moisture content as a function of time of non-fat dry milk in large boxes made from material A and stored at 40°C, 83% RH (HiAL)

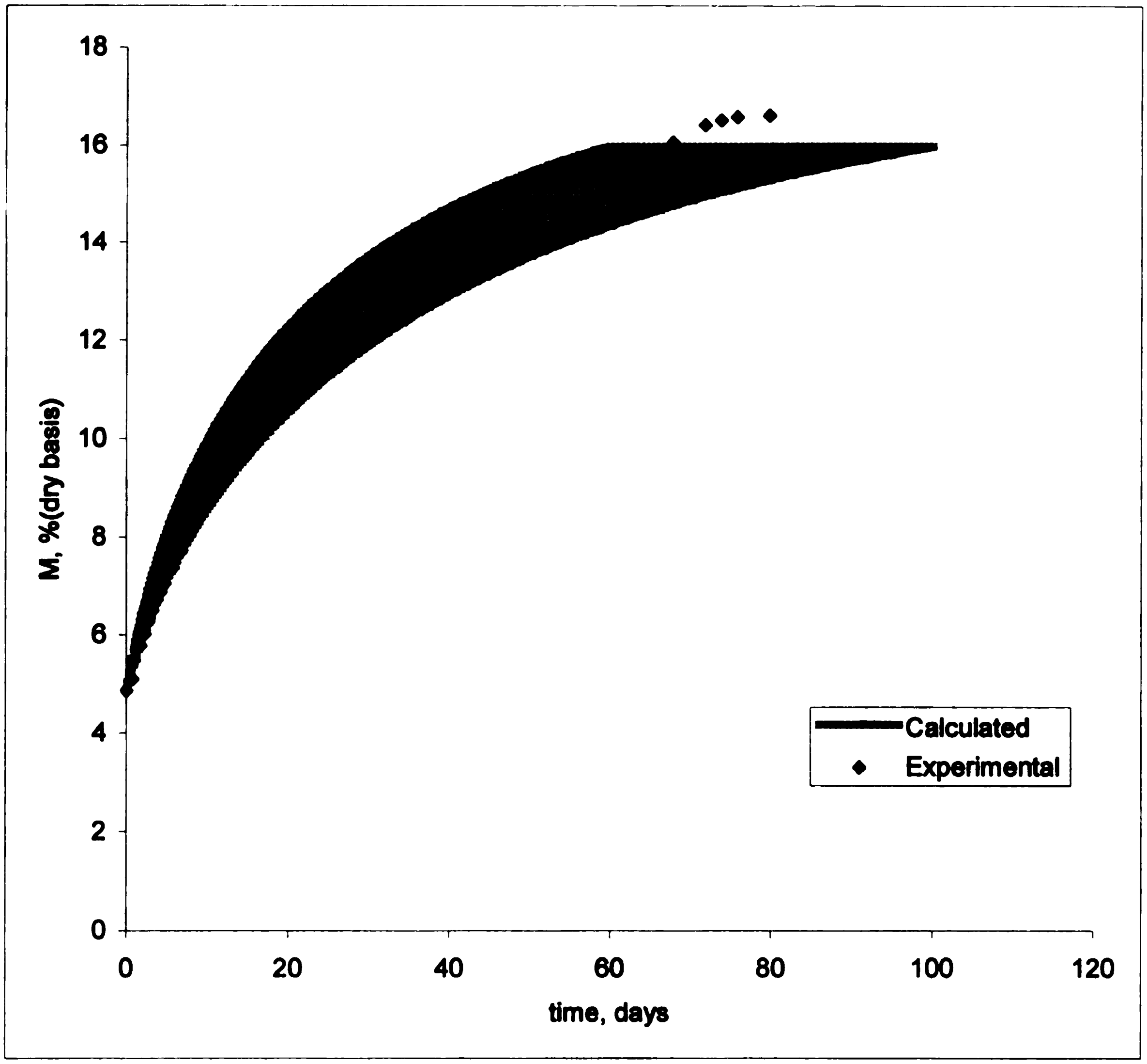

Figure 21. Predicted and experimental moisture content as a function of time of non-fat dry milk in small boxes made from material E and stored at 40°C, 83% RH (HiES)

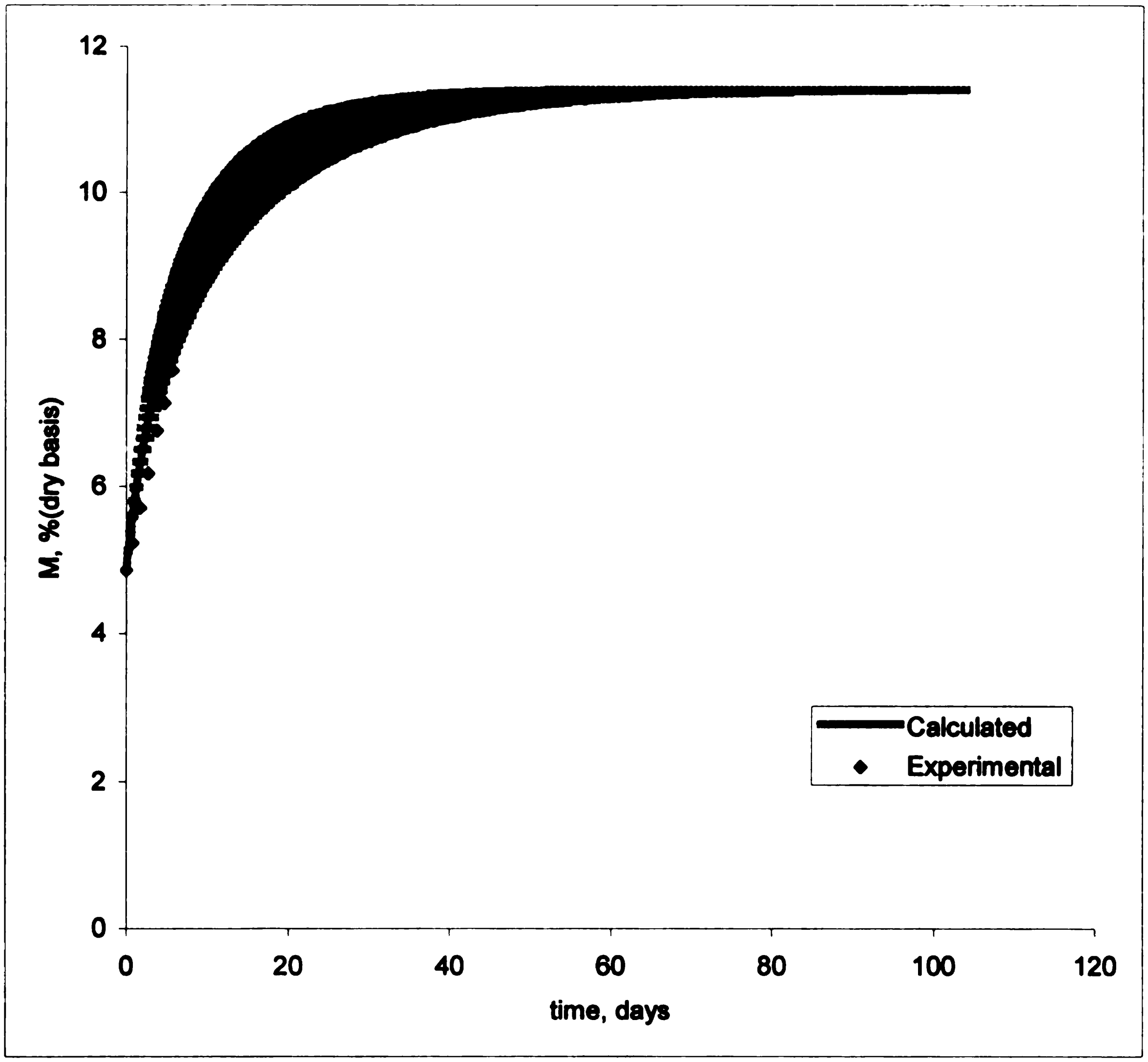

Figure 22. Predicted and experimental moisture content as a function of time of non-fat dry milk in small boxes made from material A and stored at 25°C, 67% RH (LoAS)

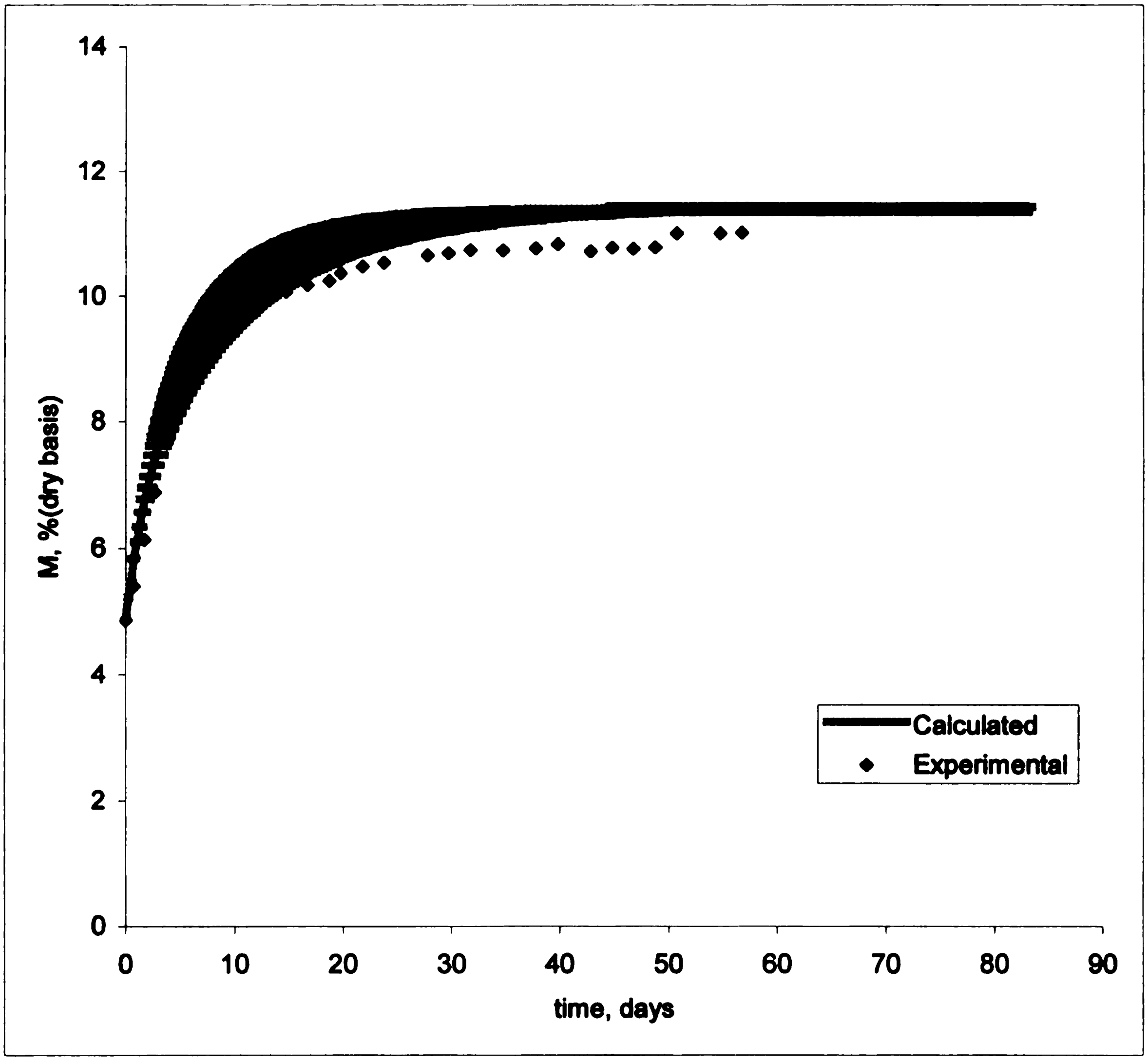

Figure 23. Predicted and experimental moisture content as a function of time of non-fat dry milk in large boxes made from material A and stored at 25°C, 67% RH (LoAL)

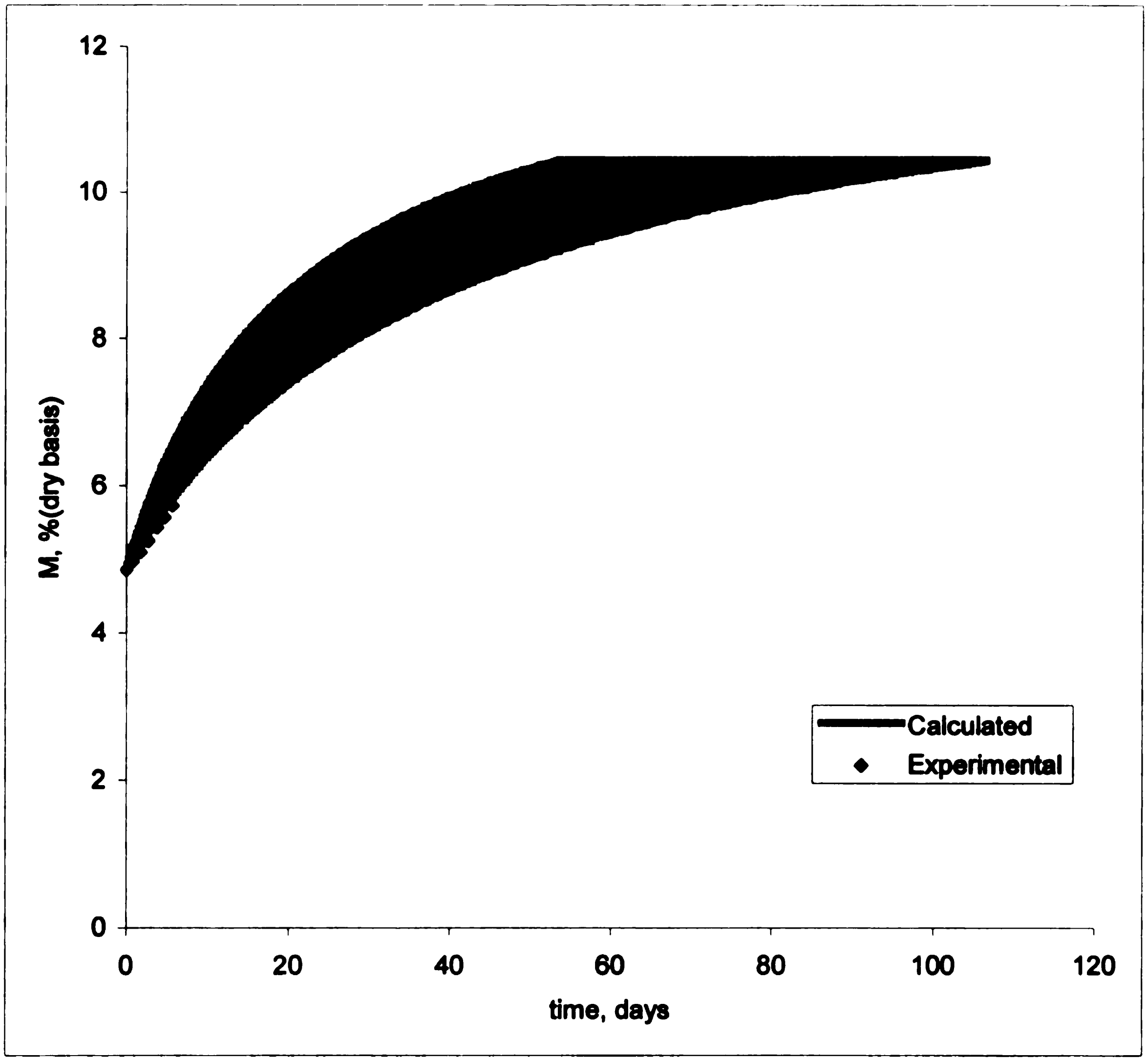

Figure 24. Predicted and experimental moisture content as a function of time of non-fat dry milk in small boxes made from material E and stored at 25°C, 67% RH (LoES)

CONCLUSION

The moisture sorption isotherms of non-fat dry milk at 20, 30, and 40°C were best described by GAB equation. The information of moisture sorption isotherm at temperature between 20 and 40°C were obtained using Lagrange interpolation method based on moisture sorption isotherm at 20, 30, and 40°C.

Barrier characteristics of Bellow and FOL style boxes were insignificantly different and both of them were free of discontinuity. Therefore, the moisture permeated into the package only through the package wall and the barrier characteristics of package were represented by the permeance of a packaging material.

The shelf life model based on GAB equation and permeance of packaging material were applied to predict moisture content as a function of time or to predict shelf life of non-fat dry milk. The sensitivity analysis for each parameter indicated that the shelf life was the most sensitive to the change in parameter k and the change of ratio of surface area and product dry weight while least sensitive to the change in parameter C. The predicted moisture content as a function of time at two isotherm storage condition, 40°C, 83% RH, and 25°C, 67% RH of non-fat dry milk packaged in three types of packages were validated with the actual experiment. At least up to the critical moisture content of 10%, the experimental data were within the predicted band of moisture content, which incorporated uncertainties of parameters. Therefore, the model was applicable to predict shelf life of non-fat dry milk in packages made from the combination of barrier layer and f-flute corrugated board.

APPENDICES

APPENDIX A

PARAMETER ESTIMATION OF GAB EQUATION

In order to easily estimate GAB parameters, GAB model was transformed into quadratic form by the following:

$$\frac{M}{W_m} = \frac{Cka_w}{(1-ka_w)(1-ka_w+Cka_w)} \tag{116}$$

$$\frac{W_m Cka_w}{M} = 1-ka_w+Cka_w-ka_w+k^2a_w{}^2-ck^2a_w{}^2 \tag{117}$$

$$\frac{a_w}{M} = \frac{k}{W_m}\left(\frac{1}{C}-1\right)a_w{}^2+\frac{1}{W_m}\left(1-\frac{2}{C}\right)a_w+\frac{1}{W_m Ck} \tag{118}$$

Assign

$$\alpha = \frac{k}{W_m}\left(\frac{1}{C}-1\right) = \frac{1}{W_m C}(1-C) \tag{119}$$

$$\beta = \frac{1}{W_m}\left(1-\frac{2}{C}\right) = \frac{1}{W_m C}(C-2) \tag{120}$$

$$\gamma = \frac{1}{W_m Ck} \tag{121}$$

Eqn. 118 can be rewritten as

$$\frac{a_w}{M} = \alpha a_w{}^2+\beta a_w+\gamma \tag{122}$$

Constants α, β, and γ were obtained from the quadratic regression and were employed to calculate GAB constants, C, W_m, and k as follow

Substituting eqn. 119 into eqn. 120 gives

$$k = -\frac{\alpha}{\beta}\frac{(C-2)}{(C-1)} \tag{123}$$

Substituting eqn. 123 into eqn. 120 gives

$$\frac{1}{W_m} = -\frac{\alpha\gamma}{\beta}\frac{(C-2)C}{(C-1)} \tag{124}$$

Substitute eqn. 124 into eqn. 120 gives

$$\frac{\beta^2}{(-\alpha)\gamma} = \frac{(C^2-4C+4)}{(C-1)} \tag{125}$$

Assign $X = \frac{\beta^2}{(-\alpha)\gamma}$ and eqn. 125 can be rewritten as

$$C^2-(4+X)C+(4+X) = 0 \tag{126}$$

Assign $\theta = 4+X = 4+\frac{\beta^2}{(-\alpha)\gamma}$. The solution of eqn. 126 are

$$C = \frac{\theta \pm \sqrt{\theta^2-4\theta}}{2} \tag{127}$$

Since the equation is in quadratic form, there are two possible solutions for C. Only the solution that gives positive values for all GAB constants was the right answer. Parameter W_m and k can be obtained by substitution of C into eqn. 120 and 121, respectively.

The standard deviations of C, k and W_m (S_c, S_k, S_{Wm}) was estimated using the Gauss' Law of Error Propagation and standard error of α, β, and γ (s_α^2, s_β^2, and s_γ^2) as (Taylor, 1982)

$$s_c = \sqrt{\left(\frac{\partial C}{\partial \alpha}\right)^2 s_\alpha^2 + \left(\frac{\partial C}{\partial \beta}\right)^2 s_\beta^2 \left(\frac{\partial C}{\partial \gamma}\right)^2 s_\gamma^2} \tag{128}$$

where $\frac{\partial C}{\partial \alpha} = \frac{\beta^2}{\alpha^2\gamma}\left(\frac{1}{2}-\frac{1}{4\sqrt{\theta^2-4\theta}}\right)$

$$\frac{\partial C}{\partial \beta} = -\frac{2\beta}{\alpha\gamma}\left(\frac{1}{2}-\frac{1}{4\sqrt{\theta^2-4\theta}}\right)$$

$$\frac{\partial C}{\partial \gamma} = \frac{\beta^2}{\alpha\gamma^2}\left(\frac{1}{2} - \frac{1}{4\sqrt{\theta^2 - 4\theta}}\right)$$

$$s_k = \sqrt{\left(\frac{\partial k}{\partial \alpha}\right)^2 s_\alpha^2 + \left(\frac{\partial k}{\partial \beta}\right)^2 s_\beta^2 \left(\frac{\partial k}{\partial \gamma}\right)^2 s_\gamma^2} \tag{129}$$

where $\frac{\partial k}{\partial \alpha} = \frac{1}{\sqrt{\beta^2 - 4\alpha\gamma}}$

$$\frac{\partial k}{\partial \beta} = \frac{1}{2\gamma}\left(\frac{\beta}{\sqrt{\beta^2 - 4\alpha\gamma}}\right)$$

$$\frac{\partial k}{\partial \gamma} = \frac{1}{2\gamma^2\sqrt{\beta^2 - 4\alpha\gamma}}\left(\beta\sqrt{\beta^2 - 4\alpha\gamma} + 2\alpha\gamma - \beta^2\right)$$

$$s_{W_m} = \sqrt{\left(\frac{\partial W_m}{\partial \alpha}\right)^2 s_\alpha^2 + \left(\frac{\partial W_m}{\partial \beta}\right)^2 s_\beta^2 \left(\frac{\partial W_m}{\partial \gamma}\right)^2 s_\gamma^2} \tag{130}$$

where $\frac{\partial W_m}{\partial \alpha} = \frac{2\gamma}{\sqrt{\left(\beta^2 - 4\alpha\gamma\right)^3}}$

$$\frac{\partial W_m}{\partial \beta} = \frac{\sqrt{2}\beta}{\sqrt{\left(\beta^2 - 4\alpha\gamma\right)^3}}$$

$$\frac{\partial W_m}{\partial \gamma} = \frac{2\alpha}{\sqrt{\left(\beta^2 - 4\alpha\gamma\right)^3}}$$

APPENDIX B

EXPERIMENTAL AND CALCULATED MOISTURE SORPTION ISOTHERMS

Table 24. Experimental and calculated (with GAB equation) moisture sorption isotherm data for non-fat dry milk at 20°C

Relative Humidity	Moisture content, % (dry basis)				
	1	2	3	Average	Calculated
0.0 ± 0.00	0.0000	0.0000	0.0000	0.00 ± 0.00	0.00
8.4 ± 0.05	4.2399	4.2282	4.2220	4.23 ± 0.01	4.26
23.1 ± 0.05	4.8680	4.8303	4.8349	4.84 ± 0.02	5.42
34.0 ± 0.25	6.0755	6.0240	6.0311	6.04 ± 0.03	6.24
47.3 ± 0.25	8.9686	8.9797	8.9617	8.97 ± 0.07	7.75
50.4 ± 0.25	8.0227	8.0413	8.0294	8.03 ± 0.01	8.16
64.9 ± 0.25	11.6198	11.5736	11.5514	11.58 ± 0.03	11.10
75.6 ± 0.25	14.3704	14.3408	14.3350	14.35 ± 0.02	14.54
81.3 ± 0.25	17.0415	16.9302	16.9120	16.96 ± 0.07	17.84
94.5 ± 0.25	38.8087	37.8571	N/A	38.45 ± 0.51	35.05

Table 25. Experimental and calculated (with GAB equation) moisture sorption isotherm data for non-fat dry milk at 30°C

Relative Humidity	Moisture content, % (dry basis)				
	1	2	3	Average	Calculated
0.0 ± 0.00	0.0000	0.0000	0.0000	0.00 ± 0.00	0.00
8.9 ± 0.05	3.8475	3.8736	3.9110	3.88 ± 0.03	3.97
23.2 ± 0.05	4.5957	4.6010	4.5447	4.58 ± 0.03	4.90
34.2 ± 0.25	6.0869	6.1267	6.0680	6.09 ± 0.03	5.73
4.66 ± 0.25	6.5827	6.5054	6.5405	6.54 ± 0.04	6.93
48.7 ± 0.25	7.1250	7.1564	7.1063	7.13 ± 0.02	7.31
63.6 ± 0.25	11.5924	11.5683	11.5989	11.59 ± 0.02	10.01
75.9 ± 0.25	14.0061	13.9898	14.0472	14.01 ±0.03	13.67
81.5 ± 0.25	16.4967	16.5089	16.5141	16.51 ± 0.01	16.39
93.5 ± 0.25	33.4394	33.5232	N/A	33.48 ± 0.06	33.81

Table 26. Experimental and calculated (with GAB equation) moisture sorption isotherm data for non-fat dry milk at 40°C

Relative Humidity	Moisture content, % (dry basis)				
	1	2	3	Average	Calculated
0.0 ± 0.00	0.0000	0.0000	0.0000	0.00 ± 0.00	0.00
9.2 ± 0.05	3.2139	3.8736	3.9110	3.67 ± 0.02	3.61
23.8 ± 0.05	4.4300	4.4168	4.4668	4.44 ± 0.02	4.53
34.3 ± 0.25	5.8055	5.9436	5.9473	5.90 ± 0.08	5.32
45.6 ± 0.25	5.9936	5.9738	6.0182	6.00 ± 0.02	6.36
47.6 ± 0.25	6.4217	6.4261	6.4432	6.43 ± 0.01	6.59
62.8 ± 0.25	9.6050	9.6113	9.6262	9.61 ± 0.01	8.99
77.5 ± 0.25	13.6980	13.6740	13.6780	13.68 ± 0.01	13.99
79.6 ± 0.25	16.3945	16.4363	16.4294	16.42 ± 0.02	14.53
91.3 ± 0.25	27.338	27.3216	27.2586	27.31 ± 0.04	28.94

APPENDIX C

POTENTIAL ERROR AND PROPOSED CORRECTION OF PARAMETER C IN GAB MODEL

As mentioned in Chapter 2, parameter C of GAB model is temperature dependent and can be correlated with temperature by the Arrhenius equation. Parameter C in GAB equation of non-fat dry milk at 20, 30, and 40°C showed the temperature dependency but the behavior did not followed the Arrhenius equation. As shown in the sensitivity analysis, GAB equation is very sensitive in the region of low water activity where it is difficult to get equilibrium moisture content value. The error could result from the insufficient number of experimental data in low water activity region. The possible cause of error and the attempt to correct the value of C parameter are discussed below.

Since it has been known from the sensitivity analysis of GAB equation that parameter C describes the moisture sorption isotherm in low water activity region, the main reason for an error in C value is the insufficient of experimental data in low water activity region. The highest sensitivity coefficient of C is at 0.01 a_w but the lowest experimental data was obtained at water activity of about 0.08. Therefore, parameter C was estimated based mostly on the extrapolated data. In order to correct the C value, more experimental data in the range of 0 to 0.08 water activity would be included in the isotherm. This would result in different value of parameter C, but not parameter k and W_m which have very low sensitivity coefficient in the low water activity range.

From the value of C at 20, 30, and 40°C in Table 13, three possibilities are: parameter C at 30°C was too high, or parameter C at 20 or 40°C was too low. In order to have a correct trend with the estimated new values, corrected values of moisture content at 0.01 a_w for three temperatures have been included into the experimental data and the new GAB parameters at each temperature were estimated. The estimated values of moisture content were obtained by lowering (for moisture sorption isotherm at 30°C) or raising (for moisture sorption isotherm at 20 or 40°C) the predicted moisture content at water activity of 0.01. Table 27 shows the predicted moisture content at water activity of 0.01 obtained from GAB equation presented in Table 9 of Chapter 3. Table 28 to 30 present the corrected moisture content and the GAB parameters estimated from the experimental data with the addition of corrected data.

Table 27. Predicted moisture content at water activity of 0.01 using GAB equation in Table 9 of Chapter 3

Temperature, °C	Moisture content, %
20	2.19
30	2.18
40	1.78

Table 28. GAB parameter at 20°C derived from the experimental data and the additional data point in low water activity region

Parameter	Corrected moisture content at a_w 0.01 added to the experimental data				
	none	2.4%	2.6%	2.8%	3.0%
C	103.55	109.14	115.37	121.24	126.85
Wm	0.04	0.04	0.04	0.04	0.04
k	0.93	0.93	0.93	0.93	0.93

Table 29. GAB parameter at 30°C derived from the experimental data and the additional data point in low water activity region

Parameter	Corrected moisture content at a_w 0.01 added to the experimental data			
	none	2.10%	1.90%	1.70%
C	124.63	120.29	110.73	100.79
Wm	0.04	0.04	0.04	0.04
k	0.95	0.95	0.95	0.95

Table 30. GAB parameter at 40°C derived from the experimental data and the additional data point in low water activity region

Parameter	Corrected moisture content at a_w 0.01 added to the experimental data					
	none	1.90%	2.00%	2.10%	2.20%	2.30%
C	95.46	111.58	116.21	120.73	124.94	129.39
Wm	0.04	0.04	0.04	0.04	0.04	0.04
K	0.96	0.96	0.96	0.96	0.96	0.96

As seen, the additional of data point in low water activity region only affected parameter C but not parameter W_m and k. In order to increase the value of parameter C at 20°C to be higher than the value of parameter C at 30°C, the corrected moisture content at 0.01 a_w had to be increased upto at least 3.0%. To lower the value of parameter C at 30°C to be in between the value of parameter C at 20 and 40°C, the corrected moisture content at 0.01 a_w had to be decreased down to 1.7% or lower. To increase the value of parameter C at 40°C to be greater than parameter C at 20 and 30°C, the corrected moisture content at 0.01 a_w had to be increased upto the minimum of 2.3%. With the corrected C parameter in the last column of Table 28 to 30, the moisture content at 0.01 a_w was calculated and compared with the original data as presented in Table 31.

Table 31 The comparison of moisture content calculated from original and corrected C value at 20 ,30, and 40°C.

Temperature, °C	Moisture content, %, at 0.01 a_w obtained from GAB using	
	Original C value	Corrected C value
20	2.19	2.50
30	2.18	1.97
40	1.78	4.73

The evaluation of possible error is made by comparing the corrected moisture content with the rest of original moisture content based on two assumptions: 1) only parameter C at one temperature was incorrect and 2) at the specific water activity, moisture content of the product subjected to low temperature is higher than those subjected to high temperature. It is obvious that the corrected C value at 40°C is too high. This reduces the possible error to either the parameter C at 20°C is too low or the parameter C at 30°C is too high. Since, in most cases, parameter C decreases with an increasing of temperature, the error of C at 20°C is likely to be incorrect and the discussion on the proposed correction is discussed below.

The proposed method to correct the value of parameter C at 20°C is based on the Arrhenius equation obtained from parameter C at 30 and 40°C. The possible value of parameter C at 20°C was obtained from the extrapolation of the Arrhenius equation was approximately 165. The additional data of moisture sorption isotherm at water activity in the range of 0 to 0.08 must be obtained to derive the exact value of parameter C.

From the sensitivity analysis of shelf life model, parameter C has very low sensitivity coefficient. Therefore, the change in parameter C would not have much impact on predicted shelf life.

APPENDIX D

WATER VAPOR TRANSMISSION AND PERMEANCE OF PACKAGING MATERIALS

Table 32. Combined water vapor transmission rate, WVTR, and permeance, R, of packaging materials at 40°C,

Material	RH, %	Combined WVTR, g/(day.m^2)					R, g/(m^2.day. mmHg)
		1	2	3	4	Average	
A	73 ± 3	62.85	38.16	50.73	42.65	49 ± 11	1.2 ± 0.3
B	73 ± 3	92.93	75.43	53.86	52.98	69 ± 19	1.7 ± 0.4
C	74 ± 3	95.23	98.92	87.46	102.92	96 ± 7	2.4 ± 0.2
D	74 ± 3	168.36	157.14	167.91	186.77	170 ± 12	4.2 ± 0.3
E	74 ± 3	16.74	20.30	22.32	21.82	20 ± 2.5	0.49 ± 0.06
Control	75 ± 3	2296.45	2295.56	2319.35	2165.36	2300 ± 70	55 ± 1.3

Table 33. Combined water vapor transmission rate, WVTR, and permeance, R, of packaging material A and E at 30°C, 75±1 %RH

Material	Combined WVTR, g/(day.m^2)					R, g/(m^2.day. mmHg)
	1	2	3	4	Average	
A	36.28	38.19	42.72	-	39 ± 3	1.6 ± 0.1
E	10.50	14.56	8.35	-	11 ± 3	0.46 ± 0.1

Table 34. Combined water vapor transmission rate, WVTR, and permeance, R, of packaging material A and E at 25°C, 67% RH

Material	Combined WVTR, g/(day.m^2)					R, g/(m^2.day. mmHg)
	1	2	3	4	Average	
A	28.81	27.38	30.88	24.67	27 ± 2	1.8 ± 0.2
E	5.41	7.64	8.12	6.21	6.8 ± 1.2	0.44 ± 0.07

APPENDIX E

SENSITIVITY ANALYSIS OF SHELF LIFE MODEL

$$\chi_C = \frac{100W_d \cdot k \cdot W_m (((C \cdot M_f(RH \cdot k-100)+100 \cdot W_m)+M_f(100-RH \cdot k)) \cdot (C(RH \cdot M_i \cdot k-100(M_i-W_m))-M_i \cdot RH \cdot k-100)) \cdot \ln((C(M_f \cdot RH \cdot k-}{p_s \cdot R \cdot A(C-1)^2(C(M_f(RH \cdot k-100)+100 \cdot W_m)+M_f(100-RH \cdot k)) \cdot (C(RH \cdot M_i \cdot k-100(M_i-W_m))-M_i(RH \cdot k-100)) \cdot (RH \cdot k-100)^2}$$

$$\frac{100)+100W_m)+M_f(100-RH \cdot k))/(C(RH \cdot M_i \cdot k-100(M_i-W_m))-M_i \cdot (RH \cdot k-100)))+100 \cdot C \cdot W_m(100-RH \cdot k) \cdot (C-1) \cdot (M_f-M_i))}{(C(RH \cdot M_i \cdot k-100(M_i-W_m))-M_i(RH \cdot k-100)) \cdot (RH \cdot k-100)^2} \qquad (131)$$

$$\chi_k = \frac{\begin{array}{c} 100 \cdot W_d \cdot (C \cdot W_m(C(M_f(RH \cdot k-100)+100W_m)+M_f(100-RH \cdot k))(C(RH \cdot M_i \cdot k-100(M_i-W_m))-M_i(RH \cdot k-100))(RH \cdot k+100) \cdot \ln((C \\ \hline (M_f(RH \cdot k-100)+100W_m+M_f(100-RH \cdot k))/(C(RH \cdot M_i \cdot k-100(M_i-W_m))-M_i \cdot (RH \cdot k-100)))+(100-RH \cdot k)(C-1)(M_f-1)(C^2(M_f(RH^2 \cdot \end{array}}{p_s \cdot R \cdot A(C-1)(C(M_f(RH \cdot k-100)+100W_m)+M_f(100-RH \cdot k))}$$

$$\frac{M_i \cdot k^2+100 \cdot RH \cdot k(W_m-2M_i)+10000(M_i-W_m)+100W_m(RH \cdot k(M_i+W_m)+(2 \cdot C100-RH \cdot k)(M_f(RH \cdot M_i \cdot k-50(2M_i-W_m))+50M_i \cdot W_m)}{(C(RH \cdot M_i \cdot k-100(M_i-W_m))-Mi(RH \cdot k-100))(RH \cdot k-100)^3}$$

$$\frac{+(M_f \cdot M_i(RH \cdot k-100)^2)}{} \qquad (132)$$

$$\chi_{W_m} = \frac{100 \cdot C \cdot W_d \cdot k((C(M_f(RH \cdot k-100)+100W_m)+M_f(100-RH \cdot k))(C(RH \cdot M_i \cdot k-100(M_i-W_m))-M_i(RH \cdot k-100)) \cdot \ln((C(M_f(RH \cdot k-}{p_s \cdot R \cdot A(1-C)(C(M_f(RH \cdot k-100)+100W_m)+M_f(100-RH \cdot k))}$$

$$\frac{100)+100W_m+M_f(100-RH \cdot k))/(C(RH \cdot M_i \cdot k-100(M_i-W_m))-M_i \cdot (RH \cdot k-100)))+100C \cdot W_m(100-RH \cdot k)(C-1)(M_f-M_i)}{(C(RH \cdot M_i \cdot k-100(M_i-W_m))-M_i(RH \cdot k-100))(RH \cdot k-100)^2} \qquad (133)$$

$$\chi_{Mi} = \frac{W_d \cdot M_i \cdot k(1-C)}{p_s \cdot R \cdot A(C \cdot (RH \cdot M_i \cdot k-100(M_i-W_m))-M_i \cdot (RH \cdot k-100))} \qquad (134)$$

$$\chi_{Wd} = \frac{k \cdot [100 \cdot C \cdot W_m \cdot \ln((C(M_f \cdot RH \cdot k-100)+100W_m)+M_f(100-RH \cdot k))/(C(RH \cdot M_i \cdot k-100(M_i-W_m))-M_i(RH \cdot k-100)))+(100-RH \cdot k)}{p_s \cdot R \cdot A(1-C)}$$

$$\frac{(C-1)(M_f-M_i)]}{(RH \cdot k-100)^2} \qquad (135)$$

$$\chi_A = \frac{100 \cdot C \cdot W_d \cdot k \cdot W_m \cdot \ln((C(M_f(RH \cdot k-100)+100W_m+M_f(100-RH \cdot k))/(C(RH \cdot M_i \cdot k-100(M_i-W_m))-M_i \cdot (RH \cdot k-100)))}{p_s \cdot R \cdot A^2 (C-1)(RH \cdot k-100)^2} +$$

$$\frac{W_d \cdot k(M_f-M_i)}{p_s \cdot R \cdot A^2 (RH \cdot k-100)^2} \qquad (136)$$

$$\chi_R = \frac{100 \cdot C \cdot W_d \cdot k \cdot W_m \cdot \ln((C(M_f(RH \cdot k-100)+100W_m+M_f(100-RH \cdot k))/(C(RH \cdot M_i \cdot k-100(M_i-W_m))-M_i \cdot (RH \cdot k-100)))}{p_s \cdot R^2 \cdot A(C-1)(RH \cdot k-100)^2} +$$

$$\frac{W_d \cdot k(M_f-M_i)}{p_s \cdot R^2 \cdot A(RH \cdot k-100)^2} \qquad (137)$$

$$\chi_{Ps} = \frac{100 \cdot C \cdot W_d \cdot k \cdot W_m \cdot \ln((C(M_f(RH \cdot k-100)+100W_m+M_f(100-RH \cdot k))/(C(RH \cdot M_i \cdot k-100(M_i-W_m))-M_i \cdot (RH \cdot k-100)))}{p_s^2 \cdot R \cdot A(C-1)(RH \cdot k-100)^2} +$$

$$\frac{W_d \cdot k(M_f-M_i)}{p_s^2 \cdot R \cdot A(100-RH \cdot k)} \qquad (138)$$

$$\chi_{RH} = \frac{W_d \cdot k^2(200 \cdot C \cdot Wm(C(M_f(RH \cdot k-100)+100W_m)+M_f(100-RH \cdot k))(C(RH \cdot M_i \cdot k-100(M_i-W_m))-M_i(RH \cdot k-100)) \cdot \ln((C}{p_s \cdot R \cdot A(C-1)(C(M_f(RH \cdot k-100)+100W_m)+M_f(100-RH \cdot k))(C(RH \cdot M_i \cdot k-100(M_I-W_m)-M_i(RH \cdot k-100))(RH \cdot k-100))(RH \cdot k-100)^3}$$

$$\frac{(M_f(RH \cdot k-100)+100W_m+M_f(100-RH \cdot k))/(C(RH \cdot M_i \cdot k-100(M_i-W_m))-M_i \cdot (RH \cdot k-100)))+(100-RH \cdot k)(C-1)(M_f-M_i)(C^2}{p_s \cdot R \cdot A(C-1)(C(M_f(RH \cdot k-100)+100W_m)+M_f(100-RH \cdot k))}$$

$$\frac{(M_f(RH^2 \cdot M_i \cdot k^2+100 \cdot RH \cdot k(W_m-2M_i)+10000(M_i-W_m))+100 \cdot W_m(RH \cdot M_i \cdot k-100(M_i-2W_m)))+2 \cdot C(100-RH \cdot k)(M_f(RH \cdot M_i k-}{(C(RH \cdot M_i \cdot k-100(M_I-W_m)-M_i(RH \cdot k-100))(RH \cdot k-100))(RH \cdot k-100)^3}$$

$$\frac{50(2M_i-W_m))+50M_i \cdot W_m)+M_f M_i(RH \cdot k-100)^2))}{} \qquad (139)$$

$$\chi_{(A/Wd)} = \frac{100 \cdot C \cdot W_d \cdot k \cdot W_m \cdot \ln((C(M_f(RH \cdot k-100)+100W_m+M_f(100-RH \cdot k))/(C(RH \cdot M_i \cdot k-100(M_i-W_m))-M_i \cdot (RH \cdot k-100)))}{p_s \cdot R \cdot (A/W_d)^{2} \cdot (C-1)(RH \cdot k-100)^2} +$$

$$\frac{k(M_f-M_i)}{p_s \cdot R \cdot (A/W_d)^2 \, (RH \cdot k-100)^2} \qquad (140)$$

Table 35. Sensitivity coefficient of C at different factor combinations

Factor combination	χ_C at C value of		
	60	100	140
S_H, R_H, P_S	0.23	0.13	0.08
S_H, R_H, P_L	0.17	0.09	0.06
S_H, R_L, P_S	0.95	0.53	0.36
S_H, R_L, P_L	0.67	0.38	0.25
S_L, R_H, P_S	0.16	0.08	0.05
S_L, R_H, P_L	0.11	0.06	0.04
S_L, R_L, P_S	0.66	0.35	0.22
S_L, R_L, P_L	0.47	0.21	0.13

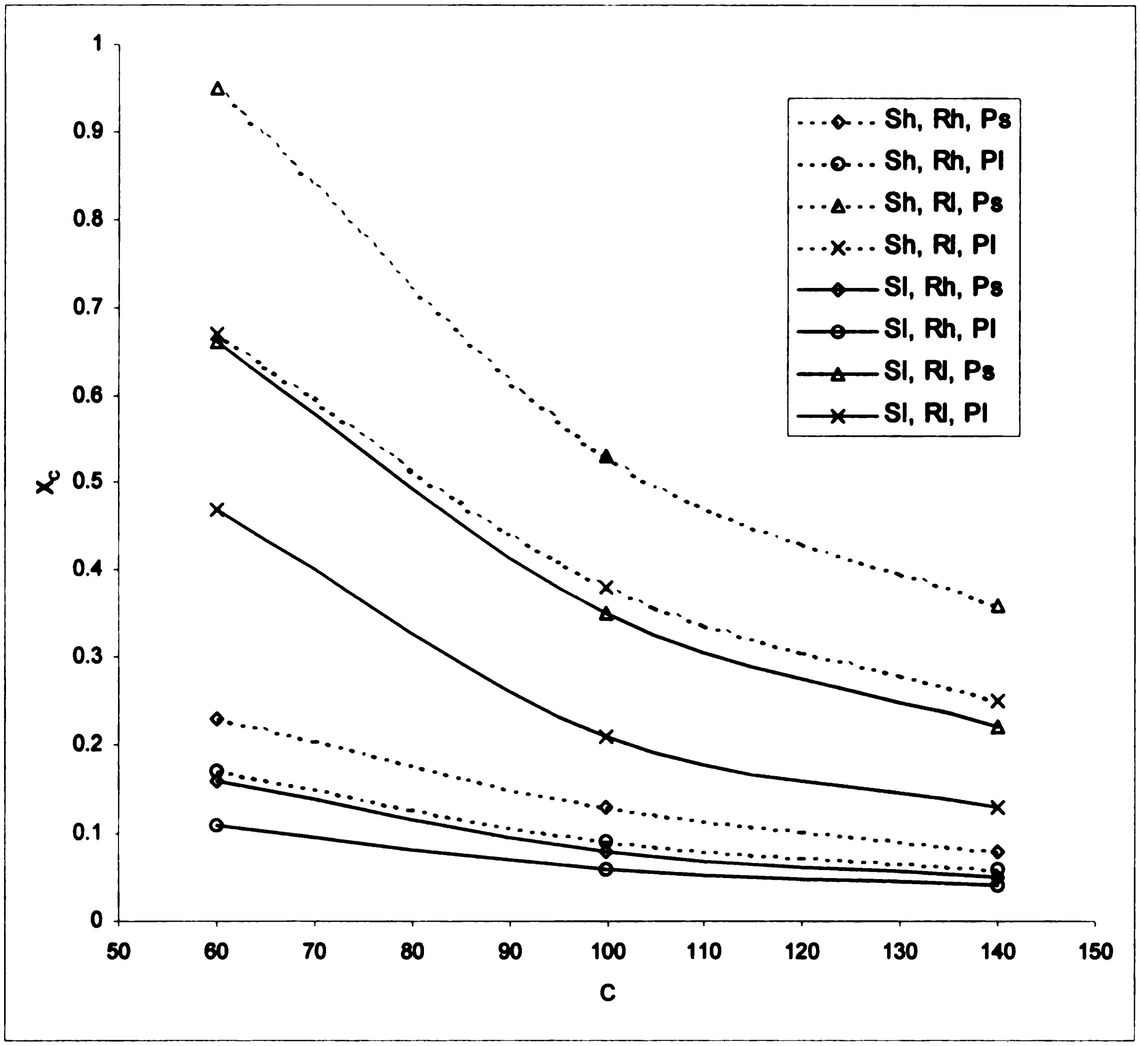

Figure 25. The plot of χ_C as a function of C at different factor combinations

Table 36. Sensitivity coefficient of k at different factor combinations

Factor combinations	χ_k at k value of				
	0.94	0.96	0.97	0.98	1.00
S_H, R_H, P_S	*	-4818	*	-517.1	-238
S_H, R_H, P_L	*	-3412	*	-366.2	-169
S_H, R_L, P_S	*	-19700	*	-2115.5	-974
S_H, R_L, P_L	*	-13900	*	-1498.3	-690
S_L, R_H, P_S	-1373	*	-267	*	-127
S_L, R_H, P_L	-970	*	-189	*	-90
S_L, R_L, P_S	-5615	*	-1094	*	-520
S_L, R_L, P_L	-3978	*	-775	*	-368

* No data

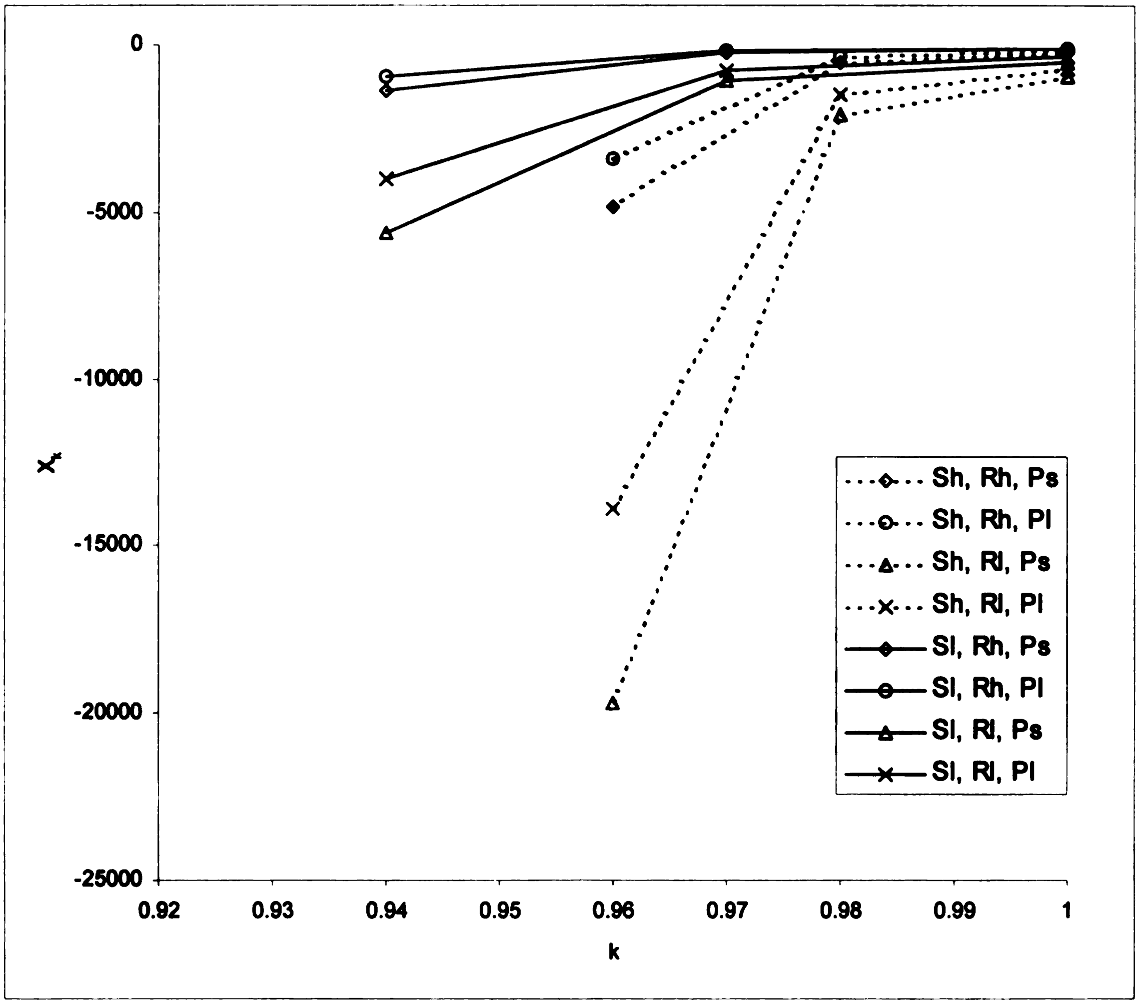

Figure 26. The plot of χ_k as a function of k at different factor combinations

Table 37. Sensitivity coefficient of W_m at different factor combinations

Factor combinations	χ_{Wm} at W_m (%) value of					
	3.6	4	4.2	4.5	4.6	5
S_H, R_H, P_S	-990	-30	*	-11	*	*
S_H, R_H, P_L	-701	-21	*	-8	*	*
S_H, R_L, P_S	-4048	-123	*	-45	*	*
S_H, R_L, P_L	-2868	-87	*	-32	*	*
S_L, R_H, P_S	*	*	-150	*	-20	-9
S_L, R_H, P_L	*	*	-141	*	-14	-7
S_L, R_L, P_S	*	*	-610	*	-84	-39
S_L, R_L, P_L	*	*	-432	*	-59	-27

* No data

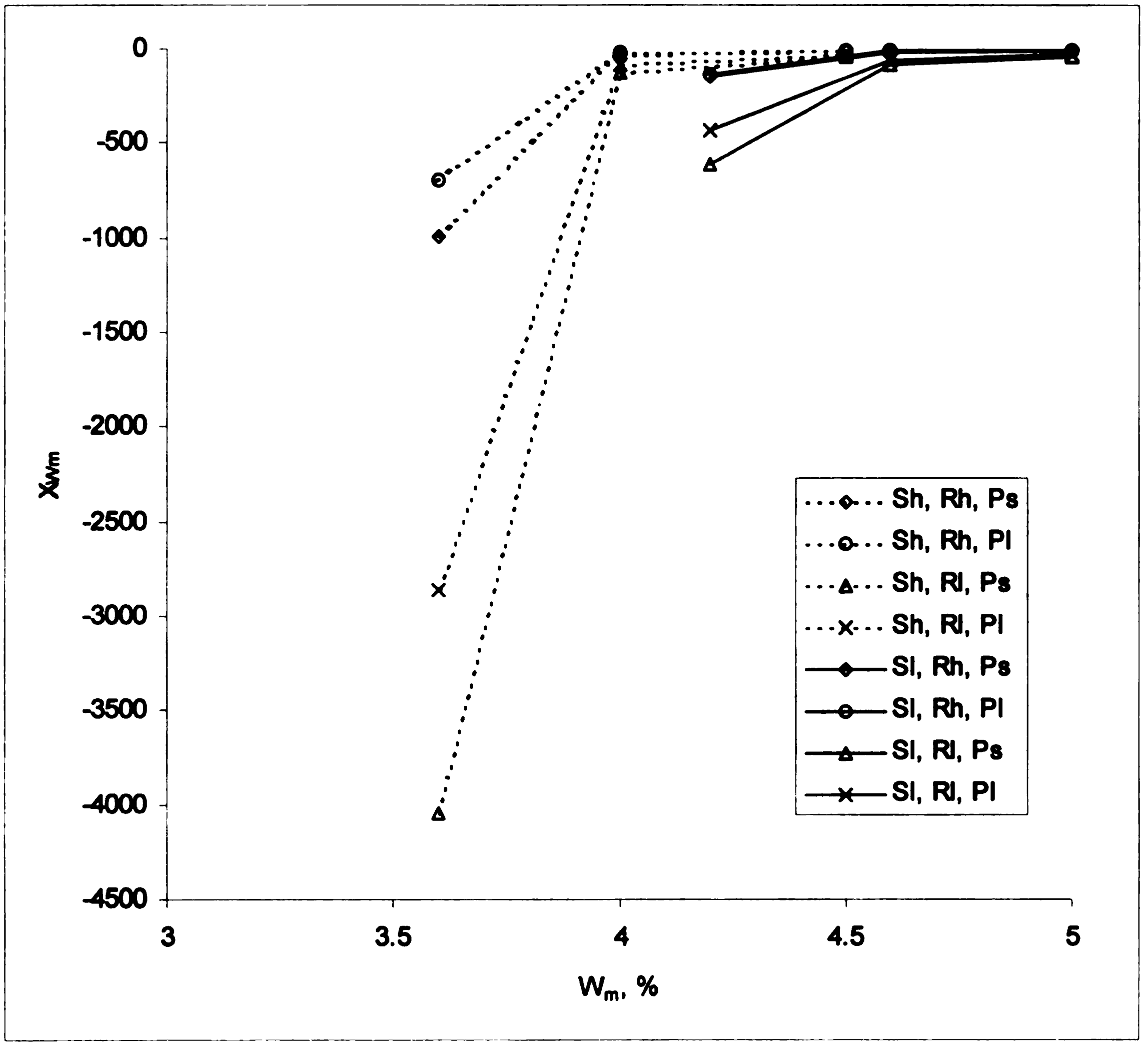

Figure 27. The plot of χ_{Wm} as a function of Wm at different factor combinations

Table 38. Sensitivity coefficient of M_i at different factor combinations

Factor combinations	χ_{Mi} at M_i (%) value of		
	3	4	5
S_H, R_H, P_S	-0.19	-0.27	-0.37
S_H, R_H, P_L	-0.13	-0.19	-0.26
S_H, R_L, P_S	-0.78	-1.10	-1.50
S_H, R_L, P_L	-0.56	-0.79	-1.06
S_L, R_H, P_S	-0.43	-0.65	-0.94
S_L, R_H, P_L	-0.30	-0.46	-0.66
S_L, R_L, P_S	-1.70	-2.60	-3.80
S_L, R_L, P_L	-1.20	-1.80	-2.70

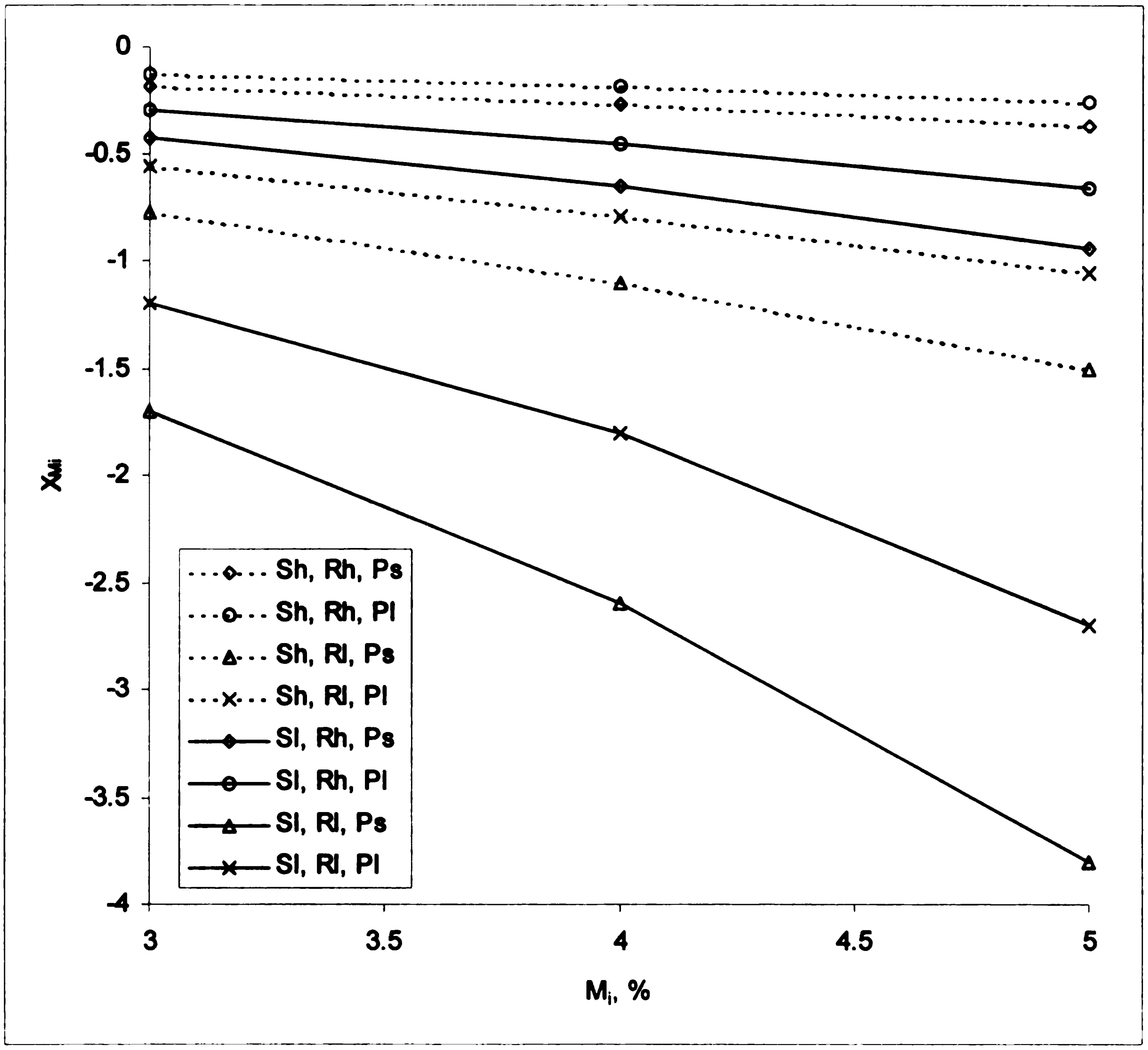

Figure 28. The plot of χ_{Mi} as a function of M_i at different factor combinations

Table 39. Sensitivity coefficient of W_d at different factor combinations

Factor combinations	χ_{Wd} at W_d (g) value of W_d							
	275	425	575	725	300	800	1300	1800
S_H, R_H, P_S	0.21	0.21	0.21	0.21	*	*	*	*
S_H, R_H, P_L	*	*	*	*	0.12	0.12	0.12	0.12
S_H, R_L, P_S	0.86	0.86	0.86	0.86	*	*	*	*
S_H, R_L, P_L	*	*	*	*	0.50	0.50	0.50	0.50
S_L, R_H, P_S	0.16	0.16	0.16	0.16	*	*	*	*
S_L, R_H, P_L	*	*	*	*	0.09	0.09	0.09	0.09
S_L, R_L, P_S	0.67	0.67	0.67	0.67	*	*	*	*
S_L, R_L, P_L	*	*	*	*	0.38	0.38	0.38	0.38

* No data

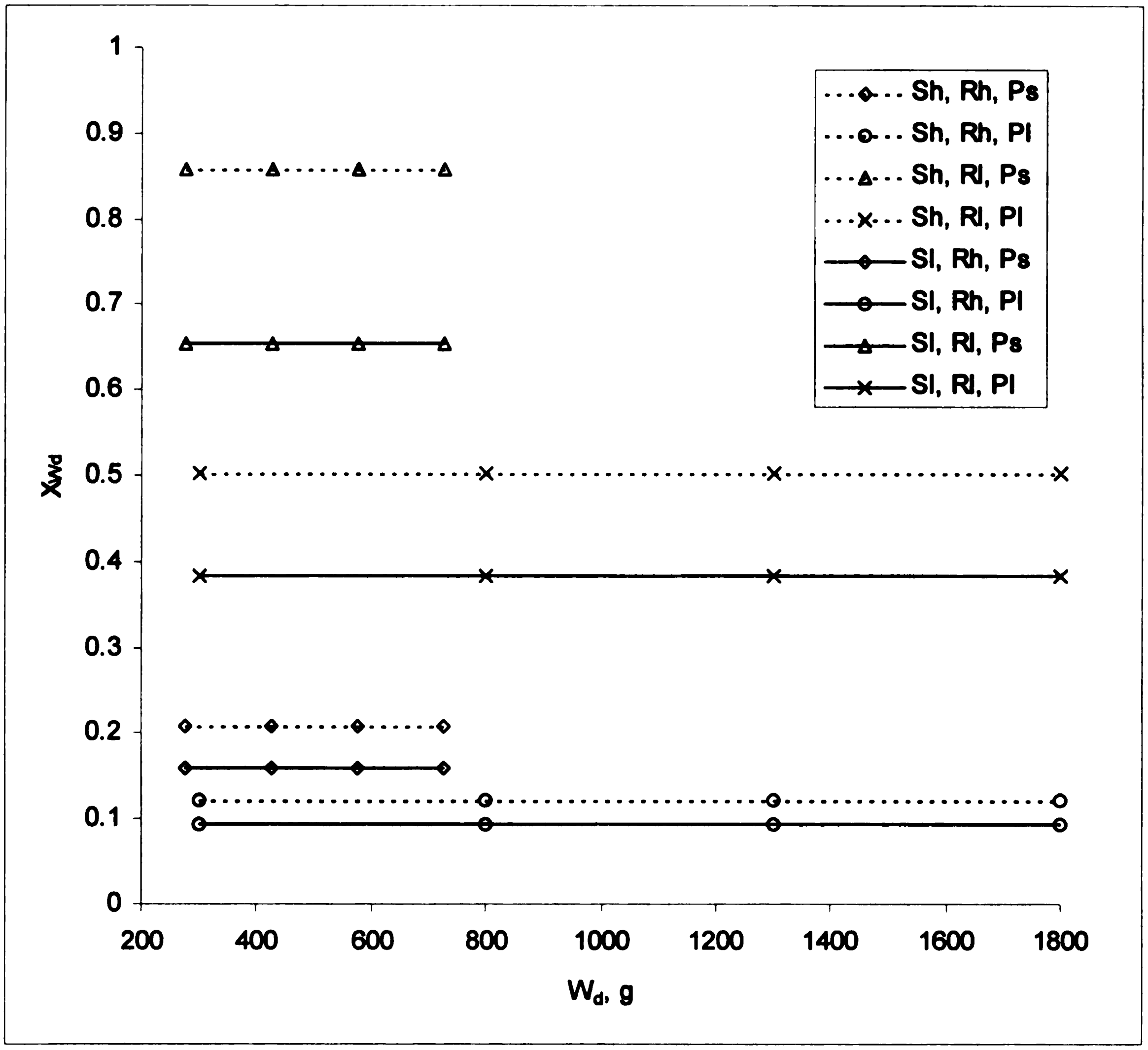

Figure 29. The plot of χ_{Wd} as a function of W_d at different factor combinations

Table 40. Sensitivity coefficient of A at different factor combinations

Factor combinations	χ_A at A (m^2) value of							
	0.115	0.125	0.135	0.145	0.215	0.225	0.235	0.245
S_H, R_H, P_S	-590.7	-500.0	-428.0	-371.6	*	*	*	*
S_H, R_H, P_L	*	*	*	*	-204.6	-186.8	-171.2	-157.6
S_H, R_L, P_S	-2416.5	-2045.8	-1753.8	-1520.3	*	*	*	*
S_H, R_L, P_L	*	*	*	*	-837.3	-764.5	-700.9	-644.8
S_L, R_H, P_S	-451.0	-381.7	-327.3	-283.7	*	*	*	*
S_L, R_H, P_L	*	*	*	*	-156.2	-142.6	-130.7	-120.3
S_L, R_L, P_S	-1845.5	-1561.9	-1339.0	-1160.7	*	*	*	*
S_L, R_L, P_L	*	*	*	*	-639.2	-583.7	-535.0	-492.3

* No data

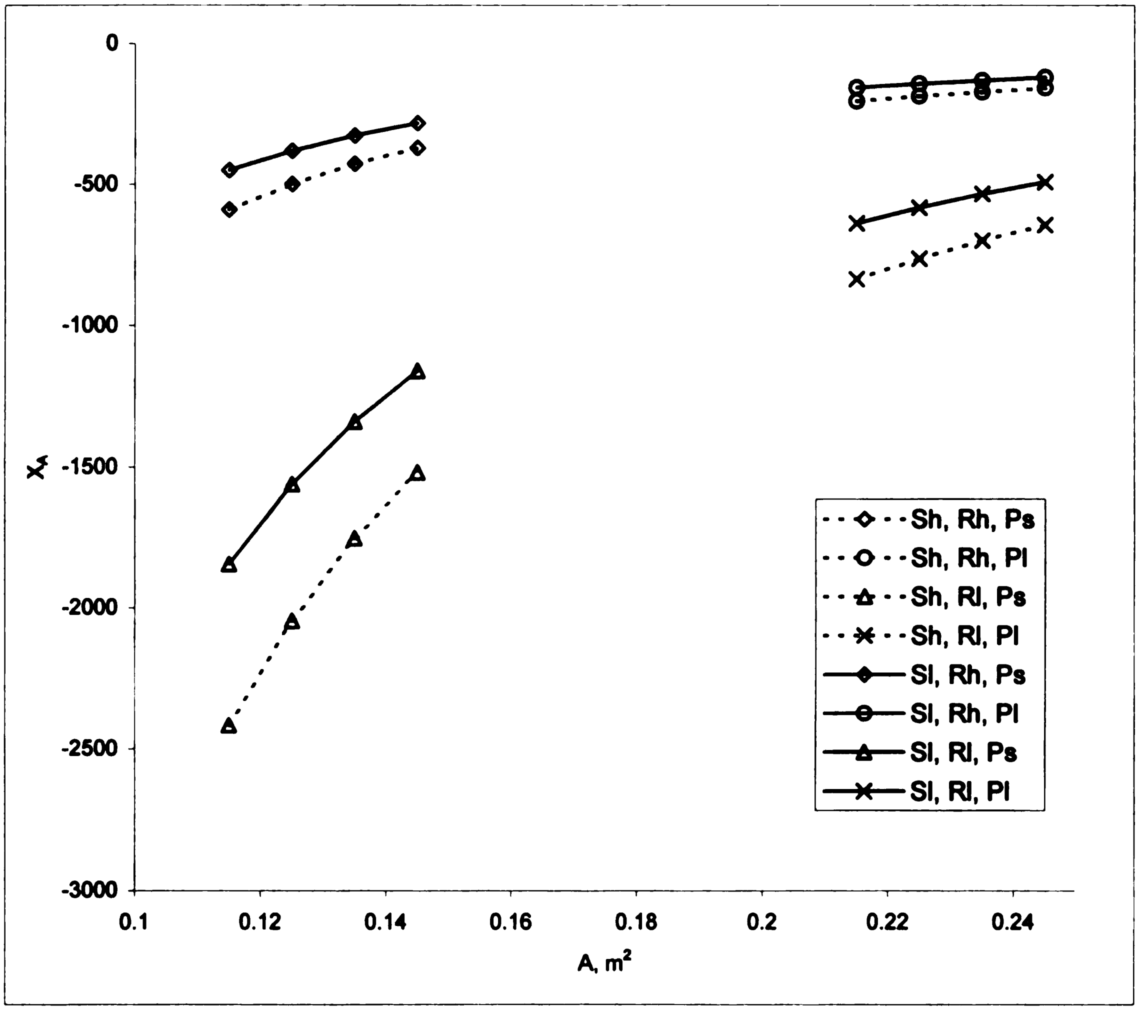

Figure 30. The plot of χ_A as a function of A at different factor combinations

Table 41. Sensitivity coefficient of A/W$_d$ at different factor combinations

Factor combinations	$\chi_{A/Wd}$ at A/W$_d$, m^2/g value of			
	0.0001	0.0003	0.0005	0.0007
S_H, R_H	-2.84	-0.03	-0.01	-0.01
S_H, R_L	-11.6	-0.13	-0.05	-0.02
S_L, R_H	-2.16	-0.02	-0.01	-0.004
S_L, R_L	-8.86	-0.1	-0.03	-0.02

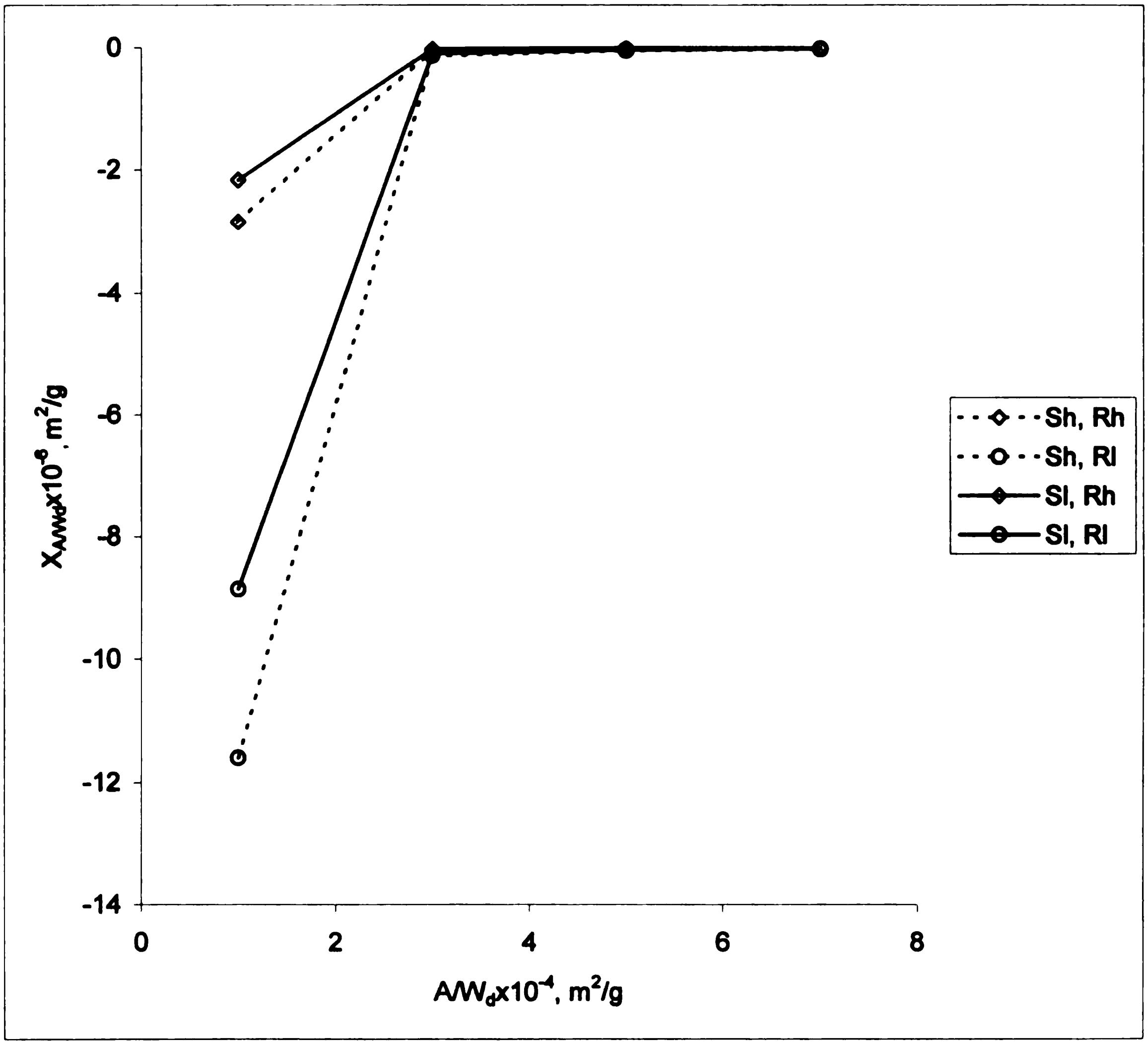

Figure 31. The plot of $\chi_{A/Wd}$ as a function of A/W$_d$ at different factor combinations

Table 42. Sensitivity coefficient of R at different factor combinations

Factor combinations	χ_R at R (g/m^2.day.mmHg) value of			
	0.4	0.9	1.4	1.9
S_H, P_S	-649	-128	-53	-29
S_H, P_L	-460	-91	-38	-20
S_L, P_S	-495	-98	-40	-22
S_L, P_L	-350	-69	-29	-16

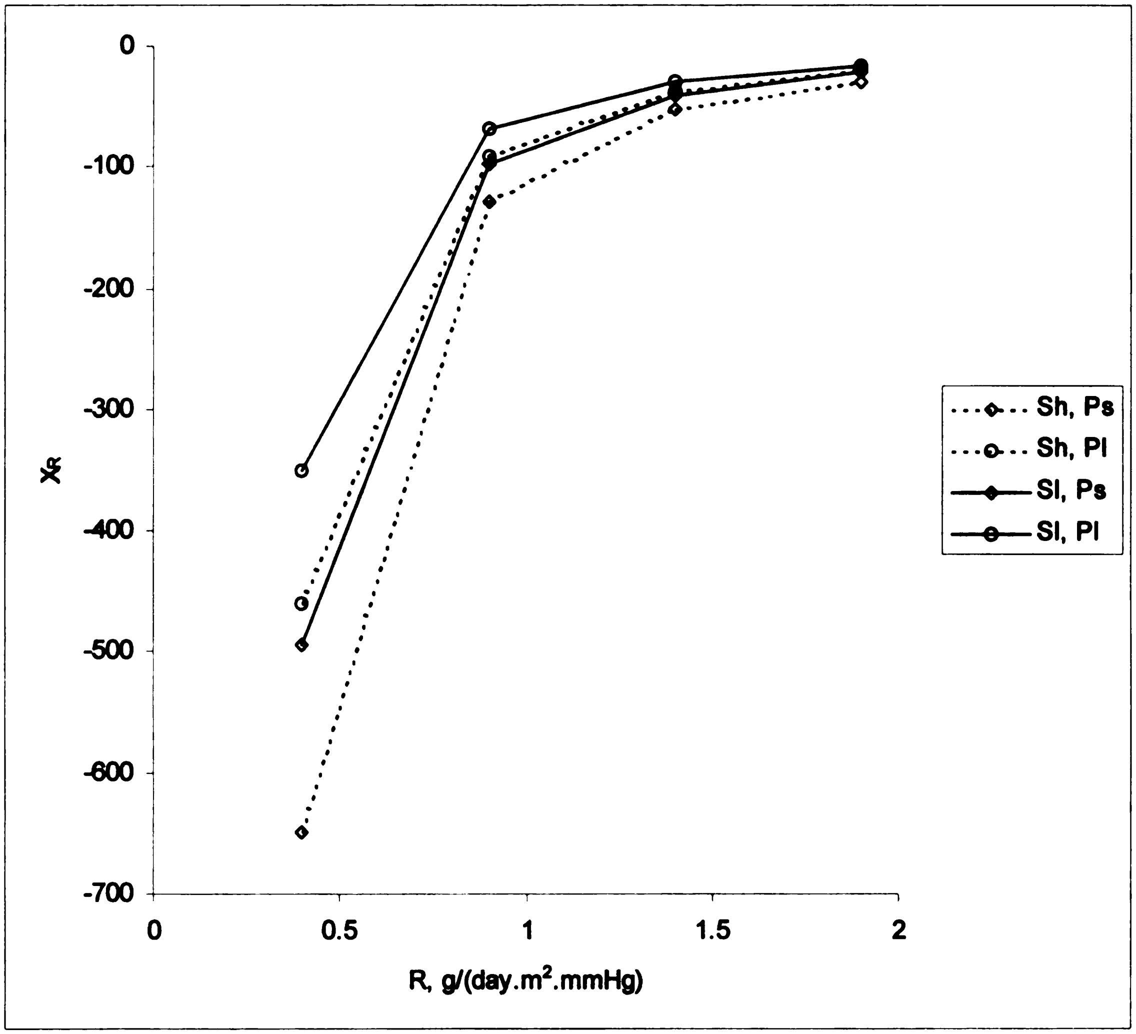

Figure 32. The plot of χ_R as a function of R at different factor combinations

Table 43. Sensitivity coefficient of p_s at different factor combinations

Factor combinations	χ_{Ps} at p_s (mmHg) value of				
	9.209 (10°C)	17.535 (20°C)	31.824 (30°C)	55.324 (40°C)	92.51 (50°C)
S_H, R_H, P_S	-37.6	-10.4	-3.2	-1.0	-0.4
S_H, R_H, P_L	-26.6	-7.4	-2.2	-0.7	-0.3
S_H, R_L, P_S	-153.9	-42.4	-12.8	-4.3	-1.5
S_H, R_L, P_L	-109.0	-30.0	-9.1	-3.0	-1.1
S_L, R_H, P_S	-11.8	-3.2	-1.0	-0.3	-0.1
S_L, R_H, P_L	-8.3	-2.3	-0.7	-0.2	-0.1
S_L, R_L, P_S	-48.4	-13.3	-4.0	-1.3	-0.5
S_L, R_L, P_L	-34.2	-9.4	-2.8	-1.0	-0.3

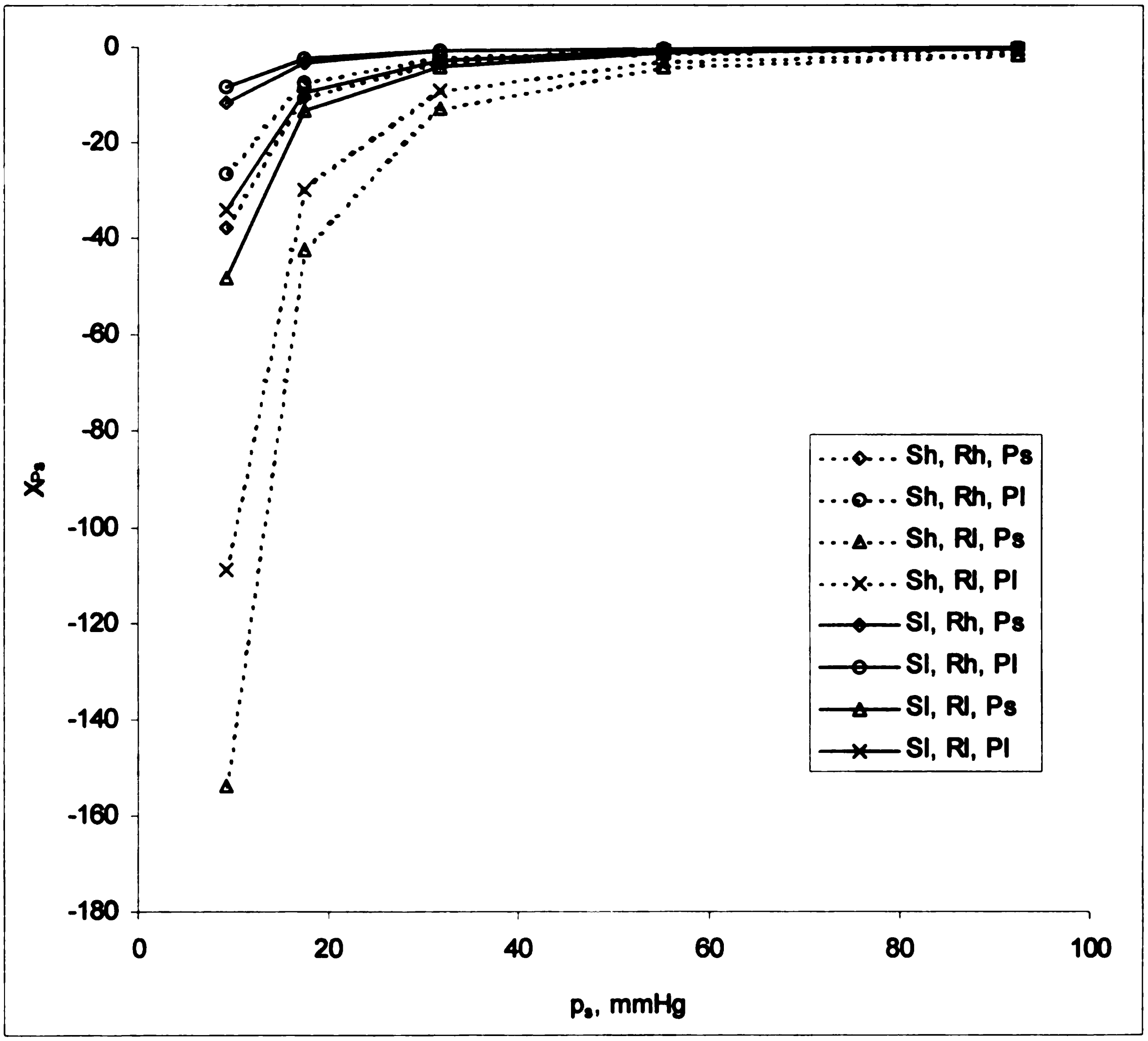

Figure 33. The plot of χ_{Ps} as a function of ps at different factor combinations

Table 44. Sensitivity coefficient of RH at different factor combinations

Factor combinations	χ_{RH} at RH (%) value of				
	50	60	70	80	90
S_H, R_H, P_S	-2.9	-8.7	-2.4	-101.3	-679.1
S_H, R_H, P_L	-2.0	-6.2	-17.0	-71.7	-480.9
S_H, R_L, P_S	-11.7	-35.5	-98.3	-414.4	-2778.1
S_H, R_L, P_L	-8.3	-25.1	-69.6	-293.5	-1967.5
S_L, R_H, P_S	-5.7	-12.8	-31.5	-95.4	-455.8
S_L, R_H, P_L	-4.0	-9.1	-22.3	-67.5	-322.8
S_L, R_L, P_S	-23.2	-52.7	-129.2	-390.4	-1864.8
S_L, R_L, P_L	-16.4	-37.3	-91.5	-276.5	-1320.7

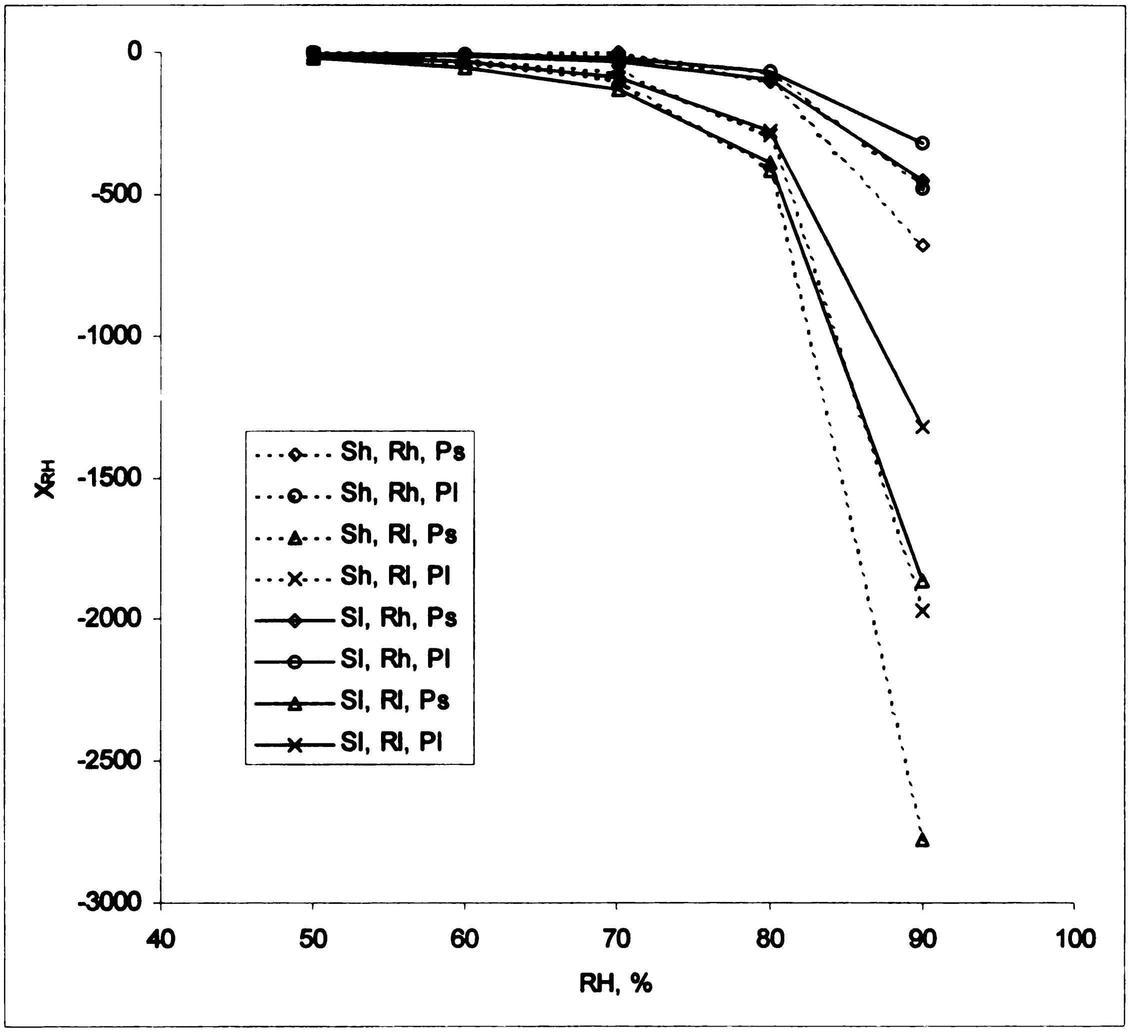

Figure 34. The plot of χ_{RH} as a function of RH at different factor combinations

APPENDIX F

ERROR ANALYSIS OF SHELF LIFE MODEL

Table 45. Percent error of parameters in shelf life model for packages at 40°C, 83% RH and 25°C, 67% RH.

Parameter	Error, %					
	HiAS	HiAL	HiES	LoAS	LoAL	LoES
C	0.06	0.06	0.06	0.04	0.04	0.04
W_m	1.09	1.09	1.09	1.19	1.19	1.19
k	11.46	11.46	11.46	11.7	11.7	11.7
p_s	0.81	0.81	0.81	0.29	0.29	0.29
RH	2.81	2.81	2.81	0.16	0.16	0.16
M_i	0.82	0.82	0.82	0.82	0.82	0.82
W_d	0.44	0.21	0.28	0.06	0.17	0.11
R	25	25	12.24	11.11	11.11	15.91

The absolute error of shelf life value was calculated by Gauss' Law of Error Propagation based on the error of model parameters as follow:

$$\delta t = \sqrt{\begin{array}{l}\left(\frac{\partial t}{\partial C}\cdot\delta C\right)^2+\left(\frac{\partial t}{\partial W_m}\cdot\delta W_m\right)^2+\left(\frac{\partial t}{\partial k}\cdot\delta k\right)^2+\left(\frac{\partial t}{\partial p_s}\cdot\delta p_s\right)^2+\\\left(\frac{\partial t}{\partial RH}\cdot\delta RH\right)^2+\left(\frac{\partial t}{\partial M_i}\cdot\delta M_i\right)^2+\left(\frac{\partial t}{\partial W_d}\cdot\delta W_d\right)^2+\left(\frac{\partial t}{\partial R}\cdot\delta R\right)^2\end{array}} \qquad (141)$$

Where δ represents absolute error

With Gauss' Law of Error Propagation, the percent error of shelf life for non-fat dry milk at certain final moisture content were calculated as:

$$\text{Error, \%} = \frac{\delta t}{t}\times 100 \qquad (142)$$

and percent error of predicted shelf life for non-fat dry milk packaged in different packages at 40°C, 83 %RH and 25°C, 67 %RH are presented in Table 46 and 47, respectively.

Table 46. Percent error of shelf life for non-fat dry milk in three different packages stored at 40°C, 83% RH.

Mf	Error, %		
	HiAS	HiAL	HiES
5	34.79*	33.01*	33.63*
7	32.80*	32.80*	24.86*
9	38.23*	38.13*	31.28*
11	49.49*	47.59*	42.48*
13	66.52	66.38	62.67
15	107.40	107.62	105.00
17	258.35	258.40	257.69

* data used for construction x-axis error bar

Table 47. Percent error of shelf life for non-fat dry milk in three different packages stored at 25°C, 67% RH.

Mf	LoAS	LoAL	LoES
5	38.4	38.46	38.18
6	26.19*	26.31*	28.43*
7	29.86*	29.68*	32.22*
8	36.40*	36.51*	38.40*
9	48.92	49.15	50.14
10	77.33	77.35	78.34

* data used for construction x-axis error bar

The error that each parameter contributed to the total error at certain moisture content of each package and storage condition are graphically presented in Figure 35 to 40.

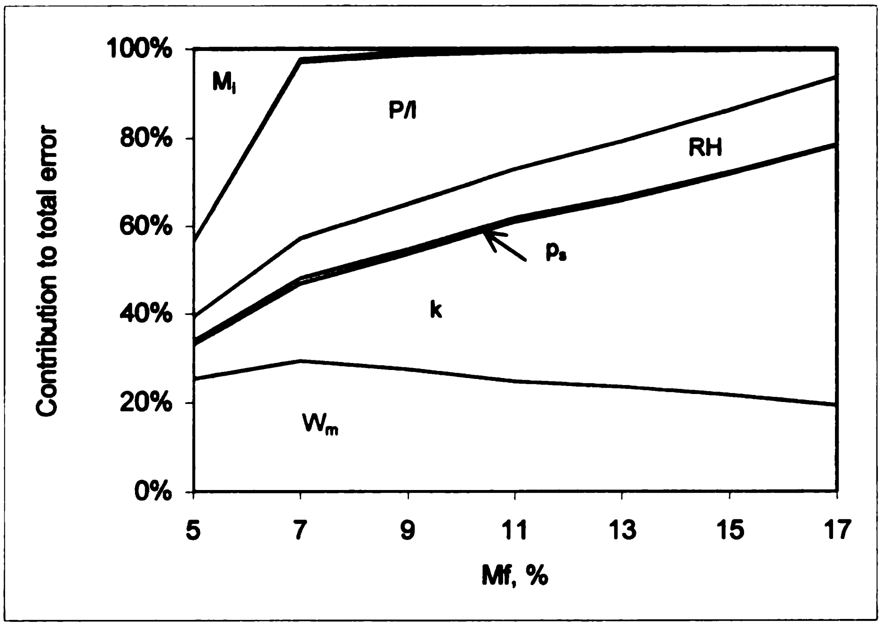

Figure 35. Contribution of error from each model parameters to total error in shelf life of non-fat dry milk packaged in small boxes made from material A and stored at 40°C, 83% RH (HiAS)

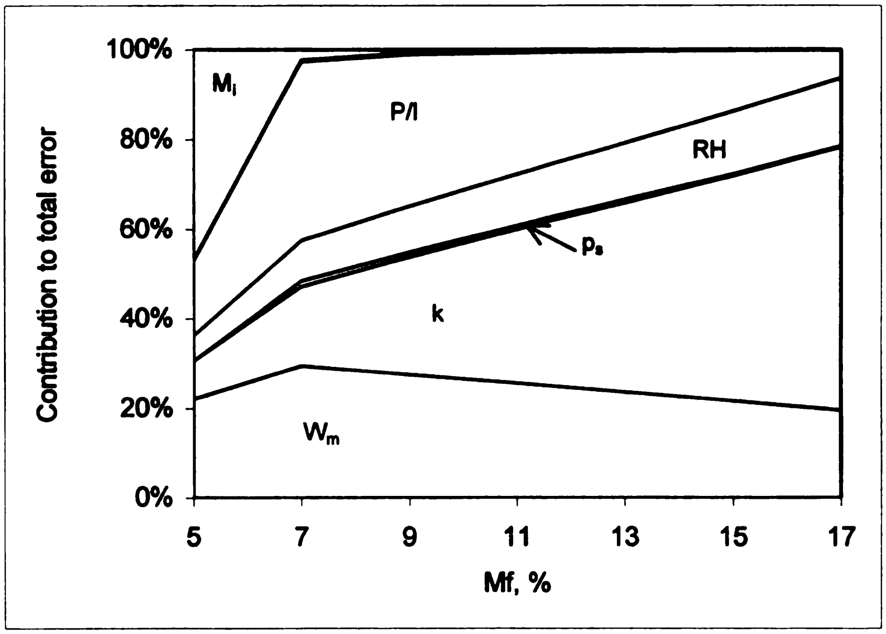

Figure 36. Contribution of error from each model parameters to total error in shelf life of non-fat dry milk packaged in large boxes made from material A and stored at 40°C, 83% RH (HiAL)

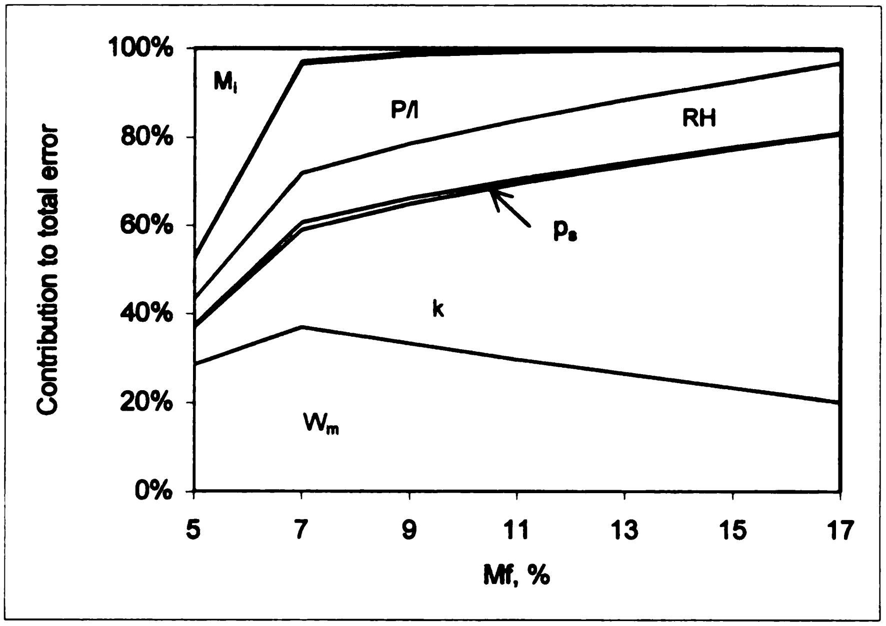

Figure 37. Contribution of error from each model parameters to total error in shelf life of non-fat dry milk packaged in small boxes made from material E and stored at 40°C, 83% RH (HiES)

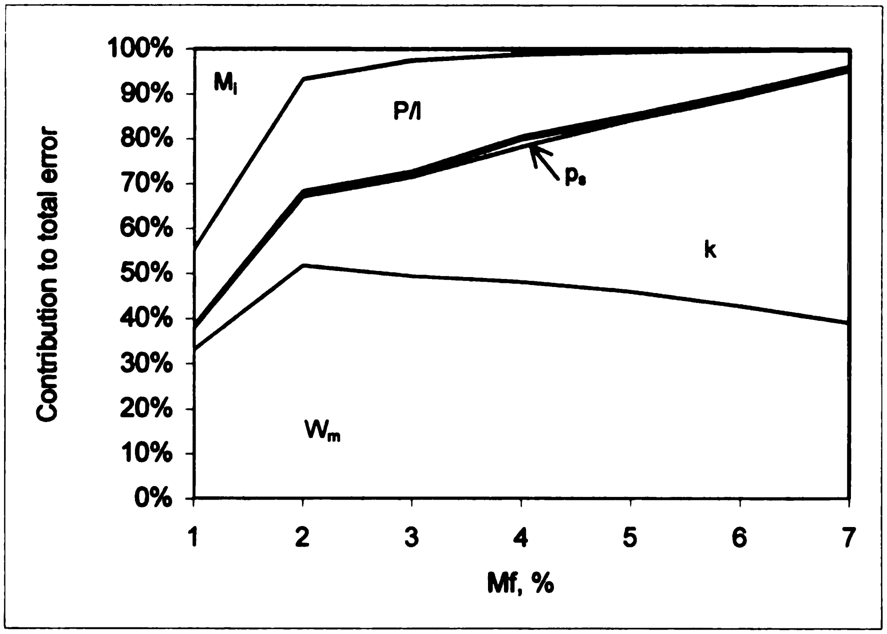

Figure 38. Contribution of error from each model parameters to total error in shelf life of non-fat dry milk packaged in small boxes made from material A and stored at 25°C, 67% RH (LoAS)

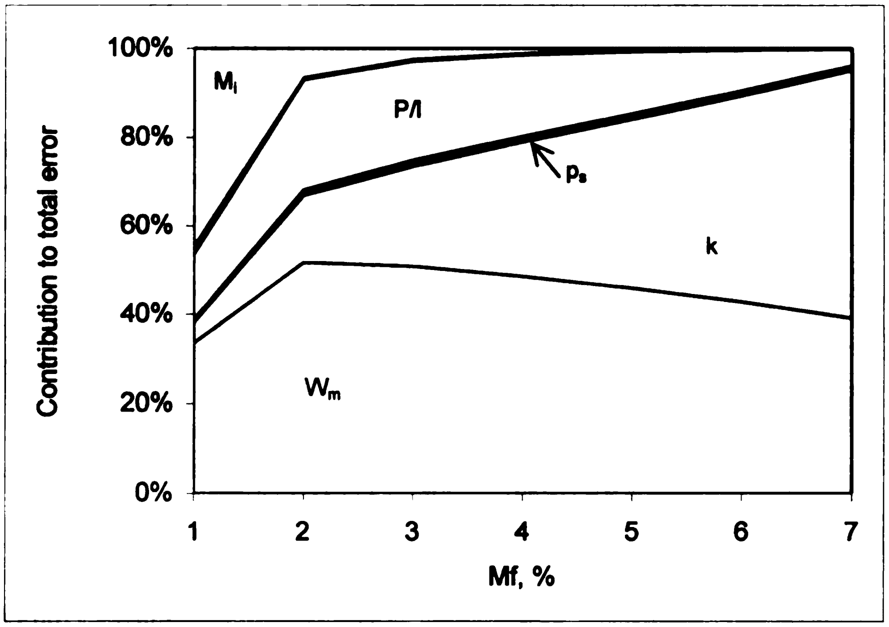

Figure 39. Contribution of error from each model parameters to total error in shelf life of non-fat dry milk packaged in large boxes made from material A and stored at 25°C, 67% RH (LoAL)

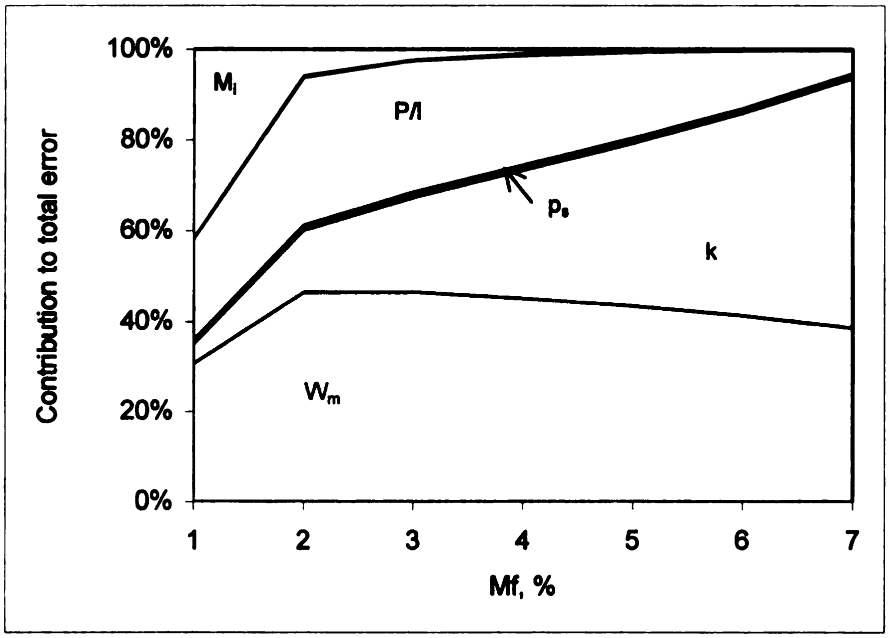

Figure 40. Contribution of error from each model parameters to total error in shelf life of non-fat dry milk packaged in small boxes made from material E and stored at 25°C, 67% RH (LoES)

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