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MARIA DE FATIMA FILIPE POCAS

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Maria de Fátima Filipe Poças

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ABSTRACT

MODELING THE MOISTURE TRANSFER OF TWO-COMPONENT FOOD PRODUCTS IN A FLEXIBLE PACKAGE

By

Maria de Fátima Filipe Poças

Most deterioration reactions of foods are greatly affected by the food's moisture content. To prevent spoilage of dry products a packaging system able to provide an adequate protection against moisture uptake is necessary. Mathematical modeling is a useful technique for shelf-life prediction at the packaging development and optimization stages. The application of this technique to two-component foods was the main objective of this work. A mathematical model correlating the products moisture sorption characteristics, the packaging properties and the storage conditions was developed and a computer program was prepared based on the model. The program selects the isotherm equation that best fits the experimental isotherms (Henderson, Chen, Oswin, Halsey or GAB) and calculates the change in components' moisture content or the mixture shelf-life. Experimental validation with breakfast cereal and powder chocolate packaged in two different packaging materials was carried out. The model tends to overestimate the moisture content of the components, in particular for the cereal and for longer storage periods. Deviations seem to be dependent on the packaging material barrier, which affects the relative tendency of the components to absorb moisture simultaneously.

To my husband João

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PREFACE

This thesis is divided into three chapters. In Chapter I, a literature review on relevant topics for the main subject is presented. Chapter II (Modeling the moisture content of two-component food products in a flexible package. Model development) and Chapter III (Modeling the moisture content of two-component food products in a flexible package. Model validation) were prepared in article format. A Reference section is presented at the end of each chapter.

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LIST OF SYMBOLS

A - packaging surface area

a_{wo} - external water activity

a_w - internal water activity

A_o, A_1, A_2 - parameters from non-linear moisture isotherms

b - slope of the linear moisture isotherms

EMC - equilibrium moisture content (dry basis)

IMC - initial moisture content (dry basis)

IR - infra red

l - film thickness

L - dimensionless number (ratio between moisture permeance in the food to the permeance in the packaging material)

Mi - moisture content of product i (dry basis)

Mmix - moisture content of the mixture (dry basis)

OPP - oriented polypropylene

PE - polyethylene

PE/barrier - polyethylene coextruded with a barrier material

P - film permeability coefficient

p^s - water vapor saturation pressure

p_o, p_i - vapor pressure of water outside and inside the package

RH - relative humidity

R - relative percent root mean square of the difference between the experimental and calculated values of moisture content

S - root mean square of the difference between the experimental and calculated values of moisture content

t - time

U - average of relative percent difference between the experimental and calculated values of moisture content

Wi - dry weight of component i

Yf - final wet weight

Yi - initial wet weight

Z - mixture wet weight

INTRODUCTION

The control of moisture gain or loss during storage of packaged products is of prime importance in the food industry for safety, marketing, economic and regulatory reasons. Particularly for dry foods, the packaging system should be designed to provide protection against moisture uptake. Shelf-life determination is required to develop and optimize the packaging system. Mathematical modeling is useful for estimating shelf-life by reducing the time and cost of experimental shelf-life determination.

The change in societies' life-styles has led to great developments in food products processing and preservation, impelled by consumer demands for reduced time and effort for meals' preparation. An increasing number of combined or multicomponent food products is now marketed. Additionally, concern with environment protection and economic constrains have led to a generalized trend in reducing packaging materials and avoiding over-packaging without reducing products' protection or packaging user-friendliness.

In moisture-sensitive multicomponent foods, moisture is transferred from products having higher water activity to those with lower water activity. At equilibrium, all the products will have the same water activity and dry products, such as breakfast cereal, may loose their desirable crispness while semi-moist components, such as dried fruits, may dry out to moisture content levels lower than the acceptable values.

In a moisture-permeable package, there is a moisture transfer between the food product and the external environment. The rate of moisture transfer is governed by the difference between the water vapor pressure in the package head-space and the water vapor pressure in the environment. If the diffusion of moisture within the food product is fast compared to the diffusion across the packaging barrier, the food product reaches equilibrium with the head-space vapor pressure and the product's moisture content may be described by its isotherm.

Shelf-life modeling of single products has been reported. However, for multicomponent foods, studies have only focused on the prediction of mixture sorption behavior from the sorption characteristics of individual components and assumed no moisture transfer across the packaging barrier. Nevertheless, shelf-life studies have been reported using a linear sorption isotherm equation or equations with limited range of water activity.

The development of a more general mathematical model to predict the moisture change over storage time and the shelf-life of two-component foods was the main goal of this research. A computer program to perform the model calculations was prepared and experimental validation was carried out. The model takes into consideration the whole isotherm and not only a linear part of it: the Henderson, Chen, Oswin, Halsey and GAB equations may be selected for the shelf-life calculations. Experimental validation of the model was performed with mixtures of breakfast cereal and powder chocolate packaged into different materials.

CHAPTER I

LITERATURE REVIEW

Introduction

Moisture content and water activity are critical parameters affecting the shelf life of most foods: textural quality, chemical and biochemical reactions and microbial growth rates are greatly affected by those parameters.

Water activity, describing the availability of water to play a role on physical, chemical and biochemical reactions, has been used to explain the influence of moisture on reaction rates. Recently, the glass transition theory from polymer science, has been introduced on food preservation, particularly for intermediate and high moisture foods (Nelson and Labuza, 1994; Chirife and Pilar Buera, 1994). The relation between glass transition temperature and food stability has been seen with increasing interest to help understanding the influence of water on reactions of food deterioration or spoilage.

Moisture content and equilibrium water activity of a food product are related to each other by the food sorption isotherm. Several equations have been used to mathematically describe sorption data of different groups of food products. A review of those equations is presented in this Chapter. The equations are listed in Appendix A. A review on the work devoted to the prediction of moisture sorption behavior of mixed or multicomponent products from individual component's behavior is also presented in this Chapter.

The control of moisture uptake or loss during storage is one of the major protection functions of the food package. Fast and reliable methods for shelf life prediction are of great interest as a tool for packaging development and optimization. Mathematical models correlating the characteristics of the product, the package properties and the environmental conditions are less time consuming and have lower cost than other techniques of shelf-life determination. A review on shelf-life models developed for products, whose shelf-life may be regarded as solely dependent on moisture content, is also presented.

1. Review on Food Moisture Sorption Isotherm Equations

Water binding to food products takes place by the following mechanisms: (i) adsorption as a monolayer to specific sites by molecular forces, (ii) multilayer absorption consisting of water molecules hydrogen bonded and (iii) absorption with free water in the interstitial pores. These mechanisms correspond to different ranges of equilibrium water activity (a_W). Monolayer adsorption corresponds to a_W up to ca. 0.3, at which most deterioration reactions have a minimum rate. The second mechanism corresponds to the medium range of a_W in the sorption isotherm that is often a straight line in this range. At high a_W, free water is capable of acting as a solvent and microbial growth may occur.

Most foods' sorption isotherms show hysteresis behavior, i.e., the moisture content is lower on equilibrium by adsorption than by desorption. This has important implications with respect to food stability, since foods adjusted to the desired a_W by desorption rather than by adsorption, may deteriorate more rapidly because of their higher moisture content.

A large number of equations have been proposed to describe the moisture sorption behavior of foods. Some are based on theoretical principles and some are proposed due to its fitting capability to experimental data. The models can be classified into kinetic models based on a molecular monolayer of water, kinetic models based on multilayer sorption and a condensed film, models imported from the polymer literature and empirical models (Peleg, 1993).

Chirife and Iglesias (1978) reviewed the equations existing in the literature and compiled twenty-three equations, discussing its origin, range of applicability and use. Some of these equations were mathematically equivalent and some were limited to a specific range of a_W or type of foods.

Boquet *et al.* (1978) and Boquet *et al.* (1979) evaluated equations with two and three parameters for fitting experimental data of moisture sorption of fruits, meats, milk products, proteins, starchy foods and vegetables. The authors studied the following two-parameter equations: Bradley, Caurie, Halsey, Henderson, Iglesias and Chirife, Kuhn, Mizrahi and Oswin equations. The Halsey and the Oswin models were appointed as the more versatile ones (Boquet *et al.*, 1978). The three-parameter equations studied were the Brunauer-Emmet-Teller (BET), Chen, Hailwood and Horrobin and Young and Nelson equations. The Hailwood and Horrobin equation, which is mathematically equivalent to the Guggenheim-Anderson-de Boer (GAB) equation, was considered very versatile (Boquet *et al.*, 1979). It was also noted that some of the simpler two-parameter equations give, in some cases, fits of comparable or even better accuracy than some of the three-parameter equations, pointing out that the use of a third-parameter may not be always worthwhile.

Lomauro *et al.* (1985a) and Lomauro *et al.* (1985b) compared the accuracy of the Halsey, Oswin, Iglesias and Chirife equations (two parameters) and the GAB equation (three parameters) to describe moisture sorption of several types of foods (fruits, vegetables and meat products, milk, coffee, tea, nuts, oilseeds, spices and starchy foods). They concluded that the GAB equation gives a very good fit over a wide range of a_W (up to 0.9), for most food isotherms exhibiting a sigmoid shape curve. The equation also gives a better evaluation of the amount of water tightly bound by the primary sorption sites (Bizot, 1983), which is related to the physical and chemical deterioration in dehydrated foods (Chirife and Iglesias, 1978).

Saravacos *et al.* (1986) used the D'Arcy-Watt equation (five parameters) to fit experimental data of raisin's isotherms at various temperatures. The best fit over a wide range of a_W (0.1 - 0.9) was obtained with the five-parameter D'Arcy-Watt equation as compared to the Halsey and GAB equations.

An empirical double power law four-parameter equation was proposed by Peleg (1993). Its fitting capabilities to sorption data of different food products, including raisin, were compared with the GAB equation. Better results were obtained with the double power law equation than with the GAB.

The criteria commonly followed to evaluate the goodness of fit of the experimental data, is the average of relative percent difference between the experimental and calculated values of moisture content (U), expressed as

$$U = \frac{100}{n} \sum_{i}^{n} \left| \frac{Mi - Mi^*}{Mi} \right| \qquad (1)$$

where Mi is the experimental moisture content, Mi* is the calculated and n is the number of experimental data points.

Boquet *et al.* (1978) suggested the use of the root mean square of the deviations (S), expressed as

$$S = \sqrt{\frac{1}{n} \sum_{i}^{n} (Mi - Mi^*)^2} \qquad (2)$$

to compare the fitting abilities of the different equations when applied to the same experimental data.

The relative percent root mean square (R) has also been used (Bizot, 1983), expressed as

$$R = \sqrt{\frac{1}{n}\sum_{1}^{n}\left|\frac{Mi - Mi^*}{Mi}\right|^2} \times 100 \qquad (3)$$

which combines both concepts described above.

A list of the equations to describe the isotherms referred to above is presented in the Appendix A.

2. Review on Multicomponent Food Isotherms Equations

In packages of multicomponent food products, a transfer of moisture occurs not only between the products and the environment, but also between the components. At equilibrium, all components will have the same a_W and the final moisture content of each component will influence the quality and shelf-life of the mixed product (Hong et al, 1986; Gal, 1983; Labuza, 1984). The prediction of equilibrium a_W is therefore very important when formulating a moisture sensitive multicomponent food.

The prediction of water sorption behavior of a mixture from the individual components has been studied by several authors: Iglesias *et al* . (1980), Chinachoti and Steinberg (1985), Chinachoti and Steinberg (1988), Leiras and Iglesias (1991), Lang and Steinberg (1980), Lang and Steinberg (1981), Nieto and Toledo (1989) and Lang *et al.* (1981). Water is assumed to be independently bonded to each product as described by equation (4):

$$M_{mix} = \frac{\sum W_i M_i}{\sum W_i} \qquad (4)$$

where M_{mix} is the moisture content of the mixture, M_i is the moisture content of product i before mixing and W_i is the dry weight of component i.

Interactions between the mixture components may result in either a decreased or an increased water sorption by the mixture as compared to the moisture content predicted by equation (4), particularly in mixtures prepared by any method other than by simple physical mixing, such as wet mixing followed by freeze-drying.

The predicted values of moisture content of mixtures of protein and carbohydrates were almost always higher than the measured ones (Iglesias *et al.*, 1980), but mixtures of sucrose-protein sorbed more water than the calculated (Chinachoti and Steinberg, 1988). In both cases, mixtures were obtained by freeze-dehydration of water solutions or suspensions of the components.

Solubilization of components such as salt and sugar, may also yield to deviations from the predicted behavior, as found in cake mixes, specially at high a_w where experimental moisture contents were greater than the predicted (Leiras and Iglesias, 1991). Interactions involving hydrogen bonds between the components competing with hydrogen bonds with water may explain the lower sorption of mixtures of sodium chloride and starch that showed a decreased water sorption at a_w above 0.75 as compared to the expected values obtained from the mass balance (Chinachoti and Steinberg, 1985).

Mixtures of starch, casein, sugar, salt, propylene glycol and ground beef in binary and ternary combinations prepared by hand mixing, have shown a good agreement between the predicted values of moisture content calculated by equation (4) and the measured values (Lang and Steinberg, 1980).

In an attempt to include interaction parameters Nieto and Toledo (1989) applied an empirical approach using a factorial design of 4x3 levels of combinations of NaCl, non-fat dry milk and lard added to minced fish to produce a fish sausage. Although with good agreement between the experimental and predicted values, the regression equation was limited to the factors and respective levels used in the validation experiment.

Lang *et al.* (1981) followed a thermodynamic approach, using an enthalpy balance, rather than a mass balance described by equation (4). The hypothesis tested was that the total partial enthalpy change for the water of a mixture is equal to the sum of the partial enthalpy changes for the water of the individual ingredients at the same a_W. This was tested for starch, casein, sucrose and starch-casein and starch-sucrose combinations.

Salwin and Slawson (1959) derived an equation to calculate the equilibrium relative humidity of a dehydrated mixture from the dry weight of the components, the initial relative humidity for each component and the slopes of the isotherms. Linear isotherms between the initial and the equilibrium relative humidity were assumed. They found good agreement between the calculated and the experimental final moisture content, although they were working over a narrow range of relative humidity. This is appointed as a major drawback, because at higher relative humidity, the normal s-shaped isotherms show more curvature and therefore the assumption of linear isotherm is no longer valid (Lang and Steinberg, 1981).

Iglesias *et al.* (1979) assumed the concept of additivity of the components' isotherms, calculating a mixture isotherm from the weight percentage of each component times the amount it would sorb alone. The merit lies on the use of a non-linear isotherm. The BET equation is used with applicability in the range of a_W from 0.05 to 0.40.

The estimation of equilibrium a_w of mixtures may, according to the models used, raise calculation difficulties. Peleg and Normand (1992) developed a method for a_w estimation using the easy-to-use mathematical software "MathCAD" package. The method is also based on a combined weighted isotherm, and determines the mixture a_w as the root of the relation $M_{mix} - \Sigma M_i = 0$, where M_{mix} is the mixture moisture content (a function of a_w) and M_i is the initial moisture content of component i. The method was developed for a closed system (there is no moisture exchange with the environment) and allows for each component to have a different sorption isotherm equation.

3. Review on Shelf-Life Models

The interest in the development of shelf-life models for moisture sensitive products has been recognized for long time. However, most studies have focused on packages of single products. After the concepts introduced by Heiss (1958), other studies on shelf-life modeling have followed, releasing some of the assumptions originally made and increasing the complexity and applicability of the models.

Heiss (1958) discussed the relationship between moisture sorption properties of foods, the packaging film permeability and the shelf-life of the product and developed a solution based on Fick's law of diffusion. The model was modified by Karel (1967) assuming a linear isotherm and later by Labuza, Mizrahi and Karel (1972) who introduced the non-linear isotherms Oswin, Kuhn and Mizrahi, on the model. Clifford *et al.* (1977) reported a shelf-life model taking into consideration the moisture in the package head-space and assuming a linear isotherm. Peppas and Khanna (1980) developed a model using the Nernst-Plank diffusion equation combined with the non-linear isotherms BET, Halsey, Oswin and Freundlich. The model was further extended to packaging systems where the polymeric film is appreciably swollen by the diffusing water. Kim (1992) developed a model and a computer program for predicting the shelf-life of a packaged pharmaceutical tablet based on the unsteady state mass transfer of water through the package and within the tablet and used the method of finite differences to solve the model. The influence of temperature on the system was introduced by Lee (1987) considering its effect on the permeability coefficient and by Kirloskar (1991) considering its effect on the sorption isotherm.

All the above referred studies have, as one of the assumptions, constant storage temperature and relative humidity. Cardoso and Labuza (1983) developed a dynamic mathematical model to predict moisture transfer for packaged pasta under controlled unsteady state conditions of temperature and relative humidity. The influence of storage temperature and relative humidity varying as sine wave, was considered on packaging permeability and on pasta isotherm.

Although moisture transfer in a combination of foods has been studied by several authors as previously referred, a much less amount of work has been devoted to the case where the mixture is packaged in a moisture permeable package and to its implication on the shelf-life of the product. In multicomponent foods, it is assumed that the amount of water sorbed at any a_w is equal to a weighted average of the moisture each component would absorb alone and a mixture isotherm could be derived. This approach was followed by Iglesias *et al.*, 1979 using the BET model to describe the mixture sorption isotherm. However, this model is only applicable in the a_w range 0.05 - 0.40. Furthermore, no experimental validation of the model was presented.

Hong, Bakshi and Labuza (1986) developed a computer-aided model using the finite element method to predict moisture transfer in a multicomponent mixed system during storage, but no moisture transfer across the container barrier was assumed. The GAB equation was used to describe the products isotherm. The model derived by Salwin and Slawson (1959), previously referred, assumes linear isotherms and does also not consider moisture transfer through the packaging.

Conclusions

Among the equations proposed to describe the moisture sorption isotherms of foods, the GAB gives the best results for a great variety of foods and over a wider range of a_w. The Halsey and the Oswin equations also represent well the experimental data of several types of foods.

Moisture sorption of dried mixtures may be influenced by interactions between components, by the method of mixing and by whether drying is carried out before or after mixing. As a first approach and in the case of physical mixing, it may be assumed that mixtures sorb an amount of water equal to the weighed average of the amount that components would sorb alone.

Shelf-life studies of moisture-sensitive foods in permeable packaging have only focused on single products and have considered only either linear or the BET isotherms in the case of multicomponent products.

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CHAPTER II

MODELING THE MOISTURE CONTENT OF TWO-COMPONENT FOOD PRODUCTS IN A FLEXIBLE PACKAGE

MODEL DEVELOPMENT

Abstract

Water plays a predominant role in the physical and chemical properties of foods, as well as in the mechanisms controlling their deterioration. Moisture-sensitive products packaged in plastic containers are expected to change their moisture content during storage and distribution. The impact of the exchange of water through the packaging material in most cases determines the product's shelf life.

The development of mathematical models correlating the characteristics of a product, the packaging material properties and the environmental conditions is desirable not only as a means to reduce the time and cost of shelf-life determinations but, perhaps more importantly, as a tool for packaging design.

Shelf-life models have been developed in the past for a single product. Studies of multicomponent food however, have also been reported. Most of these studies included solely the prediction of water sorption behavior of a mixture from the individual component's behavior. In the case of shelf-life estimation, a linear isotherm equation or equations with limited water activity range of applicability were used.

In this work, a computer shelf-life program for flexible packaging containing two moisture-sensitive food products was developed. The computer program allows to select from GAB, Oswin, Halsey, Henderson and Chen equations to fit the experimental moisture sorption isotherm of the products. Computer simulated results of products storage stability are presented.

Introduction

Controlling moisture content of a product is a major concern in preserving food products. Texture and chemical deterioration rates, as well as microbial growth, are greatly affected by the water activity of foods. Moisture transfer through the packaging material limits the shelf-life of most dehydrated products packaged in flexible plastic materials.

Shelf-life models have been developed in the past for a single product: Heiss (1958), Karel (1967), Labuza, Mizrahi and Karel (1972), Clifford *et al.* (1977), Peppas and Khanna (1980), Kim (1992), Lee (1987), Kirloskar (1991), Cardoso and Labuza (1983). In packages containing multicomponent food products, a transfer of moisture also occurs from the component with higher a_W to those at lower a_W. At equilibrium, all components will have the same a_W and the final moisture content of each component will influence the quality and shelf-life of the mixed product (Hong *et al.*, 1986; Gal, 1983; Labuza, 1984). The prediction of equilibrium a_W is therefore very important, when formulating a moisture sensitive multicomponent food.

Studies on the prediction of water sorption behavior of mixed multicomponent foods from the individual component's behavior have also been reported: Salwin and Slawson (1959), Iglesias *et al.* (1980), Chinachoti and Steinberg (1985), Chinachoti and Steinberg (1988), Leiras and Iglesias (1991), Lang and Steinberg (1980), Lang and Steinberg (1981), Nieto and Toledo (1989) and Lang *et al.* (1981). All of these studies however, did not consider the simultaneous moisture transfer across the packaging material. In studies for shelf-life prediction, a linear sorption isotherm equation or equations with limited a_W range of applicability were used (Labuza, 1984; Iglesias *et al.*, 1979).

The transfer of moisture in packages containing multicomponent moisture-sensitive products, takes place through the packaging material and within the food components. When the diffusion coefficient of water in the packaging material is much smaller than the diffusion of water within the product, the transport through the film barrier controls the shelf-life.

For multicomponent foods, it can be assumed that the amount of water transferred through the package at any a_W, is distributed proportionally to their respective sorption isotherms. A weighed isotherm could be derived and combined with the shelf-life models previously developed. This approach was followed by Iglesias *et al.* (1979), using the BET equation to describe the mixture sorption isotherm. However, this equation is only applicable in the a_W range 0.05 - 0.40.

The objective of this work was to develop a more general mathematical model to calculate the change in moisture content over storage time and the shelf-life of a two-component packaged mixture, using the GAB, Halsey, Henderson, Oswin or the Chen equations, maintaining the individuality of each component and not using one "weighed sorption isotherm". A computer program was written and simulation runs were carried out.

Mathematical Model Development

The rate of water transport through a permeable film is given by the following equation (Labuza *et al.*, 1972):

$$\frac{dW}{dt} = \frac{P}{l} A (p_o - p_i) \tag{5}$$

Where:

W is the weight of water transported across the film, in g

t is the time, in days

P is the film permeability coefficient, in $g\mu m / m^2$ day mmHg

l is the film thickness, in μm

p_o, p_i are the vapor pressure of water outside and inside of the package, respectively, in mmHg.

Under the conditions of usage of a package (temperature and relative humidity) only the internal pressure p_i is unknown. However, it is assumed that product's moisture content is in equilibrium with p_i .

When the diffusion coefficient of water through the packaging material is several order of magnitude smaller than the diffusion coefficient of water in the air and within the product, we can assume that the packaging material controls the moisture flow between the product and the external environment. This is the case of most packaging applications of dried foods. We also assume that there is a rapid equilibrium between water and the food. The internal pressure p_i is determined by the product equilibrium moisture content and the storage temperature.

When two products A and B are packaged together, the amount of moisture dW permeating through the package is equal to the moisture change in product A plus the moisture change in product B:

$$dW = W_A\, dM_A + W_B\, dM_B \tag{6}$$

Where:

W_A, W_B are the dry weights of components A and B, respectively

dM_A, dM_B are the change in moisture content of component A and B respectively, in g /g dry weight.

Substitution of equation (6) in equation (5) and rearrangement gives:

$$W_A\, dM_A + W_B\, dM_B = \frac{P}{l} A\, p^s\, (a_{wo} - a_w)\, dt \tag{7}$$

Where:

p^s is the water vapor pressure at the storage temperature

a_{wo}, a_w are the external and internal water activity, respectively

M_A and M_B are products' equilibrium moisture content at a_w

M_A and M_B are related to the a_w through the sorption isotherm equations.

Equation (7) can be integrated to give a relationship between time and moisture content of each component.

If the shelf-life of the mixture depends on the moisture content of the components, then the integration of equation (7) will provide a mean to estimate the shelf-life of the packaged mixture.

Two cases are analyzed depending on the type of sorption isotherms considered.

Case 1 - Linear sorption isotherms

The simplified case is when the moisture sorption isotherms of the components are represented by a linear equation within the water activity range under consideration:

$$M_A = a_A + b_A\, a_w \qquad (8.a)$$

$$M_B = a_B + b_B\, a_w \qquad (8.b)$$

Where a_A, a_B, b_A and b_B are the coefficients of the linear equation.

Then

$$dM_A = dM_B \frac{b_A}{b_B} \qquad (9.a)$$

$$dM_B = dM_A \frac{b_B}{b_A} \qquad (9.b)$$

Combining equations (9) with equation (7) and integrating gives:

$$t_A = \frac{l}{P\,A\,p^s}\left(W_A + W_B \frac{b_B}{b_A}\right) \int_{M_A^1}^{M_A^2} \frac{dM_A}{a_{wo} - a_w(M_A)} \qquad (10.a)$$

$$t_B = \frac{l}{P\,A\,p^s}\left(W_A \frac{b_A}{b_B} + W_B\right) \int_{M_B^1}^{M_B^2} \frac{dM_B}{a_{wo} - a_w(M_B)} \qquad (10.b)$$

Where:

$M_A{}^1$ and $M_B{}^1$ are the initial moisture content of component A and B, respectively t_A and t_B represents the time required to achieve the moisture content $M_A{}^2$ and $M_B{}^2$, respectively.

The analytical integration of this equations gives:

$$t_A = \frac{l}{PAp^s}\,(W_A b_A + W_B b_B)\ln\left[\frac{a_{wo} - a_w\left(M_A^1\right)}{a_{wo} - a_w\left(M_A^2\right)}\right] \qquad (11.a)$$

$$t_B = \frac{l}{PAp^s}\,(W_A b_A + W_B b_B)\ln\left[\frac{a_{wo} - a_w\left(M_B^1\right)}{a_{wo} - a_w\left(M_B^2\right)}\right] \qquad (11.b)$$

Where:

$a_w\,(M_A)$ and $a_w\,(M_B)$ represent the head-space water activity, in equilibrium with the components' moisture content. Superscripts 1 and 2 refer respectively for initial and final moisture content conditions

The shelf-life is considered as the lowest of t_A and t_B needed to reach $M_A{}^2$ and $M_B{}^2$ which are the critical values for product acceptance.

Case 2 - General case of non-linear isotherm

When the linear equation is too simplistic to represent real problems, the whole isotherm needs to be considered in the model and a numerical integration of equation (7) will be necessary.

Let us assume that the sorption isotherms equations of components A and B are described by,

$$M_A = f\,(a_w) \tag{12.a}$$

$$M_B = g\,(a_w) \tag{12.b}$$

Where $f(a_w)$ and $g(a_w)$ are the sorption equations for component A and B, respectively.

Considering the inverse functions of the isotherms, a_w can be expressed as a function of the components' equilibrium moisture content, M_A and M_B, respectively:

$$a_w = f^{-1}\,(M_A) \tag{13.a}$$

$$a_w = g^{-1}\,(M_B) \tag{13.b}$$

We assume that there is equilibrium between the moisture content of the two products and therefore:

$$M_A = f\left[g^{-1}\,(M_B)\right] \tag{14}$$

and

$$M_B = g\left[f^{-1}\,(M_A)\right] \tag{15}$$

Therefore dM_B can be expressed as a function of dM_A:

$$dM_B = D\;dM_A \tag{16}$$

Where the function D is defined as:

$$D(M_A) \equiv \frac{dM_B}{dM_A} = \frac{d\left[g\left[f^{-1}(M_A)\right]\right]}{dM_A} \tag{17}$$

The expression of dM_A as a function of dM_B gives:

$$D(M_B) \equiv \frac{dM_A}{dM_B} = \frac{d\left[f\left[g^{-1}(M_B)\right]\right]}{dM_B} \tag{18}$$

The function D can be obtained analytically or numerically.

Equation (7) rearranged can then be integrated

$$t_A = \frac{l}{PAp^s} \int_{M_A^1}^{M_A^2} \frac{W_A + W_B\, D(M_A)}{a_{wo} - a_w\,(M_A)}\, dM_A \tag{19.a}$$

$$t_B = \frac{l}{PAp^s} \int_{M_B^1}^{M_B^2} \frac{W_B + W_A\, D(M_B)}{a_{wo} - a_w\,(M_B)}\, dM_B \tag{19.b}$$

to calculate the shelf-life or to predict the moisture content over storage time.

A computer program was developed in MS-DOS QBasic language, to perform the above calculations. The program is presented in Appendix B together with flow charts describing the sub-routines. A flow chart of the sub-routine to calculate the shelf-life, is presented in Figure 1.

The program calculates the coefficients of the Henderson, Chen, Oswin, Halsey and GAB moisture sorption isotherm equations for each component based on moisture sorption data by linear regression (first four equations) and by second order polynomial regression (GAB equation). The form used for each equation is presented in Table 1. To evaluate the goodness of the fit, the relative percent root mean square of the difference between the experimental and the calculated moisture content (R) was used as indicated by equation (20):

$$R = \sqrt{\frac{1}{n}\sum_{i}^{n}\left|\frac{M_i - M_i^*}{M_i}\right|^2} \times 100 \tag{20}$$

where M_i is the experimental moisture content, M_i^* is the calculated moisture content and n is the number of experimental data points.

The equation presenting the best fit of the moisture sorption data may be selected to calculate the shelf-life or to calculate the moisture content of each component for different storage periods of time.

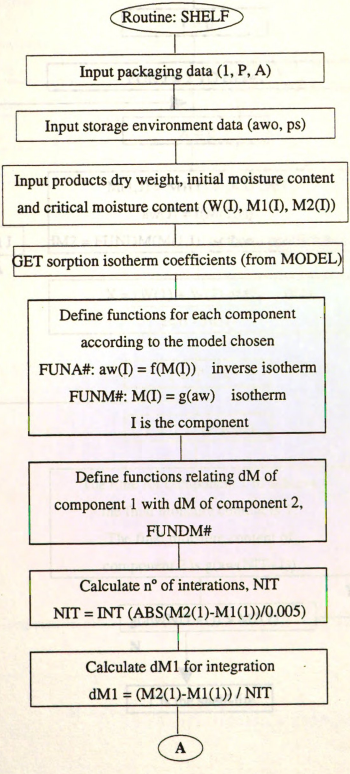

Figure 1 - Flow chart of the program sub-routine for shelf-life calculation

Figure 1 (cont'd)

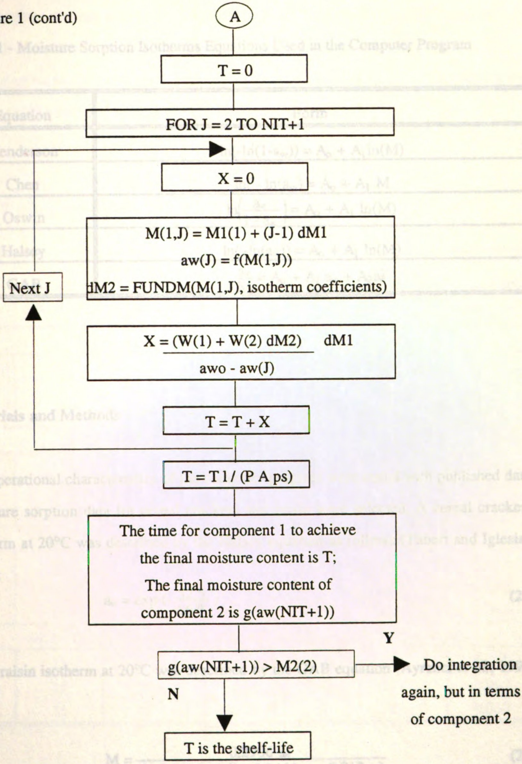

Table 1 - Moisture Sorption Isotherms Equations Used in the Computer Program

Equation	Form
Henderson	$\ln(-\ln(1-a_w)) = A_o + A_1 \ln(M)$
Chen	$\ln(- \ln(a_w) = A_o + A_1 M$
Oswin	$\ln\left(\frac{a_w}{1 - a_w}\right) = A_o + A_1 \ln(M)$
Halsey	$\ln(-\ln(a_w)) = A_o + A_1 \ln(M)$
GAB	$\frac{a_w}{M} = A_o + A_1 a_w + A_2 a_w^2$

Materials and Methods

The operational characteristics of the computer program were tested with published data. Moisture sorption data for cereal crackers and raisin were selected. A cereal cracker's isotherm at 20°C was described by the Halsey equation as follows (Tubert and Iglesias, 1986):

$$a_w = \exp\left(- \frac{52.5}{M^{1.91}}\right) \tag{21}$$

and a raisin isotherm at 20°C was described by the GAB equation (Ayranci *et al.*, 1990) as:

$$M = \frac{0.2906\, a_w}{(1- 0.9466 a_w)\,(1 - 0.9466 a_w + 2.912 a_w)} \tag{22}$$

The program was run with four sets of data in order to predict the storage stability curves for different conditions of (i) components' weight ratio, (ii) storage water activity, (iii) packaging barrier properties and (iv) total weight to packaging area ratio. Three runs were performed for each set. Table 2 summarizes the conditions used.

Table 2 - Conditions used in the computer simulation

Run	cereal weight, g	raisin weight, g	total weight, g	a_w	l/P, µm/ gµm/m^{2}day mmHg	Packaging area, m^2
Set A: To evaluate the influence of components weight ratio						
1	10	20	30	0.80	25 / 1.5	0.045
2	15	15	30	0.80	25 / 1.5	0.045
3	20	10	30	0.80	25 / 1.5	0.045
Set B: To evaluate the influence of storage water activity						
1	15	15	30	0.80	25 / 1.5	0.045
2	15	15	30	0.75	25 / 1.5	0.045
3	15	15	30	0.70	25 / 1.5	0.045
Set C: To evaluate the influence of packaging barrier properties						
1	15	15	30	0.80	25 / 2.5	0.045
2	15	15	30	0.80	25 / 1.5	0.045
3	15	15	30	0.80	30 / 1.5	0.045
Set D: To evaluate the influence of total weight to packaging area ratio						
1	15	15	30	0.80	25 / 1.5	0.045
2	20	20	40	0.80	25 / 1.5	0.045
3	25	25	50	0.80	25 / 1.5	0.050

For all the runs the initial moisture content was considered to be 0.077 g/g for the cereal and 0.09 g/g for the raisin.

Results and Discussion

Figures 2, 3, 4 and 5, present the results of the computer simulation using sets of data A, B, C and D from Table 2. In each case the moisture content of both components packaged are simulated for runs 1, 2 and 3. The calculated values are presented in Appendix C.

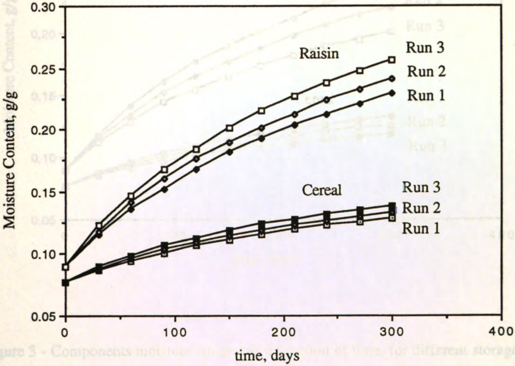

Figure 2 - Components moisture content as a function of time, for different components weight ratio (runs 1, 2 and 3). Simulated results using set of data A from Table 2

Figure 2 shows that increasing the ratio of the lower moisture product leads to an increased moisture uptake. This illustrates the influence of the mixture formulation when shelf-life is a concern.

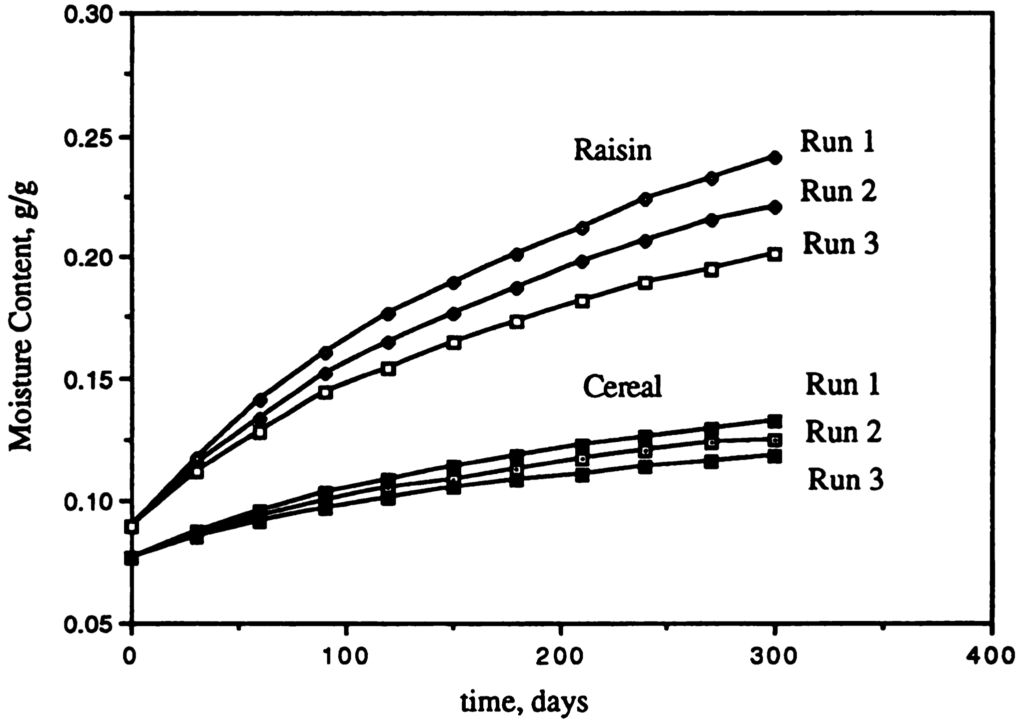

Figure 3 - Components moisture content as a function of time, for different storage water activities (runs 1, 2 and 3). Simulated results using set of data B from Table 2

The influence of storage relative humidity may be seen in Figure 3. As expected, the simulated curves indicate that storing at higher relative humidity gives lower shelf-life times. In most cases the storage environment conditions fluctuate over a range of relative humidity and temperature. The use of the program can bring significant time and cost savings when designing the packaging system. The assessment of the shelf life at different storage conditions can lead to correct packaging specifications providing information on the moisture barrier required and avoiding over-packaging.

The influence of the packaging moisture barrier properties is presented in Figure 4. As expected, the higher the packaging resistance to moisture transfer, i.e., the higher the l/P ratio, the longer the shelf-life. The use of different packaging materials or of different material's thickness may be assessed.

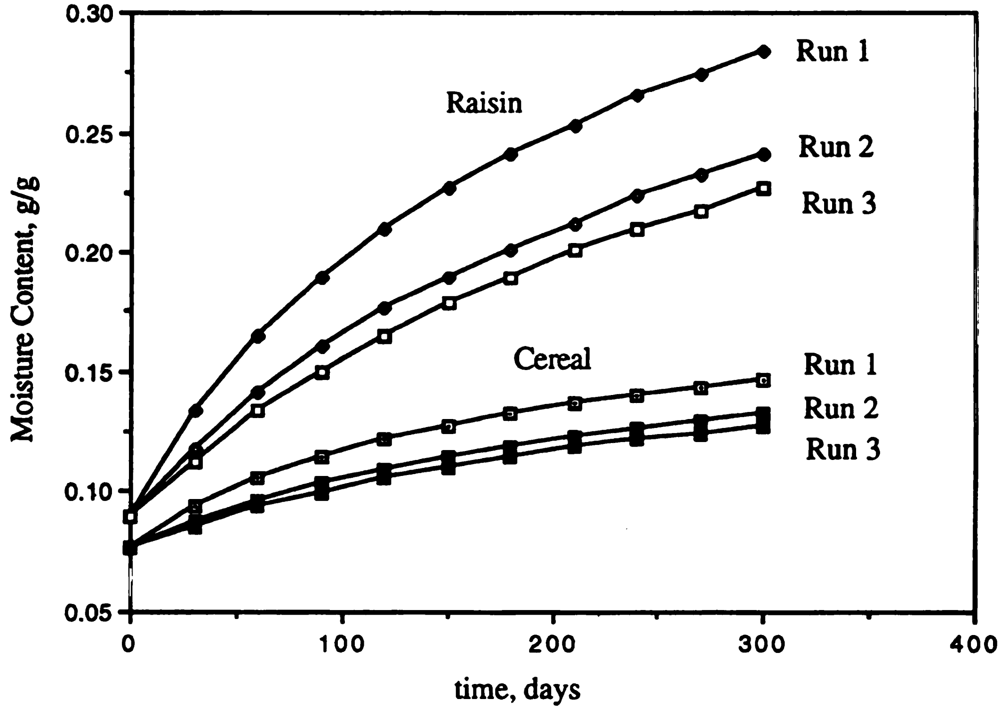

Figure 4 - Components moisture content as a function of time, for different packaging barrier properties (runs 1, 2 and 3). Simulated results using set of data C from Table 2

The influence of the ratio - total components' weight to packaging area available for moisture transfer - may be assessed from Figure 5. The simulated curves indicate that the higher this ratio, the lower the moisture content of each component for the selected time, as expected.

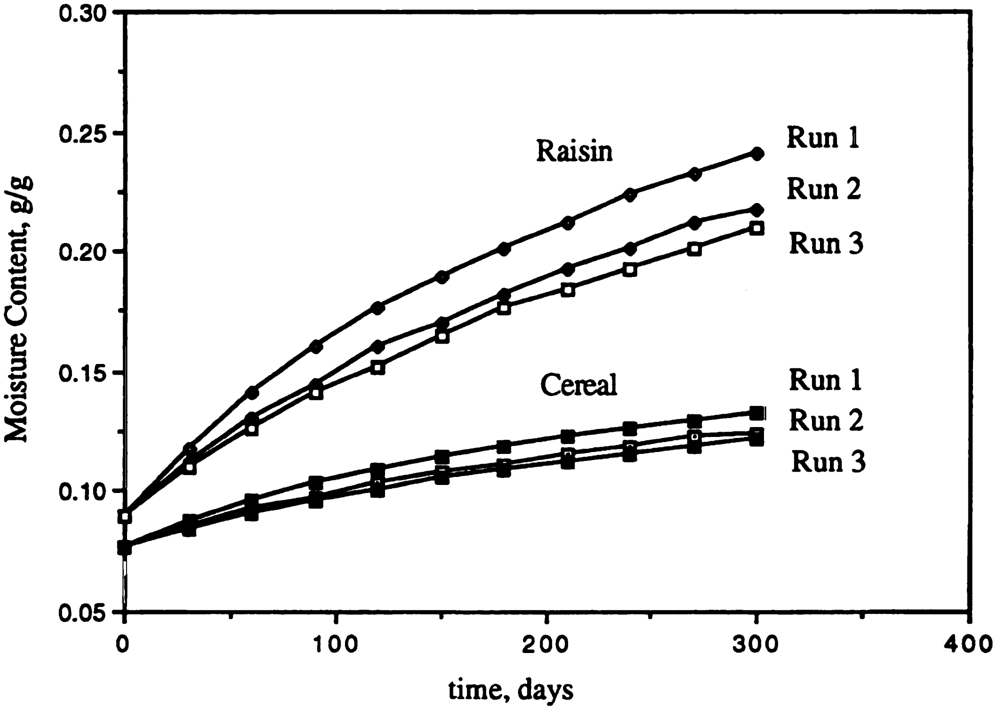

Figure 5 - Components moisture content as a function of time, for different total weight to packaging area ratio (runs 1, 2 and 3). Simulated results using set of data D from Table 2

Conclusions

The simulation program is a useful tool for packaging design and optimization. Packaging variables including the type of package, product composition, storage conditions, time and cost can thus be analyzed.

The model developed assumes that the mixed products are in equilibrium in all periods of time. This may not always be the case, depending on the relative resistance to moisture transfer within the products itself to the packaging barrier. Additionally, it also assumes that products do not interact and therefore that moisture is independently bonded to each product. Experimental validation is presented in Chapter III.

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CHAPTER III

MODELING THE MOISTURE CONTENT OF TWO-COMPONENT FOOD PRODUCTS IN A FLEXIBLE PACKAGE

MODEL VALIDATION

Abstract

Shelf-life computer models are increasingly used as a means to save time and cost of shelf-life determinations. In particular models for moisture-sensitive products have been developed and successfully used in packaging design and optimization of single products packaged in permeable packaging.

A mathematical model and a computer program to calculate the shelf-life and to predict the change in moisture content over storage time of a two-component mixture, were developed and presented in Chapter II. The objective of this work was to experimentally validate the model and to assess the accuracy with which it estimates the moisture content change of the packaged mixture components.

Mixtures of breakfast cereal and powder chocolate were used in the experiments. The food components moisture isotherms and the packaging water vapor transmission rate were determined and used in the model to predict the change in components moisture content over storage time. The model predicted values were compared to those obtained experimentally, for different components weight ratio and for two packaging materials (OPP and PE).

The model tended to overestimate the components moisture content, in particular the cereal's and for longer storage periods. Deviations seem to be dependent on the packaging material barrier, which affected the relative tendency of the components to absorb moisture simultaneously.

Introduction

Shelf-life prediction of food products is of great importance in packaging development and packaging optimization. Computer modeling is a useful tool that provides rapid analysis and design. The accuracy of the model depends on how good the physical-chemical characteristics of the product(s), package and environmental conditions are represented in the model.

Many deterioration processes occurring in food products are associated with gain or loss of moisture and with the product's final water activity (a_W). Dried products tending to absorb moisture become soft and lose their desirable crispness or begin to develop off-flavors. Intermediate moisture products may either gain or lose moisture becoming either gummy, sticky or hard.

Shelf-life modeling of moisture-sensitive single foods has been the focus of a considerable attention (Cardoso and Labuza, 1983), but not multicomponent or mixed products packaged together. A mathematical model, presented in Chapter II, was developed to calculate the shelf-life of a two-component mixture packaged in a permeable package. The model is based on the equation that describes the steady state transmission rate of moisture through a permeable film and on a moisture balance for the two components. The following equation was obtained for the case of non-linear isotherms:

$$t_i = \frac{l}{PAp^s} \int_{M_i^1}^{M_i^2} \frac{W_i + W_B\, D(M_i)}{a_{wo} - a_w\,(M_i)}\, dM_i \qquad (23)$$

where:

i is the component of interest and B the second component

P is the film permeability coefficient, in $g\mu m / m^2$ day mmHg

l is the film thickness, in μm

A is the package surface area available for moisture transfer, in m^2

p^s is the water vapor pressure at the storage temperature, in mmHg

W_i, W_B are respectively the dry weights of components i and B, in g

dM_i is the change in moisture content of component i, in g /g dry weight

a_{wo}, is the external water activity

$a_w (M_i)$ represent the head-space water activity, in equilibrium with the moisture content of component i

M_i^1 , M_i^2 are the initial and final moisture content of component i, respectively

t_i represents the time required to component i to achieve the moisture content M_i^2

$D(M_i)$ is defined as a function of M_i relating the slopes of the components isotherms at each a_w

The model assumes that: (i) the shelf-life of the mixture depends on the moisture content change of the components; (ii) the storage temperature and relative humidity are constant; (iii) the amount of water vapor in the package head-space is negligible compared with the products' moisture content; (iv) both components of the mixture reach fast equilibrium with the package's head-space relative humidity; (v) the components do not show hysteresis behavior on moisture sorption isotherms; (vi) the transfer of water through the package is always at steady state; (vii) the packaging material controls the rate of water transfer; and (viii) moisture is independently bonded to each components according to its sorption isotherm.

The equilibration of the products' moisture content with the package head-space relative humidity depends on the relative resistance to moisture transfer within the products to the packaging barrier. A dimensionless number (L), similar to the Sherwood number, may be useful to assess the applicability of assumption (vii) (Taoukis *et al., 1988*). The L number was defined as the ratio between the permeance of moisture in the food and the permeance in the packaging material. For high values of L, control of moisture transfer by the packaging material may be assumed, while for low values of L the moisture diffusion within the food is the controlling mechanism and therefore assumption (vii) cannot be applied.

Additionally to the above considerations on external and internal relative resistance, the shelf-life model developed also assumes that moisture is independently bonded to each product: the products behave as if packaged individually in what concerns the equilibrium moisture content. However, interactions between the mixture components may result in either a decreased or an increased water sorption by the mixture as compared to the individual components. Hydrogen bonds between components that compete with hydrogen bonds with water may result in a decreased water sorption, and solubilization of minor constituents at high a_w may result in an increased water sorption (Iglesias *et al.*, 1990; Chinachoti and Steinberg, 1988; Leiras and Iglesias, 1991; Chinachoti and Steinberg, 1985).

The objective of this work was to experimentally validate the model presented in Chapter II. To achieve this goal, the food products isotherms and the packaging water vapor transmission rate were determined. Different mixtures of two products were packaged and stored. The change in products moisture content over time was monitored and compared to the model predicted values.

Materials and Methods

Food Products Samples

Food products from a single lot were obtained through Portuguese companies. Breakfast cereal (brand CREPITAS) and powder chocolate (brand SUCHARD EXPRESS) were supplied by Nestlé (Lisboa, Portugal). The ingredients of breakfast cereal included: corn, sugar, wheat, honey, vegetable oil, malt extract, salt and non-fat dry milk. The powder chocolate composition included: sugar, non-fat cacao, lecithin and salt. Raisin (brand GLOBO) was supplied by A Colmeia do Minho (Seixal, Portugal). Raisin was chopped into ca 3 mm thick slices in order to decrease equilibration time in isotherms measurements.

Products were preconditioned before experiments: to get adsorption isotherms and for the validation experiments, cereal and powder chocolate were pre-dried at 103°C overnight and raisin at 60°C under vacuum for 48 hr; to get desorption isotherms, products were equilibrated at 75% relative humidity for one week.

Packaging Materials

Oriented polypropylene (OPP) coextruded with a thermosealable layer at both faces, with 25 μm thickness, was supplied by the converter Sociedade Portuguesa La Cellophane (Gaia, Portugal). Polyethylene coextruded with a barrier material (PE/barrier), of 65 μm total thickness, currently used for the breakfast cereal, was supplied by Nestlé. Low density polyethylene (30 μm), was supplied by the producer Monteiro Ribas (Porto, Portugal). The characterization of the packaging materials is presented in Appendix D.

For the validation experiments pouches of these materials were sealed using an impulse sealer. The pouches integrity was checked by electrolytic testing (Axelson *et al.* 1990), using a potential difference of 10V, 1% NaCl solution as electrolyte and steel electrodes.

Products Moisture Content

Moisture content of cereal and powder chocolate was determined by AOAC 925.09 method: 2 g of product were dried in vacuum oven (75°C, less than 20 mbar) until constant weight.

Raisin's samples were prepared according to the AOAC 934.06 method for moisture content determination: 5 g of raisin were pulped and mixed with 2 g of pre-dried sand, moistened with water and mixed thoroughly; the mixture was evaporated to dryness on a steam bath and then dried in the oven at 103°C for 4 plus 1/2 hour.

Moisture Sorption Isotherms

Products isotherms were determined at 25°C by equilibrating samples (3 replicates) at different relative humidity values. The relative humidity was created inside closed containers (20 cm height and 18 cm diameter) with saturated solutions of the following salts: Lithium Bromide (6%), Lithium Chloride (11%), Potassium Acetate (23%), Magnesium Chloride (33%), Potassium Carbonate (45%), Magnesium Nitrate (55%), Sodium Nitrite (63%), Sodium Chloride (73%), Ammonium Sulfate (82%) and Potassium Nitrate (93%). The relative humidity inside the containers was frequently monitored with a calibrated hygrometer (Rotronic AG, Basserdorf, Switzerland).

The initial moisture content was determined as described above and samples were weighed initially and after equilibration. A mass balance between the initial and final stages gives that the initial amount of water plus the weight gain is equal to the final amount of water. This can be expressed as:

$$\frac{IMC}{IMC + 1} Y_i + (Y_f - Y_i) = \frac{EMC}{EMC + 1} Y_f \qquad (24)$$

where Y_f is the final weight, Y_i is the initial weight, and IMC and EMC are the initial and the equilibrium moisture content in g/g (dry basis), respectively. This expression can be simplified to calculate the equilibrium moisture content as follows:

$$EMC, g/g = Y_f \frac{1 + IMC}{Y_i} - 1 \qquad (25)$$

Film Permeability

Water vapor transmission rate of packaging films was determined by an infrared sensor method (ASTM F1249), using a PERMATRAN W200 (Mocon Inc., Minneapolis, USA) The equipment was calibrated with polyester reference films supplied by Mocon Inc. Three replicates per material were tested at 25°C with 100% and with 75% of relative humidity as driving force. The first was obtained with water in the lower chamber of the cell, while the second was obtained with a saturated solution of NaCl. After calibration with 100% of relative humidity as driving force, the transmission rate of the reference film was measured with the saturated salt solution. The actual value of relative humidity in the lower chamber of the cell was found by dividing the transmission rates of the material as indicated in Appendix D.

Water vapor transmission rate of the pouches was also determined by the gravimetric method (ASTM D3079). Three pouches of each material (15 cm x 15 cm) with silica gel as desiccant, were stored in a chamber at 25 °C and 75 % relative humidity and weighed daily, until constant increase of weight. Empty pouches were also stored to evaluate the moisture sorption by the material itself.

Model Validation Experiments

For model validation two experiments were carried out. In the first experiment mixtures of cereal and powder chocolate were packaged in 20cm x 20cm pouches of OPP and stored in a chamber (Aralab, Lisboa, Portugal) at 25 °C and 75% relative humidity. Mixtures of different ratios of cereal to powder chocolate were prepared: 33/67, 50/50 and 67/33. Pouches were weighed weekly and twice a month, two pouches of each mixture were tested for moisture content determination of each product. Five pouches of each product itself were also prepared and weighed weekly.

In the second experiment mixtures of cereal and powder chocolate in a ratio of 50/50 were packaged in PE pouches and stored as above. The sampling was done weekly. Three pouches of each single product were also prepared.

Results and Discussion

Moisture Sorption Isotherms

Figures 6 - 8 present the experimental and the calculated GAB values of sorption isotherms for cereal, powder chocolate and raisin at 25°C, respectively. Tables 3 - 7 show the fitting of the experimental sorption data with the Henderson, Chen, Oswin, Halsey and GAB equations. Experimental values of sorption isotherms are presented in Tables E.1, E.2 and E.3 of Appendix E.

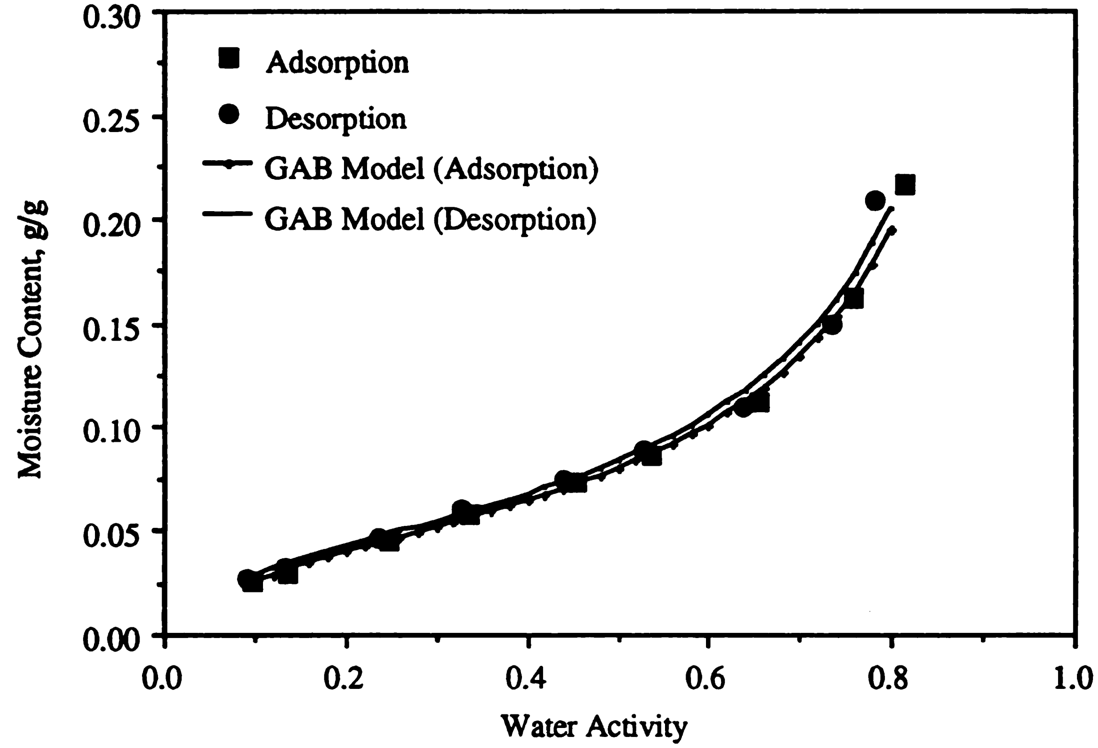

Figure 6 - Moisture adsorption and desorption isotherms of cereal at 25°C

As seen in Figures 6 and 7 both cereal and powder chocolate did not show significant hysteresis behavior. Both products appear to reach equilibrium within two days.

Raisin presented a sorption isotherm characteristic of the high sugar foods (Figure 8). At low a_w, high sugar products show low moisture contents since water is thought to be adsorbed at the surface of crystalline sugar. At high a_w, high sugar products show a significant increase of water content due to dissolution of crystalline sugar.

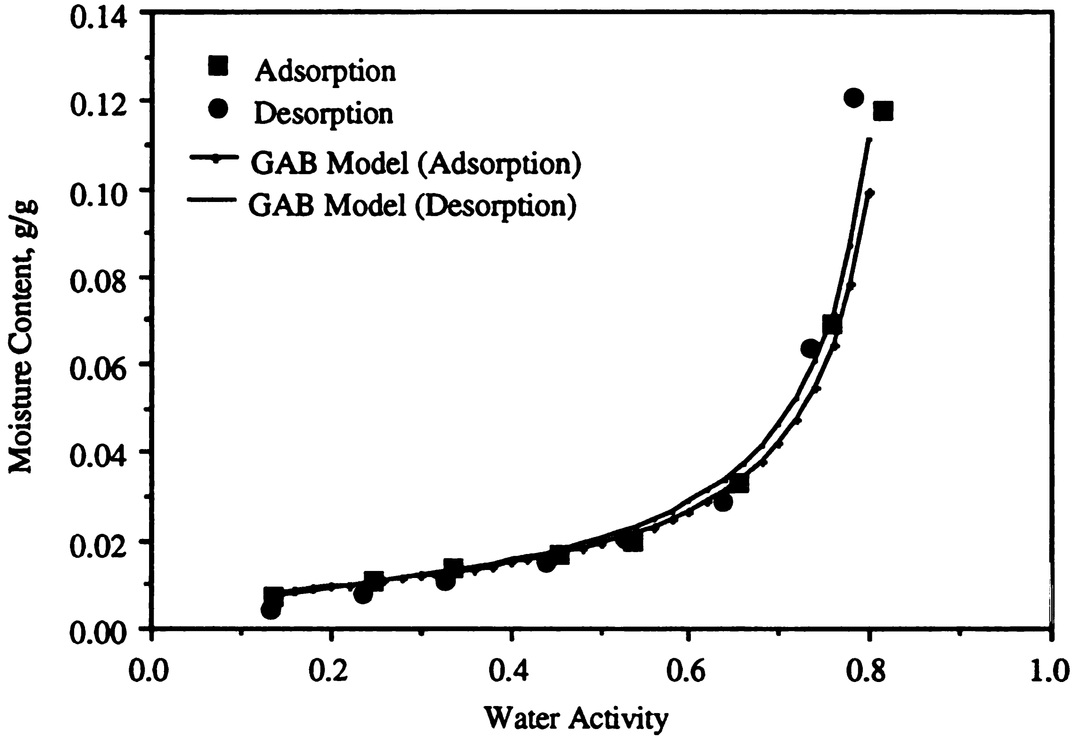

Figure 7 - Moisture adsorption and desorption isotherms of powder chocolate, at 25 °C

This results in a phase conversion of the crystalline sugar into amorphous sugar, as indicated by the presence of syrup exudation. Raisin adsorption-desorption isotherms showed hysteresis behavior. As seen in Figure 8, this product presented a significant higher moisture content when equilibrated by desorption than by absorption. Similar results were reported by Bolin (1980).

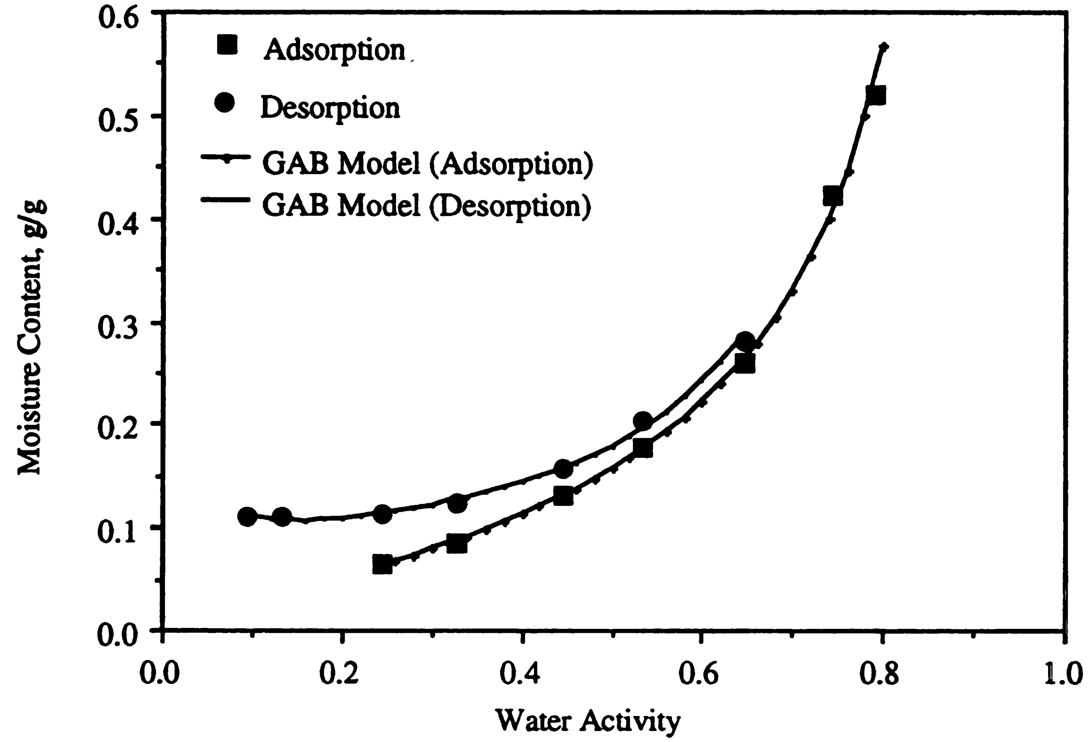

Figure 8 - Moisture adsorption and desorption isotherms of raisin at 25 °C

Even when raisin was cut in small pieces of about 3 mm, the equilibration time was around 15 days, much larger than for cereal or powder chocolate (ca. 2 days). This indicates a very low diffusion coefficient of water within the raisin. Lomauro and Bakshi (1985) reported a value of 4.17×10^{-13} m^2/s. Depending on the value of the packaging film permeance, the water diffusion through the packaging material may not be the controlling step and therefore the model is not applicable.

Since raisin showed sorption hysteresis and a very low water diffusion coefficient, it could not be used to validate the computer model. Therefore, validation experiments were carried out with cereal and powder chocolate mixtures.

The GAB equation showed the best fit for all the products. The goodness of fit was evaluated by calculating the relative percent root mean square of the difference between the experimental and the calculated moisture content (R), presented in Tables 3 to 7. The Halsey and the Oswin equations also represent well the experimental data, while the Chen equation yields a poor fit.

The amount of water tightly bound by the primary adsorption sites (monolayer value) was calculated from the parameters of the GAB equation. The following values of moisture content and equilibrium water activity were obtained: cereal - 0.0458 g/g ($a_w = 0.25$), powder chocolate - 0.0086 g/g ($a_w = 0.16$), raisin - 0.1059 g/g ($a_w = 0.38$).

Table 3 - Henderson equations fitting experimental sorption data

Adsorption Equation	Desorption Equation
Cereal	
$a_w = 1 - \exp(-17.322\ M^{1.342})$ R = 11.5	$a_w = 1 - \exp(-19.317\ M^{1.411})$ R = 11.4
Powder Chocolate	
$a_w = 1 - \exp(-13.518\ M^{0.827})$ R = 34.4	$a_w = 1 - \exp(-3.337\ M^{0.481})$ R = 11.4
Raisin	
$a_w = 1 - \exp(-2.835\ M^{0.802})$ R = 8.2	$a_w = 1 - \exp(-18.467\ M^{2.065})$ R = 19.1

Table 4 - Chen equations fitting experimental sorption data

Adsorption Equation	Desorption Equation
Cereal	
$a_w = \exp(-2.404 \exp(-12.845\ M))$ R = 37.5	$a_w = \exp(-2.540 \exp(-12.980\ M))$ R = 33.7
Powder Chocolate	
$a_w = \exp(-1.264 \exp(-17.997\ M))$ R = 173.0	$a_w = \exp(-1.098 \exp(-10.445\ M))$ R = 510.0
Raisin	
$a_w = \exp(-1.422 \exp(-3.726\ M))$ R = 39.1	$a_w = \exp(-4.149 \exp(-8.592\ M))$ R = 22.5

Table 5 - Oswin equations fitting experimental sorption data

Adsorption Equation	Desorption Equation
Cereal	
$a_w / (1-a_w) = 80.238\ M^{1.774}$ $R = 5.7$	$a_w / (1-a_w) = 83.680\ M^{1.830}$ $R = 7.0$
Powder Chocolate	
$a_w / (1-a_w) = 72.675\ M^{1.160}$ $R = 25.4$	$a_w / (1-a_w) = 9.488\ M^{0.658}$ $R = 99.1$
Raisin	
$a_w / (1-a_w) = 8.199\ M^{1.154}$ $R = 3.1$	$a_w / (1-a_w) = 62.302\ M^{2.570}$ $R = 16.7$

Table 6 - Halsey equations fitting experimental sorption data

Adsorption Equation	Desorption Equation
Cereal	
$a_w = \exp(-0.034\ M^{-1.173})$ $R = 5.5$	$a_w = \exp(-0.036\ M^{-1.182})$ $R = 6.3$
Powder Chocolate	
$a_w = \exp(-0.030\ M^{-0.825})$ $R = 16.8$	$a_w = \exp(-0.136\ M^{-0.453})$ $R = 98.3$
Raisin	
$a_w = \exp(-0.140\ M^{-0.850})$ $R = 3.4$	$a_w = \exp(-0.052\ M^{-1.583})$ $R = 12.6$

Table 7 - GAB equations fitting experimental sorption data

Adsorption Equation	Desorption Equation
Cereal	
$a_w / M = 2.351 + 17.289\, a_w - 18.836\, a_w^2$ $R = 3.3$	$a_w / M = 1.960 + 17.422\, a_w - 18.719\, a_w^2$ $R = 4.9$
Powder Chocolate	
$a_w/M = 5.384 + 104.668\, a_w - 126.618 a_w^2$ $R = 5.1$	$a_w/M = 9.489 + 85.221\, a_w - 110.133\, a_w^2$ $R = 39.7$
Raisin	
$a_w/M = 3.904 + 1.363\, a_w - 5.594\, a_w^2$ $R = 2.4$	$a_w/M = -0.368 + 14.185\, a_w - 15.720\, a_w^2$ $R = 2.6$

Film Permeability

Values of the packaging materials permeance were experimentally determined. The results are presented in Table 8. The detailed values are presented in Appendix D.

Table 8 - Materials permeance (g/m^2 day mmHg) at 25 °C

Method	IR	IR	Gravimetric
Δ RH, %	100	74.3	72.8
OPP	0.0734	0.0737	0.0679
PE/barrier	0.0293	0.0310	0.0286
PE	0.1326	0.1462	0.1349

As seen in Table 8, the permeance values of the packaging materials were within 8%, which indicated good agreement between the different methods used. Table 8 also shows that the permeance values of these materials were not affected by different driving forces. The good agreement between the permeance values obtained by the gravimetric method and the IR method additionally shows that the seals were efficient in what concerns moisture transfer and therefore they were appropriate for the validation experiments (this was confirmed by the electrolytic testing). The results obtained for the empty pouches in the gravimetric method (Figure D.2 in Appendix D) shows that the moisture absorption by the packaging material itself can be neglected, as compared to the materials' water vapor transmission rate.

Validation Experiment 1

Experimental validation of the computer model was carried out by monitoring the change in moisture content with time of each component of the packaged mixtures. The experimental values of moisture content were then compared to the calculated values by the computer model .

Experimental conditions:

Mixture components - cereal and powder chocolate
Pre-conditioning conditions - 103 °C (± 1°C) air oven, overnight
Initial moisture content of components - cereal - 0.0038 g/g ± 0.0003 g/g
powder chocolate - 0.0020 g/g ± 0.0002 g/g
Average storage conditions - temperature - 25.5 °C ± 0.9 °C
relative humidity - 73.6 % ± 2.3%
Packaging film - OPP
Average pouches surface area - 0.0748 m^2 (±0.0023 m^2)

Table 9 presents the average of cereal and powder chocolate dry weights in the pouches for the validation experiment 1. Experimental values of moisture content as a function of storage time are presented in Table 10. The individual pouches weight gain values are presented in Appendix F. Table 11 shows the moisture content values for each component, predicted by the computer model, using the GAB equation to describe the components isotherms.

Table 9 -Validation 1. Cereal and powder chocolate dry weights *

Ratio Cereal / Powder chocolate	Cereal, g	Powder chocolate, g
33/67	9.588 ± 0.837	19.874 ± 0.992
50/50	14.092 ± 0.946	13.340 ± 1.170
67/33	18.799 ± 0.899	10.139 ± 1.349
100/0	20.045 ± 0.903	-
0/100	-	20.366 ± 1.812

* total weight ≈ 30 g

Table 10 - Experimental moisture content* (g/g) of components as a function of storage time (days). Validation 1

		time, days						
Mixture	Components	0	15	28	43	51	64	80
33/67	Cereal	0.0038	0.0542	0.0774	0.0873	0.0876	0.0843	0.0900
	Pow. chocolate	0.0020	0.0092	0.0171	0.0223	0.0259	0.0274	0.0340
50/50	Cereal	0.0038	0.0457	0.0742	0.0808	0.0890	0.0857	0.0794
	Pow. chocolate	0.0020	0.0070	0.0135	0.0210	0.0263	0.0247	0.0271
67/33	Cereal	0.0038	0.0432	0.0654	0.0811	0.0804	0.0827	0.0808
	Pow. chocolate	0.0020	0.0052	0.0116	0.0192	0.0193	0.0218	0.0254
100/0	Cereal	0.0038	0.0452	0.0654	0.0825	0.0883	0.0964	0.1038
0/100	Pow. chocolate	0.0020	0.0215	0.0290	0.0347	0.0367	0.0397	0.0419

* each value is the average of two pouches

Table 11 - Values of components moisture content (g/g) as a function of storage time (days), predicted by the computer model at experiment 1 conditions

		time, days							
Mixture	Components	15	22	28	38	43	51	64	80
33/67	Cereal	0.0683	0.0823	0.0913	0.1023	0.1063	0.1123	0.1193	0.1253
	Pow.chocolate	0.0161	0.0202	0.0232	0.0273	0.0289	0.0314	0.0347	0.0377
50/50	Cereal	0.0613	0.0753	0.0853	0.0963	0.1003	0.1073	0.1143	0.1223
	Pow.chocolate	0.0143	0.0181	0.0212	0.0250	0.0265	0.0293	0.0323	0.0361
67/33	Cereal	0.0543	0.0683	0.0773	0.0883	0.0933	0.1003	0.1083	0.1163
	Pow.chocolate	0.0126	0.0161	0.0187	0.0222	0.0239	0.0265	0.0297	0.0332
100/0	Cereal	0.0553	0.0703	0.0793	0.0913	0.0963	0.1033	0.1113	0.1193
0/100	Pow. chocolate	0.0277	0.0319	0.0347	0.0387	0.0398	0.0420	0.0444	0.0469

In Figures 9 - 12 the experimental values are compared to the values predicted by the model. Figure 9 refers to cereal and powder chocolate packaged individually, while Figures 10, 11 and 12 refer to mixtures with the following cereal to powder chocolate ratios: 33/67, 50/50 and 67/33, respectively.

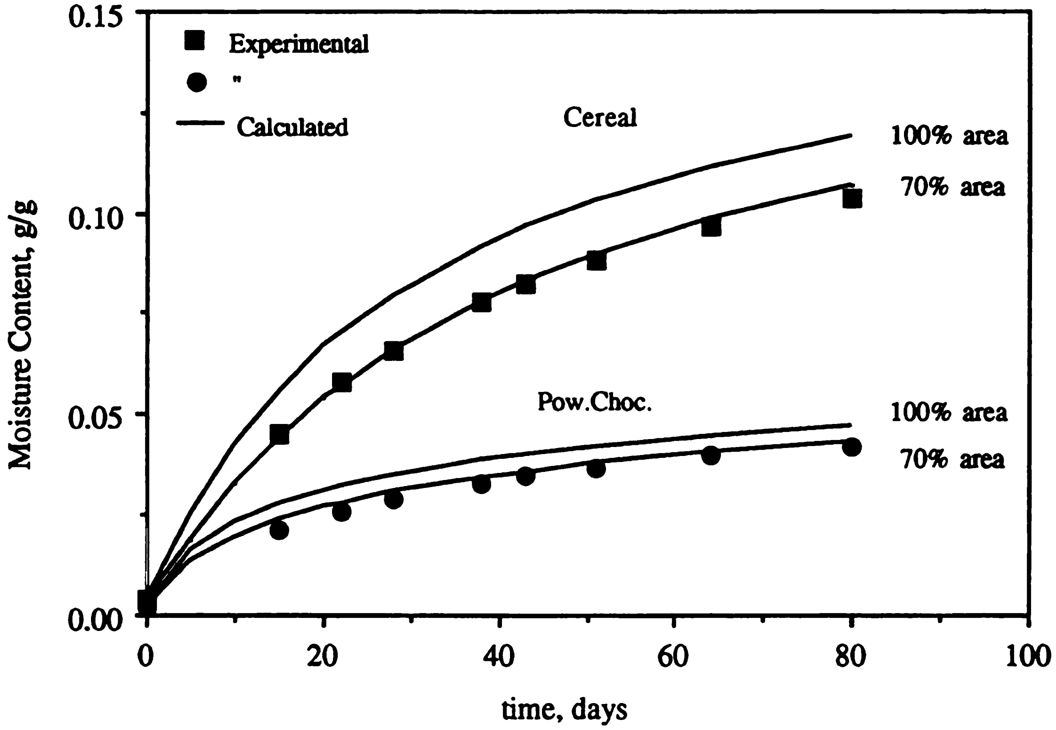

Figure 9 - Validation 1. Experimental and calculated values of moisture content for the single packaged components

From Figures 9 - 12 it appears that the experimental values are lower than what the model predicted, including the case of the mixtures 100/0 and 0/100, corresponding to each product packaged individually (Figure 9). Additionally, the moisture content of cereal, when packaged together with powder chocolate, appears to stabilize at values lower than the expected for longer storage periods (Figures 10, 11 and 12). This stabilization however, is not seen when each component is individually packaged.

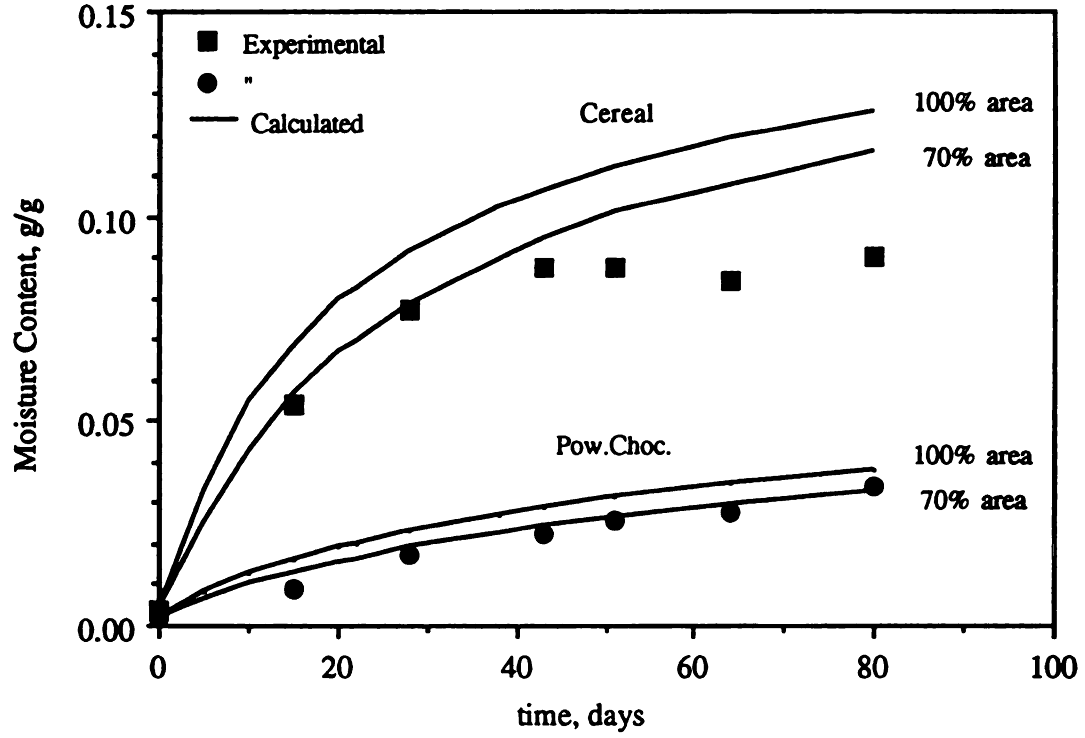

Figure 10 - Validation 1. Experimental and calculated values of moisture content for the mixture 33/67

The percent error, calculated as the difference between the experimental and predicted values of moisture content divided by the experimental values, presents values in the order of 30% for the mixtures 33/67, 50/50 and 67/33. The components packaged individually (mixtures 100/0 and 0/100) present values lower than 20%. The percent error for the individually packaged components tends to decrease with time, while in the mixtures the percent error tends to increase with time.

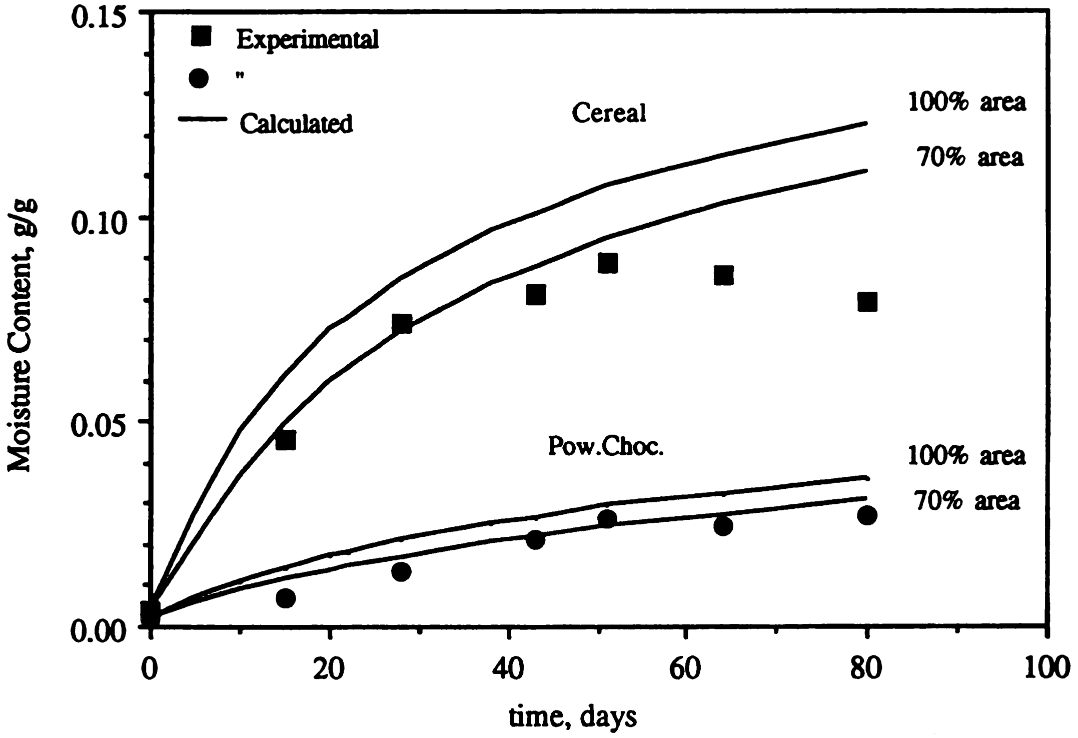

Figure 11 - Validation 1. Experimental and calculated values of moisture content for the mixture 50/50

The lower experimental values of components' moisture content may be caused by a lower rate on the moisture transfer, either due to a lower storage relative humidity, or lower pouches moisture transmission rate or lower pouches surface area available for moisture transfer. Errors associated with model assumptions may also be responsible for the higher values of moisture content predicted by the model as compared to the experimentally determined.

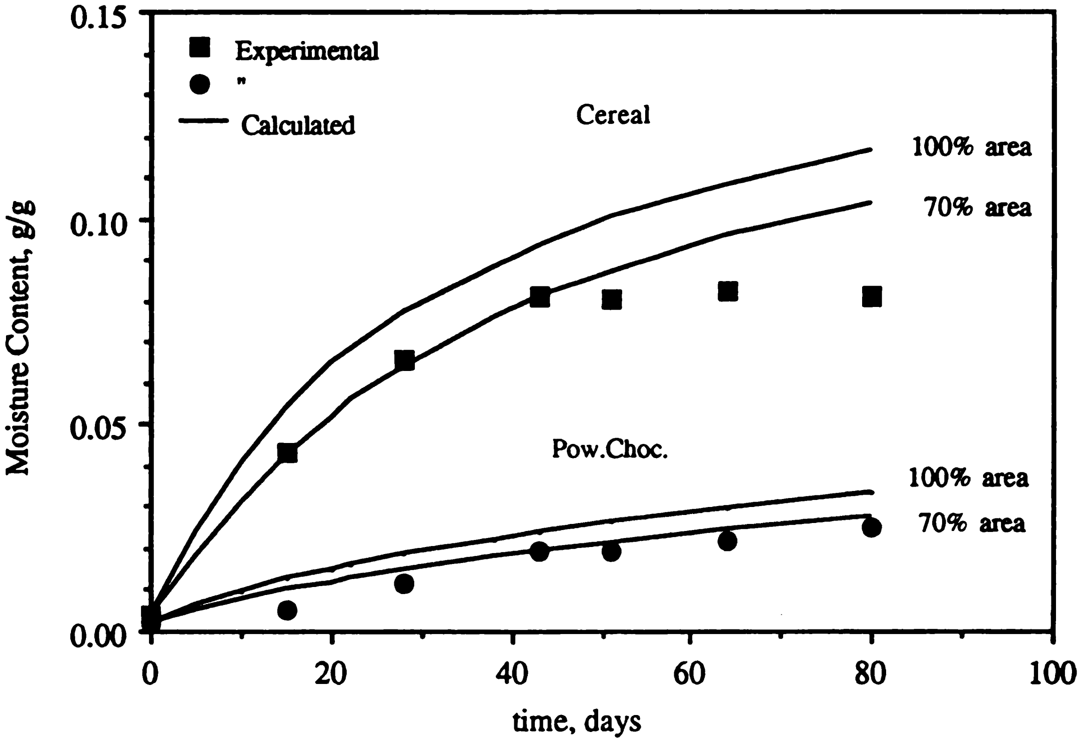

Figure 12 - Validation 1. Experimental and calculated values of moisture content for the mixture 67/33

The storage relative humidity was automatically monitored every hour and the average value over the experiment period was used in the model (a standard deviation of 2.3% was achieved over the testing period). A decrease of about 10% in the storage chamber relative humidity was recorded around the 40th day. This lower value of relative humidity remained for 3 days, which although contributing for lower values of moisture content could not account by itself for the difference between the calculated and the measured moisture content values.

The pouches' moisture transmission rate is not likely to be overestimated due to the results obtained by the different methods (the results from the gravimetric method were used in the model).

The influence of lower pouches surface area available for moisture transfer can be seen in Figures 9 - 12. The moisture content values predicted by the model, assuming that all pouches' surface was available for transfer and assuming that 30% was blocked, were plotted together with the experimental values. The pouches were flexible and not self-supporting and therefore it is possible that their surface was not totally exposed.

The model assumed that each component reaches fast equilibrium with the package's head-space relative humidity. As previously referred, the applicability of this assumption depends on the relative resistance to moisture transfer within the food components to the packaging material. For single packaged products, the higher the film permeability, the higher the deviations between the values of moisture content predicted by the model and the experimental values - the assumption of fast equilibrium between the product's moisture content and the package's head-space relative humidity is not met and the model overestimates the experimental values. This could explain the lower values obtained in this experiment. For packaged mixtures however, we have additionally assumed that moisture is independently bonded by each component according to its isotherm. For higher storage periods of time, corresponding to higher water activities, interactions between the packaged components may lead to deviations in their sorption behavior.

Following the results obtained for validation experiment 2 are presented and discussed.

Validation Experiment 2

A second experiment for model validation was carried out with a lower barrier packaging material. Similarly to validation 1, the values of components' moisture content were measured and compared to those calculated by the computer model.

Experimental conditions:

Mixture components -	cereal and powder chocolate
Pre-conditioning conditions -	103 °C air oven, overnight
Initial moisture content of components -	cereal - 0.0050 g/g ± 0.0002 g/g
	powder chocolate ≈ 0 g/g
Average storage conditions -	temperature - 25.2°C ± 0.7°C
	relative humidity - 72.9% ± 0.8%
Packaging film -	PE
Average pouches surface area -	$0.0727m^2 \pm 0.0023m^2$

Table 12 presents the average of cereal and powder chocolate dry weights in the pouches used, for the mixture 50/50 and for the components packaged individually (mixtures 100/0 and 0/100). Tables 13 and 14 present the components' moisture content over storage time determined experimentally and predicted by the model, respectively. These values are plotted in Figures 13 and 14, respectively for cereal and powder chocolate packaged individually and for the mixture 50/50.

Table 12 - Validation 2. Cereal and powder chocolate dry weights *

Ratio Cereal / Powder chocolate	Cereal, g	Powder chocolate, g
50/50	14.357 ± 0.676	14.522 ± 0.840
100/0	29.833 ± 0.067	-
0/100	-	28.926 ± 0.513

* total weight ≈ 30 g

Table 13 - Experimental moisture content* (g/g) of components as a function of storage time (days). Validation 2

		time, days							
Mixture	Components	7	14	21	24	28	31	40	50
50/50	Cereal	0.0433	0.0638		0.0873		0.0905	0.0998	0.1046
	Pow. chocolate	0.0082	0.0152		0.0226		0.0252	0.0306	0.0339
100/0	Cereal	0.0340	0.0508	0.0659		0.0798		0.0889	0.0952
0/100	Pow. chocolate	0.0168	0.0239	0.0283		0.0334		0.0363	0.0388

* each value is the average of two pouches

Table 14 - Values of components moisture content (g/g) as a function of storage time (days), predicted by the computer model at experiment 2 conditions

		time, days							
Mixture	Components	7	14	21	24	28	31	40	50
50/50	Cereal	0.0565	0.0815	0.0965	0.1015	0.1065	0.1105	0.1185	0.1245
	Pow.chocolate	0.0131	0.0199	0.0251	0.0270	0.0290	0.0307	0.0343	0.0372
100/0	Cereal	0.0395	0.0625	0.0785	0.0835	0.0895	0.0935	0.1035	0.1115
0/100	Pow. chocolate	0.0219	0.0294	0.0338	0.0352	0.0372	0.0383	0.0410	0.0433

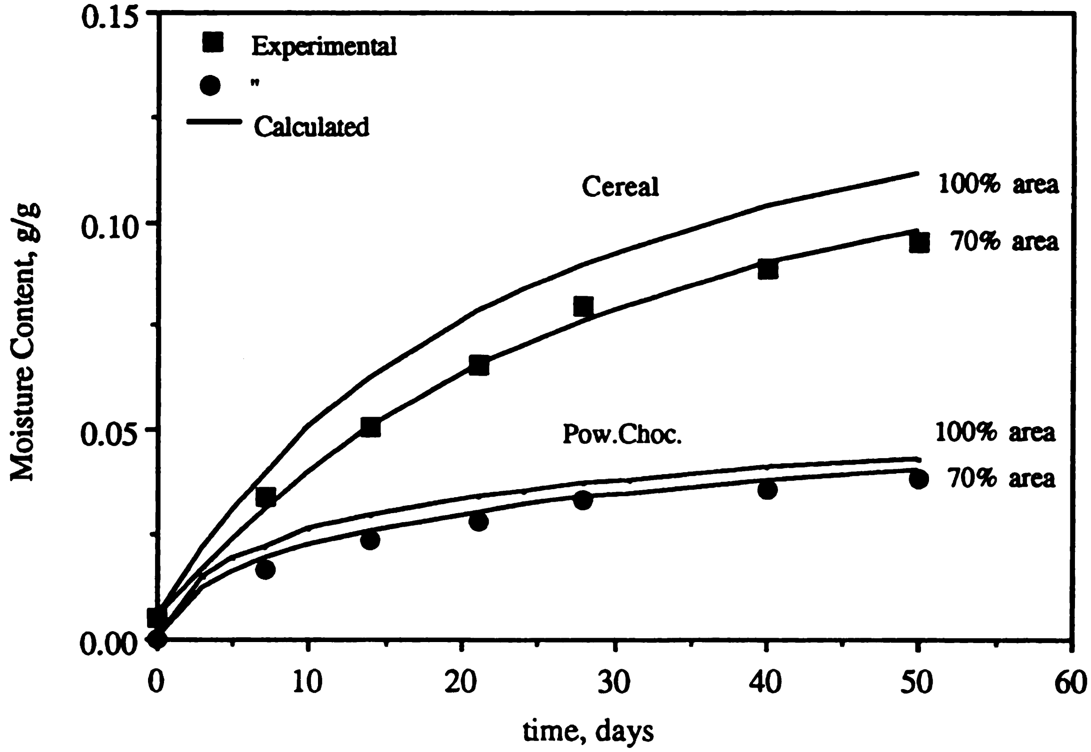

Figure 13 - Validation 2. Experimental and calculated values of moisture content for the single packaged components

Figures 13 and 14 show that the calculated and the experimental values of components' moisture content differ in a similar form as seen in validation experiment 1. The percent error between the calculated and the experimental values is 20% for the mixture 50/50 and 15% for the single components. These values are lower than those obtained in validation experiment 1.

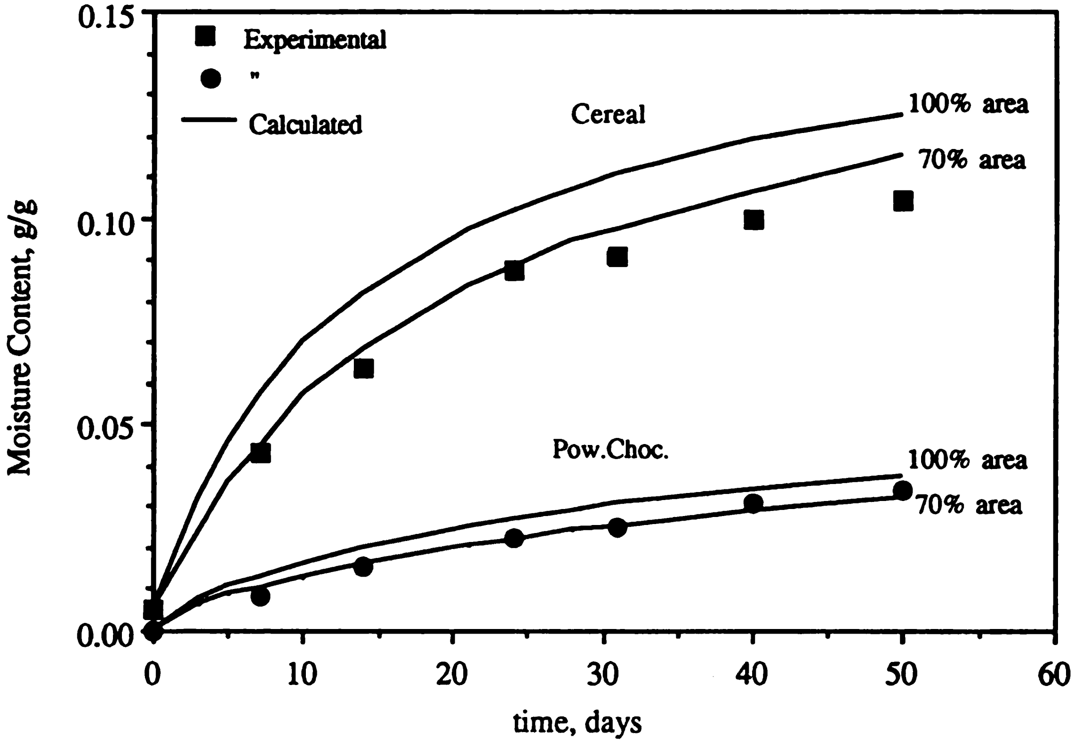

Figure 14 - Validation 2. Experimental and calculated values of moisture content for the mixture 50/50

Contrary to the results from validation experiment 1, results from validation experiment 2 presented in Figure 14, did not show a plateau of the cereal's moisture content after 35 days, at levels around 8%. Nevertheless, the difference between the calculated and the experimental values appears to increase as storage time increases. Apparently, cereal do not bind their full amount of moisture at higher water activities. Contributing to this deviation is the fact that cereal carried some part of the powder chocolate during the moisture content determination: it was very difficult to avoid that some powder was carried by the cereal's surface once the components have been mixed together. This problem was overcome by increasing the amount of cereal for moisture determination. Since the powder chocolate had a lower moisture content than the cereal, it contributed to a lower moisture content value of the later. In spite of this, this effect is not likely to low the cereal moisture content in an extent to justify the large deviation found particularly in experiment 1.

The values of cereal equilibrium moisture content were plotted against the values of powder chocolate equilibrium moisture content. Moisture content values from validation experiments 1 and 2 as well as the experimental values from the sorption isotherms are plotted in Figure 15.

It can be seen in Figure 15 that the moisture content values of the mixtures from validation experiments follow the same pattern as the moisture content values from the sorption isotherms. However, it seems that the mixing of the two components have some effect on the equilibrium moisture sorption behavior of the components. The cereal appears to absorb less water when mixed with powder chocolate, above the 7 - 8% values of moisture content. This effect seems to be larger with the pouches of OPP than with the pouches of PE and therefore it seems to increase with the decrease of packaging materials permeance.

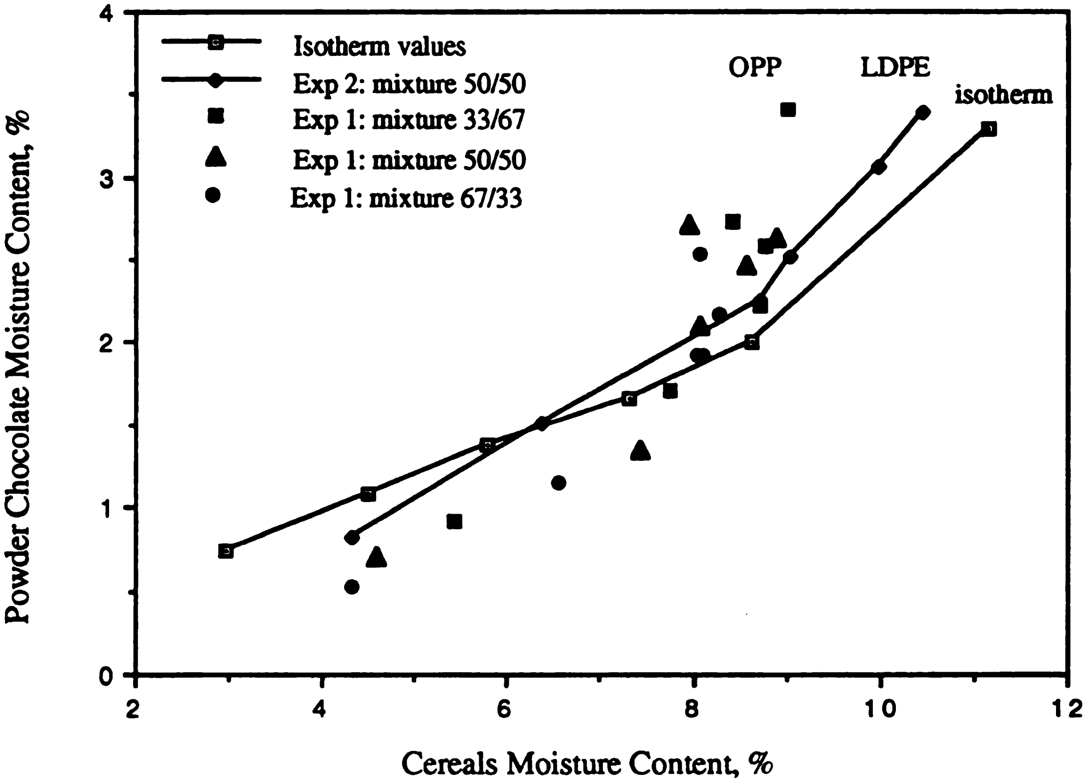

Figure 15 - Powder chocolate moisture content vs. cereal moisture content. Values from isotherm (components individual sorption behavior) and values from validation experiments (mixture sorption behavior)

In summary, several factors appear to contribute to the difference between the experimental and calculated values of the components' moisture content. Firstly, there was a non-controlled contact between the pouches during the validation experiments. This fact may account for a lower area available for moisture transfer than the actual pouches' area. Secondly, it seems that by packaging together these two products, the equilibrium moisture content of each component may be affected by the presence of the other component.

Although this is merely an observation it would be worthwhile to carry out further experiments to confirm or reject this hypothesis. Finally, it may be possible that the assumption of fast equilibrium between the head-space relative humidity and the moisture content of each component is not completely valid. Using a higher barrier material will make this assumption more valid since the diffusion time will be much larger than the moisture equilibrium time in the product.

Conclusions

The model tends to overestimate the moisture content of the components studied, in particular for the cereal and for longer storage periods. Deviation appears to be dependent on the packaging material barrier, which may affect the relative tendency of the components to absorb moisture simultaneously. Further experiments with higher barrier materials than OPP are required in order to verify how much the packaging material may affect the moisture uptake or may change the equilibrium moisture sorption behavior of the mixed components.

Further experiments are also required to verify the model assumption of components' fast equilibrium with the package's head-space relative humidity and to define a criteria for assumption's applicability.

Recommendations for future work:

- Experiments with higher as well as with lower moisture barrier packaging materials than the ones used in the validation experiments 1 and 2;
- Improved separation of mixture's components prior to moisture determination;

- Usage of sugar-free and salt-free components;
- Controlled exposure area of the pouches in the storage chamber.

It is also suggested the development and set-up of an experiment where both the package's head-space relative humidity and the components moisture content can be monitored over time. This would allow for ultimate conclusions' draft on the component moisture sorption behavior related to the moisture transfer through the packaging.

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APPENDIX A

EQUATIONS FOR MOISTURE SORPTION ISOTHERMS

The equations of the moisture sorption isotherms referred to on Chapter I, are presented below. The bibliographic references cited are listed on References section of Chapter I.

i) BET equation (Brunauer *et al.*, 1938 in Chirife and Iglesias, 1978)

$$\frac{a_w}{(1-a_w)\,M} = \frac{1}{M_m C} + \frac{a_w\,(C-1)}{M_m C}$$

M_m - is the monolayer moisture content

C - constant related to the heat net of sorption

ii) BET modified equation (Brunauer, 1945 in Chirife and Iglesias, 1978)

$$M = \left[\frac{M_m C\, a_w}{1 - a_w}\right]\left[\frac{1 - (n+1)\,a_w^n + n\, a_w^{n+1}}{1 + (C-1)\,a_w - C\, a_w^{n+1}}\right]$$

n - is the number of layers of water

iii) Bradley equation (Bradley, 1936 in Chirife and Iglesias, 1978)

$$\ln (1/a_w) = K_2 K_1^M$$

K_2 is a function of the sorptive polar groups

K_1 is a function of the dipole moment of sorbed vapor

iv) Caurie equation (Caurie, 1970)

$$\ln C = \ln C_0 - r\, a_w$$

$$C = \frac{100 - \%\ H_2O}{\%\ H_2O}$$

C_0 and r are constants

v) Chen equation (Chen, 1971 in Chirife and Iglesias, 1978)

$a_W = \exp[K + a\exp(-bM)]$

K, a, b are constants

simplified version: $a_W = \exp[-a\exp(-bM)]$

vi) Chen and Clayton equation (Chen and Clayton, 1971 in Chirife and Iglesias, 1978)

$a_w = \exp[-K_1 T^{m1} \exp(-K_2 T^{m2} M)]$

K_1, K_2, m1, m2 are constants

vii) Chung and Pfost equation (Chung and Pfost, 1967 in Chirife and Iglesias, 1978)

$\ln a_w = -\frac{a}{RT}\exp(-bM)$

a and b are constants

viii) D'Arcy -Watt equation (Saravacos *et al.*, 1986)

$$M = \frac{K1\,K2\,a_w}{1 + K1\,a_w} + K5\,a_w + \frac{K3\,K4\,a_w}{1 - K3\,a_w}$$

K1, K2, K3, K4, K5 are constants

ix) Day and Nelson equation (Day and Nelson, 1965 in Chirife and Iglesias, 1978)

$$1 - a_w = \exp\left(- j_1 T^{h1} \; M^{j2 T^{h2}}\right)$$

$j1$, $h1$, $j2$, $h2$ are constants

x) Double Power Law equation (Peleg, 1993)

$$M = k_1 a_w^{n1} + k_2 a_w^{n2}$$

k_1, k_2, n_1, n_2 are constants ($n_1 < 1$ and $n_2 > 1$)

xi) Ferro Fontan equation (Ferro Fontan *et al.* 1982 in Chirife *et al.* 1983)

$$\ln\left(\frac{\gamma}{a_w}\right) = \alpha \, M^{-r}$$

g is a parameter that accounts for the structure of sorbed water

a and r are constants

xii) GAB equation (Bizot, 1983)

$$\frac{M}{M_o} = \frac{C \, K \, a_w}{(1 - K \, a_w)(1 - K \, a_w + C \, K \, a_w)}$$

$$\text{or} \quad \frac{a_w}{M} = \alpha \, a_w^2 + \beta \, a_w + \gamma$$

M_o - monolayer moisture content

C - Guggenheim constant

K - constant correlating properties of multilayer molecules with respect to bulk liquid

xiii) Hailwood and Horrobin equation (Hailwood and Horrobin, 1946 in Chirife and Iglesias, 1978)

$$\frac{a_w}{M} = A + B\,a_w - C\,a_w^2$$

A, B and C are constants

xiv) Halsey equation (Halsey, 1948 in Chirife and Iglesias, 1978)

$$a_w = \exp\left(-\frac{K}{M^r}\right)$$

K and r are constants

xv) Halsey's modified equation (Iglesias and Chirife, 1976 g in Chirife and Iglesias, 1978)

$$a_w = \exp\left[-\exp\left(bT + c\right)M^r\right]$$

b, c and r are constants

xvi) Harkins-Jura equation (Harkins and Jura, 1944 in Chirife and Iglesias, 1978)

$$\ln a_w = B - A / M^2$$

A and B are constants

xvii) Haynes equation (Haines, 1961 in Chirife and Iglesias, 1978)

$$\ln p = (a + bM) \ln p_o + (c + dM + gM^2)$$

a, b, c, d and g are constants

p_o is the vapor pressure of pure water at a given temperature

xviii) Henderson equation (Henderson, 1952 in Chirife and Iglesias, 1978)

$$1 - a_w = \exp(-kM^n)$$

k and n are constants

xix) Iglesias and Chirife equation I (Iglesias and Chirife, 1976f in Chirife and Iglesias, 1978)

$$\ln (M + \sqrt{M^2 + M_{0.5}}) = b\, a_w + p$$

$M_{0.5}$ is the moisture content at $a_w = 0.5$

b and p are constants

xx) Iglesias and Chirife equation II (iglesias and Chirife, 1981)

$$M = A\frac{a_w}{1 - a_w} + B$$

A and B are constants

xxi) Kuhn equation (Kuhn, 1967 in Chirife and Iglesias, 1978)

$$M = \frac{a}{\ln a_w} + b$$

a and b are constants

xxii) Linear equation (Labuza *et al.*, 1972 in Chirife and Iglesias, 1978)

$M = a + b\ a_w$ a and b are constants

xxiii) Mizrahi equation (Mizrahi *et al.*, 1970 in Chirife and Iglesias, 1978)

$a_w = \frac{a + M}{b + M}$ a and b are constants

xxiii) Oswin equation (Oswin, 1946 in Chirife and Iglesias, 1978)

$M = a\left[\frac{a_w}{1 - a_w}\right]^n$ a,n are constants

xxiv) Smith equation (Smith, 1947 in Chirife and Iglesias, 1978)

$M = B - A \ln (1 - a_w)$ A, B are constants

xxv) Strohman and Yoerger equation (Strohman and Yoerger, 1967 in Chirife and Iglesias, 1978)

$\ln a_w = a \ln p_o \exp (bM) + c \exp (dM)$

a, b, c, d are contants

p_o is the vapor pressure of pure water at a given temperature

xxvi) Young and Nelson equation (Young and Nelson, 1967 a in Chirife and Iglesias, 1978)

$M_s = A\ (\theta + \alpha) + ß\ \phi$

$M_d = A\ (\theta + \alpha) + ß\ \theta\ a_{w\ max}$

s,d refer to adsorption and desorption respectively

$a_{w\ max}$ is the water activity from which desorption commenced originally

$\theta = f\ (a_w, E)$

$\phi = a_w\ q$

$\alpha = f\ (a_w, E)$

APPENDIX B

DESCRIPTION OF THE COMPUTER PROGRAM

MENU OPTIONS:
1. Create Two Files With Experimental Sorption Data
2. Modify the Sorption Data Files
3. Modelling Experimental Sorption Data
4. Calculate Shelf-Life
5. Calculate Products Moisture Content at Different Storage Periods
6. Quit

→ $\boxed{1}$ CALL CREATE

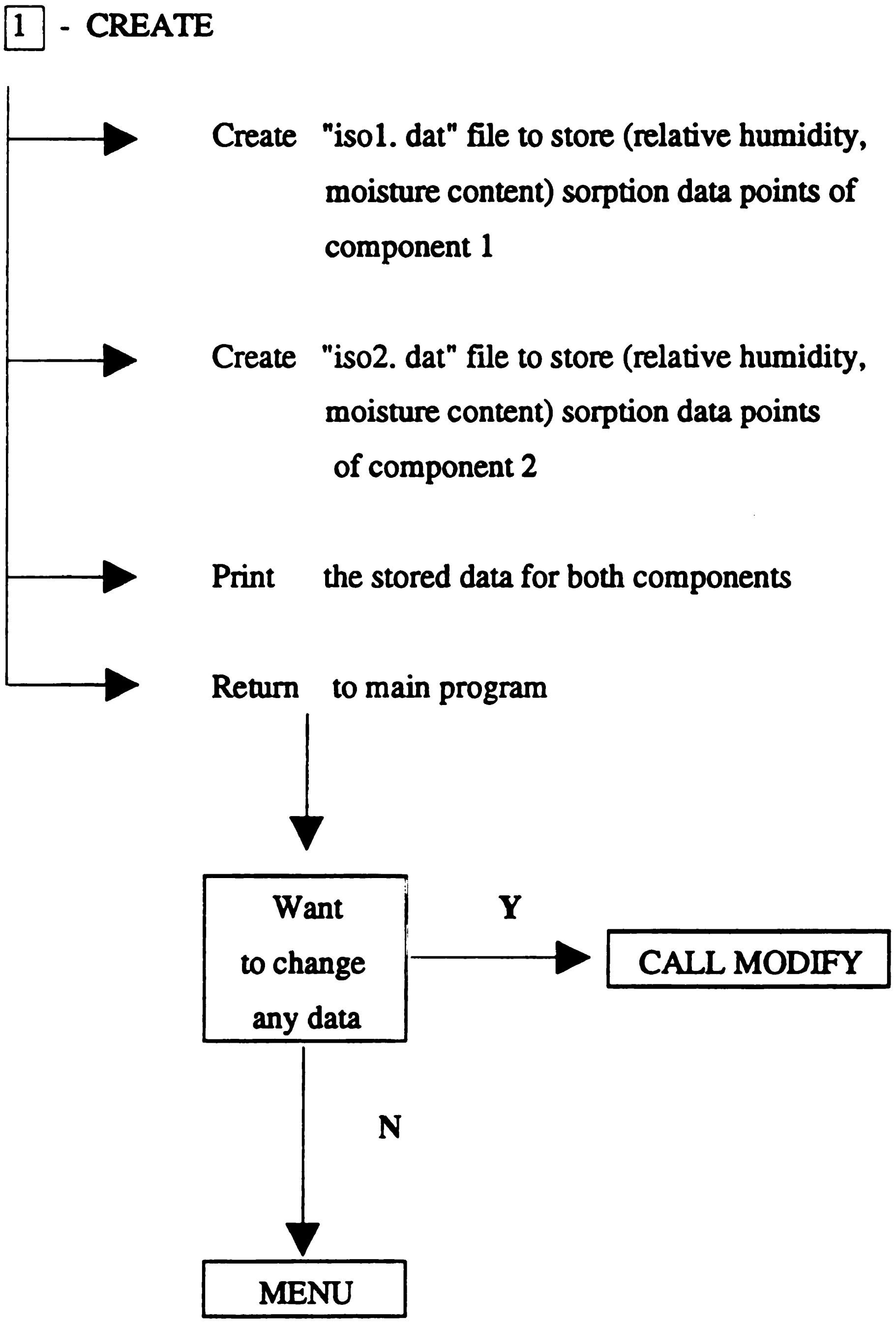
→ $\boxed{2}$ PRINT Stored Data and Call MODIFY

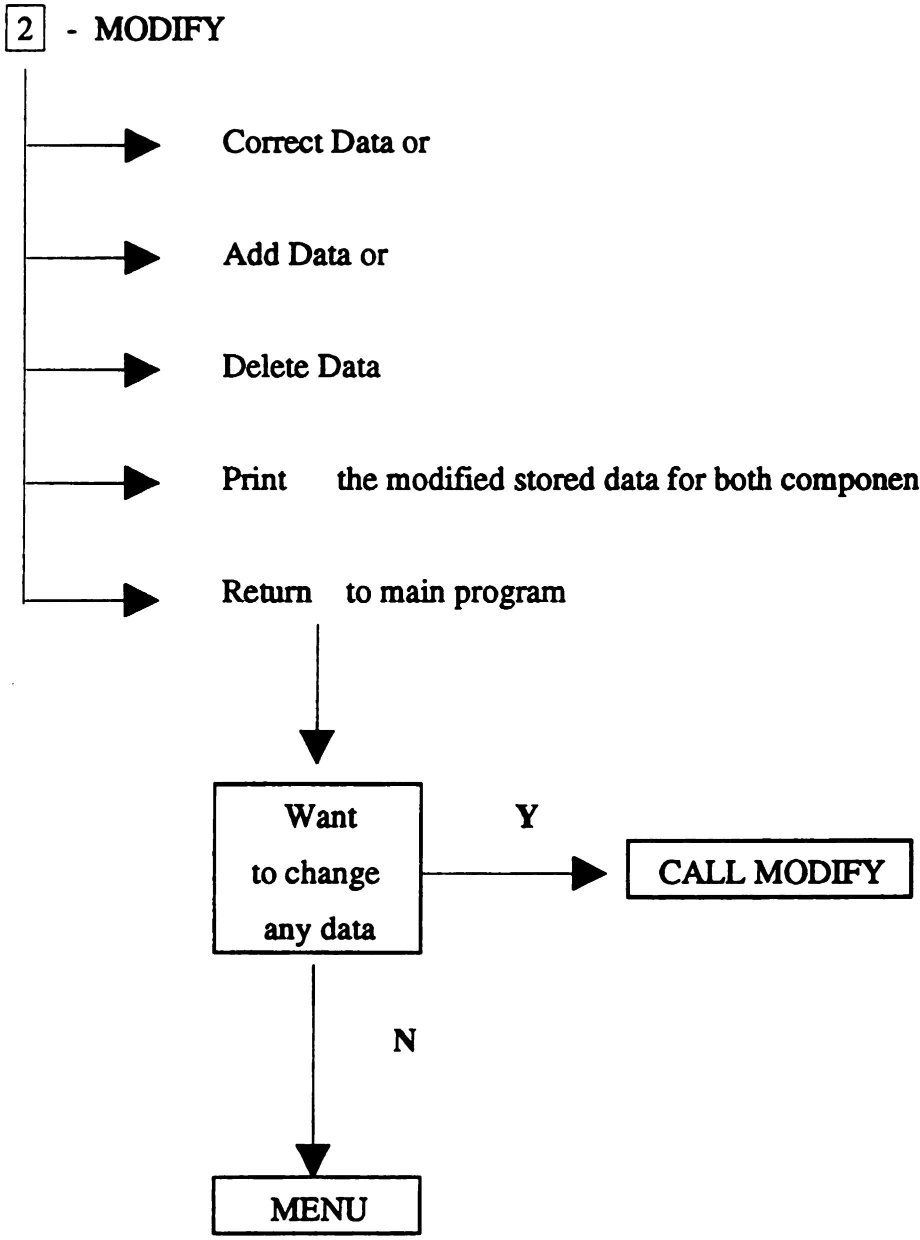
→ $\boxed{3}$ GOSUB MODEL

→ $\boxed{4}$ GOSUB SHELF

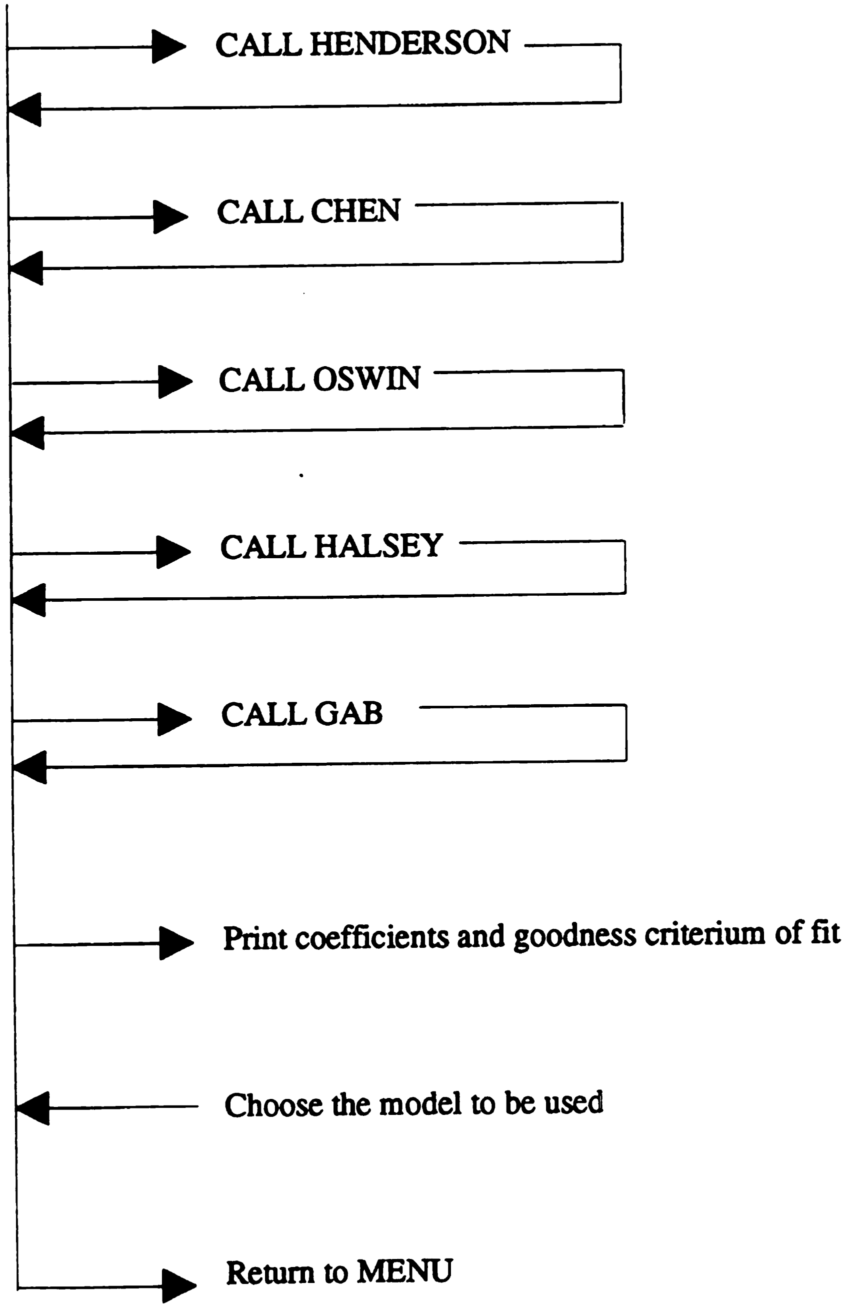
→ $\boxed{5}$ GOSUB STABILITY

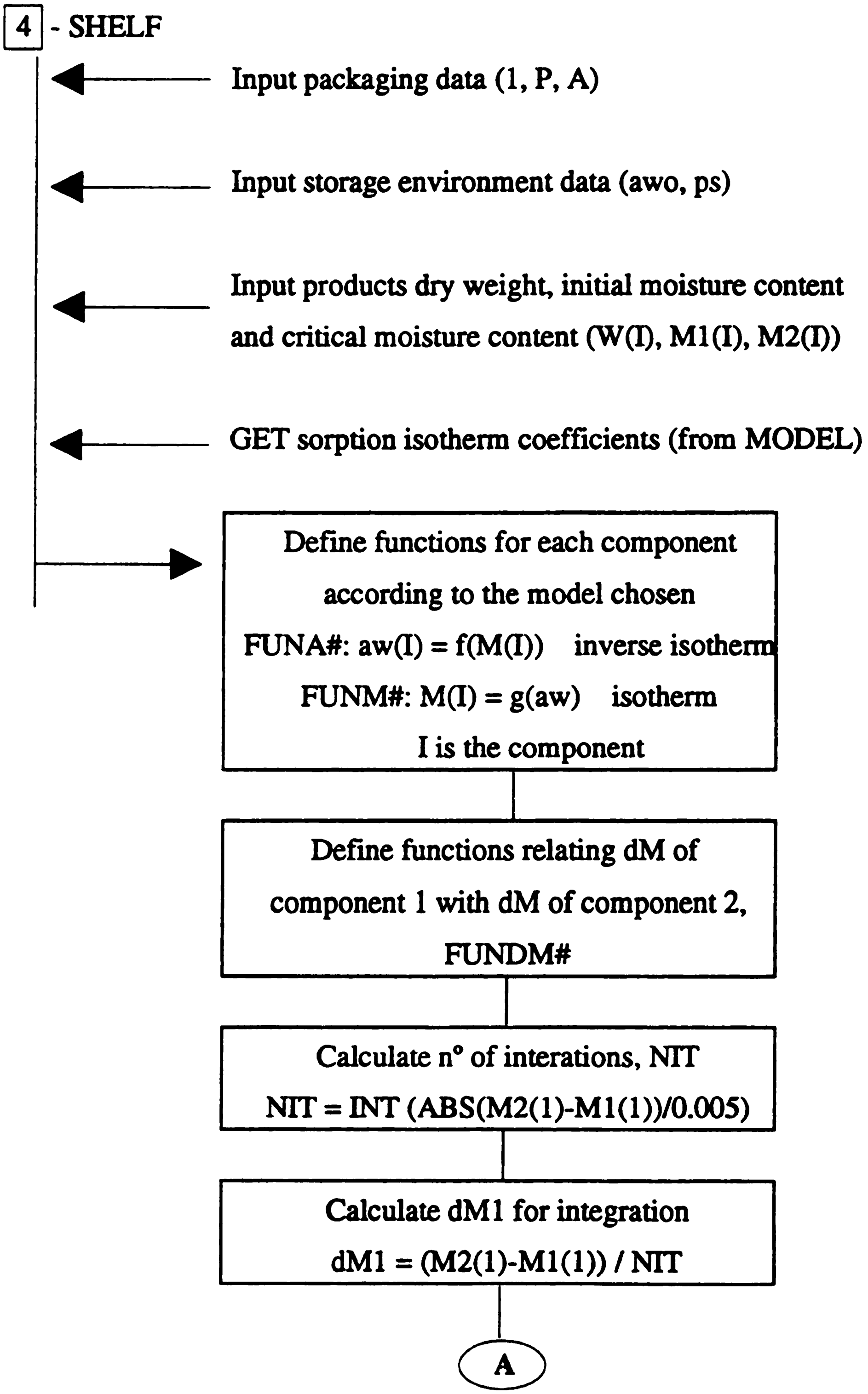
→ $\boxed{6}$ GOTO FINAL

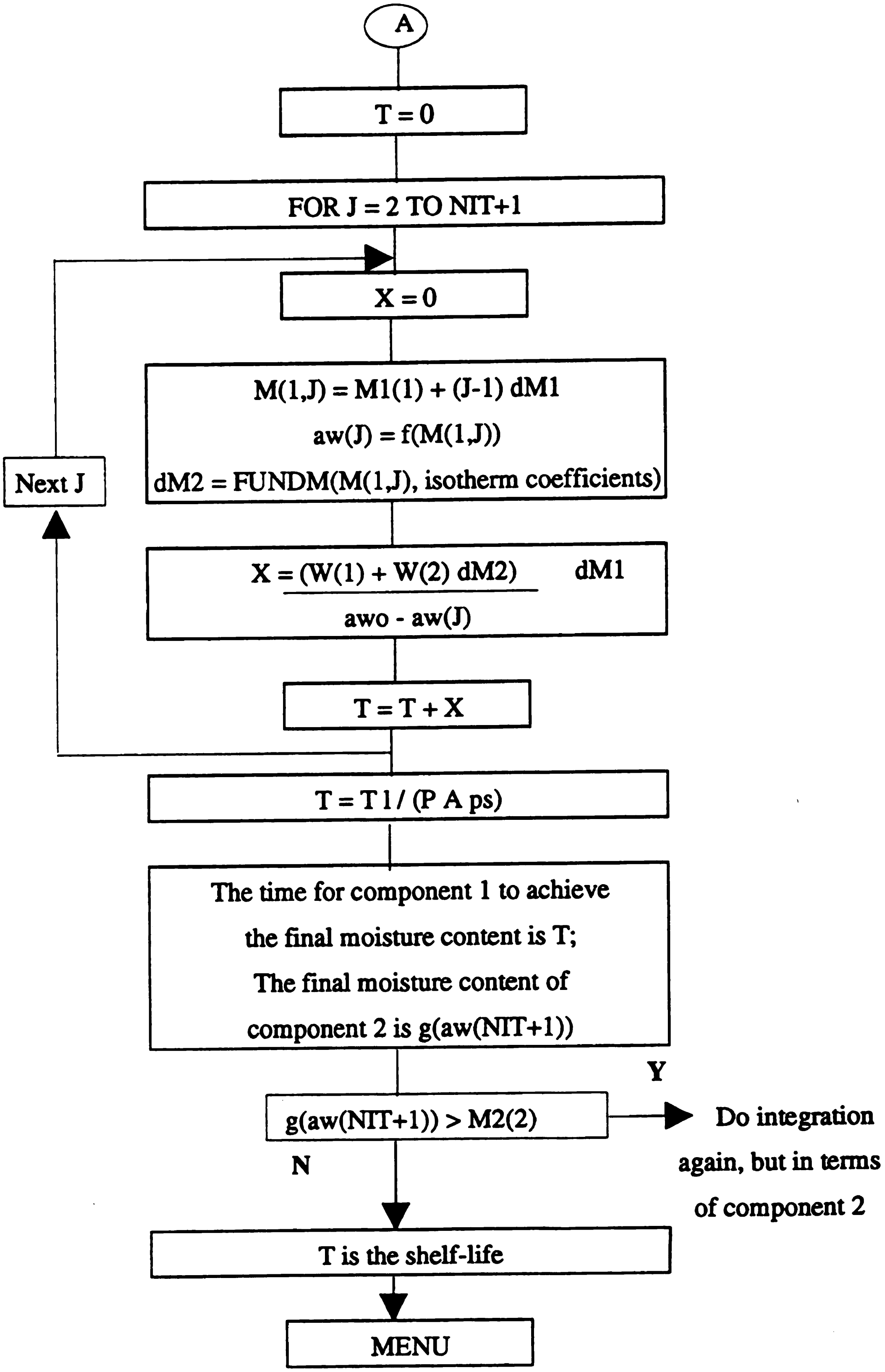

1 - CREATE
Create "iso1. dat" file to store (relative humidity, moisture content) sorption data points of component 1
Create "iso2. dat" file to store (relative humidity, moisture content) sorption data points of component 2
Print the stored data for both components
Return to main program
Want to change any data
Y
CALL MODIFY
N
MENU


2 - MODIFY
Correct Data or
Add Data or
Delete Data
Print the modified stored data for both components
Return to main program
Want to change any data
Y
CALL MODIFY
N
MENU

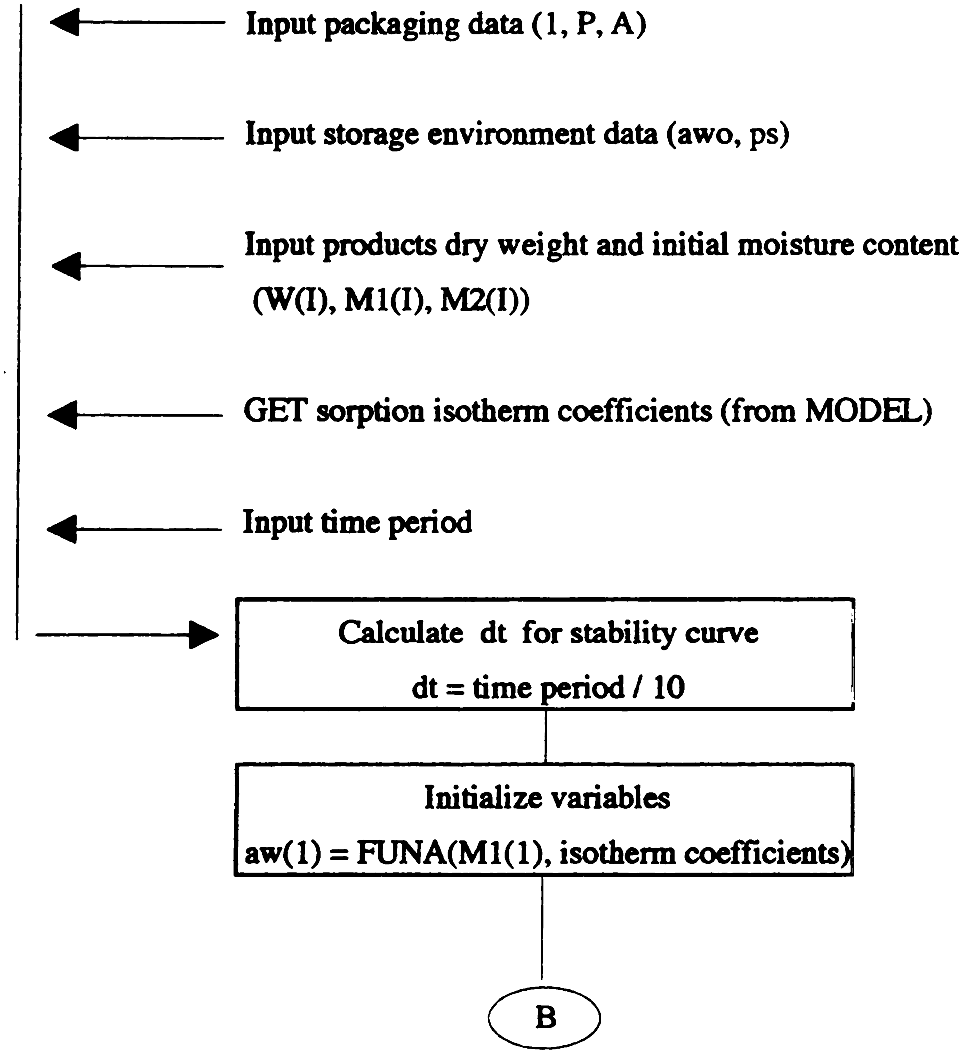
3 - MODEL

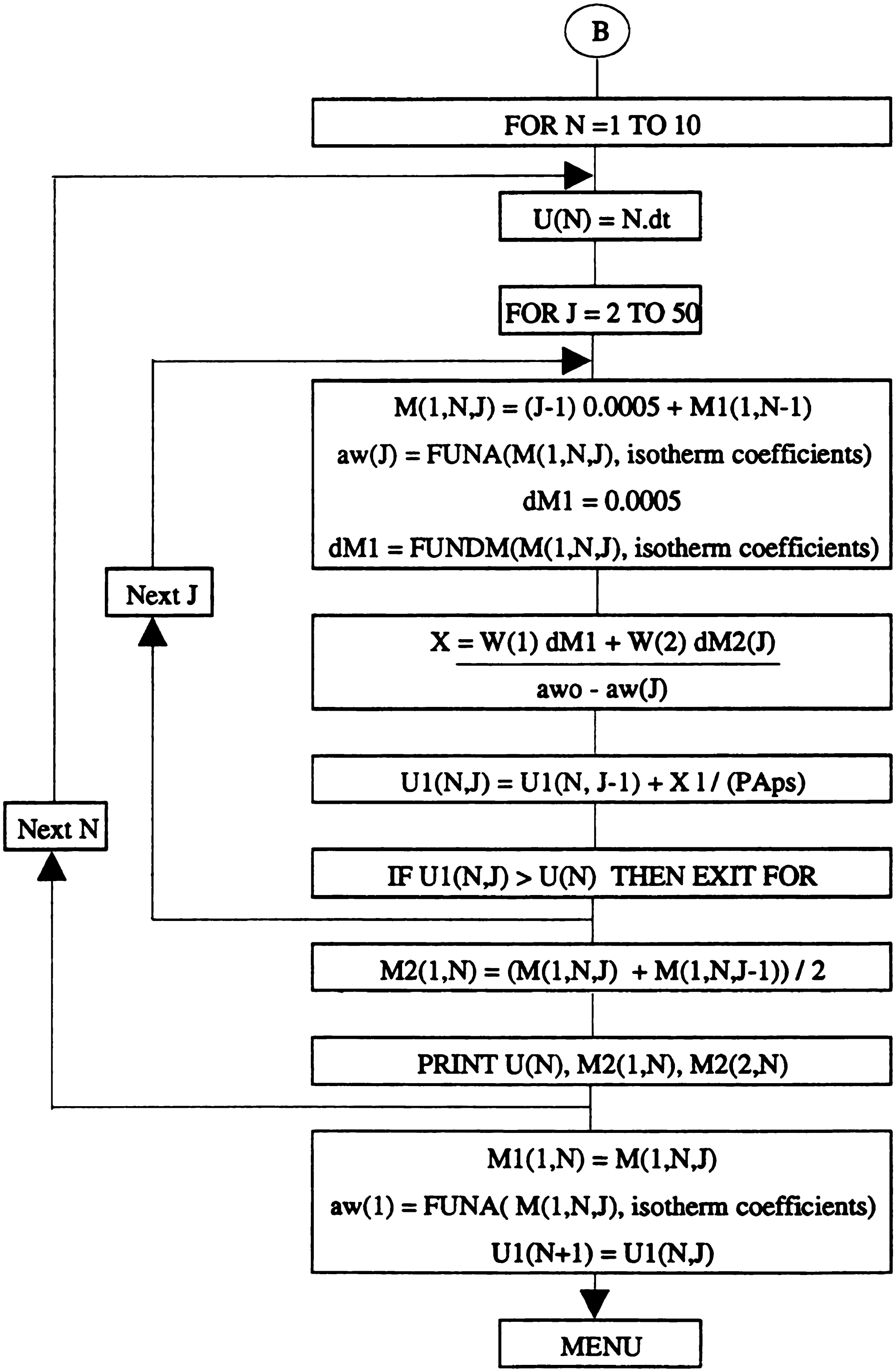

CALL HENDERSON
CALL CHEN
CALL OSWIN
CALL HALSEY
CALL GAB
Print coefficients and goodness criterium of fit
Choose the model to be used
Return to MENU


4 - SHELF
Input packaging data (1, P, A)
Input storage environment data (awo, ps)
Input products dry weight, initial moisture content and critical moisture content (W(I), M1(I), M2(I))
GET sorption isotherm coefficients (from MODEL)
Define functions for each component according to the model chosen
FUNA#: aw(I) = f(M(I)) inverse isotherm
FUNM#: M(I) = g(aw) isotherm
I is the component
Define functions relating dM of component 1 with dM of component 2, FUNDM#
Calculate n° of interations, NIT
NIT = INT (ABS(M2(1)-M1(1))/0.005)
Calculate dM1 for integration
dM1 = (M2(1)-M1(1)) / NIT
A


A
T = 0
FOR J = 2 TO NIT+1
X = 0
M(1,J) = M1(1) + (J-1) dM1
aw(J) = f(M(1,J))
dM2 = FUNDM(M(1,J), isotherm coefficients)
Next J
X = (W(1) + W(2) dM2) dM1
awo - aw(J)
T = T + X
T = T 1 / (P A ps)
The time for component 1 to achieve the final moisture content is T;
The final moisture content of component 2 is g(aw(NIT+1))
Y
g(aw(NIT+1)) > M2(2)
Do integration again, but in terms of component 2
N
T is the shelf-life
MENU

5 - STABILITY


Input packaging data (1, P, A)
Input storage environment data (awo, ps)
Input products dry weight and initial moisture content (W(I), M1(I), M2(I))
GET sorption isotherm coefficients (from MODEL)
Input time period
Calculate dt for stability curve
dt = time period / 10
Initialize variables
aw(1) = FUNA(M1(1), isotherm coefficients)
B


B
FOR N =1 TO 10
U(N) = N.dt
FOR J = 2 TO 50
M(1,N,J) = (J-1) 0.0005 + M1(1,N-1)
aw(J) = FUNA(M(1,N,J), isotherm coefficients)
dM1 = 0.0005
dM1 = FUNDM(M(1,N,J), isotherm coefficients)
Next J
X = W(1) dM1 + W(2) dM2(J) / awo - aw(J)
U1(N,J) = U1(N, J-1) + X 1 / (PAps)
Next N
IF U1(N,J) > U(N) THEN EXIT FOR
M2(1,N) = (M(1,N,J) + M(1,N,J-1)) / 2
PRINT U(N), M2(1,N), M2(2,N)
M1(1,N) = M(1,N,J)
aw(1) = FUNA(M(1,N,J), isotherm coefficients)
U1(N+1) = U1(N,J)
MENU

```
DECLARE FUNCTION FUNDM# (Q, NISO$, AWI!(), MC!, A0!(), A1!(), A2!())
DECLARE SUB PRINTDATA ()
DECLARE SUB HENDERSON (A0HE!(), A1HE!(), CORRHE!())
DECLARE SUB CHEN (A0CH!(), A1CH!(), CORRHE!())
DECLARE SUB OSWIN (A0OS!(), A1OS!(), CORROS!())
DECLARE SUB HALSEY (A0HA!(), A1HA!(), CORRHA!())
DECLARE SUB GAB (A0G!(), A1G!(), A2G!(), CORRG!())
DECLARE SUB MODIFY (MOD$)
DECLARE SUB CREATE ()
DECLARE FUNCTION FUNM# (NISO$, AWI!, A0!, A1!, A2!)
DECLARE FUNCTION FUNA# (NISO$, MC!, A0!, A1!, A2!)
DECLARE SUB PAUSA ()

'*****************************************************************************
CLS
QUAD1$ = STRING$(78, "*")
QUAD2$ = "**" + STRING$(74, " ") + "**"
PRINT : PRINT
PRINT QUAD1$: PRINT QUAD1$
PRINT QUAD2$: PRINT QUAD2$
PRINT "**"; TAB(15); "Shelf-Life Modeling of"; TAB(77); "**"
PRINT "**"; TAB(15); "Two-Component Packaged"; TAB(77); "**"
PRINT "**"; TAB(15); "Moisture-Sensitive Products"; TAB(77); "**"
PRINT "**"; TAB(15); "BY   Maria F.F. Po‡as and"; TAB(77); "**"
PRINT "**"; TAB(15); "     Ruben J. Hernandez"; TAB(77); "**"
PRINT QUAD2$: PRINT QUAD2$
PRINT "**"; TAB(40); "This program is copywrited by"; TAB(77); "**"
PRINT "**"; TAB(40); "M.F.F.Po‡as and R.J.Hernandez"; TAB(77); "**"
PRINT QUAD2$: PRINT QUAD2$: PRINT QUAD2$: PRINT QUAD2$: PRINT QUAD2$
PRINT "**"; TAB(34); "October 1995"; TAB(77); "**"
PRINT "**"; TAB(30); "School of Packaging"; TAB(77); "**"
PRINT "**"; TAB(28); "Michigan State University"; TAB(77); "**"
PRINT QUAD2$
PRINT QUAD1$: PRINT QUAD1$: CALL PAUSA
GOSUB MENU
'*****************************************************************************

TYPE Iso
 RH AS SINGLE
 MC AS SINGLE
END TYPE

DIM A1HE!(2), A0HE!(2), CORRHE!(2)
DIM A1CH!(2), A0CH!(2), CORRCH!(2)
DIM A1OS!(2), A0OS!(2), CORROS!(2)
DIM A1HA!(2), A0HA!(2), CORRHA!(2)
DIM A2G!(2), A1G!(2), A0G!(2), CORRG!(2)
'*****************************************************************************
CLEAR
MENU:
CLS
LOCATE 6, 15: PRINT "******************** MAIN MENU ********************"
LOCATE 8, 15: PRINT "1. Create Two Files with Experimental Sorption Data"
LOCATE 10, 15: PRINT "2. Modify the Sorption Data Files"
```

```
LOCATE 12, 15: PRINT "3. Modeling Experimental Sorption Data"
LOCATE 14, 15: PRINT "4. Calculate Shelf Life"
LOCATE 16, 15: PRINT "5. Calculate Products Moisture Content at"
LOCATE 17, 18: PRINT "Different Storage Periods"
LOCATE 19, 15: PRINT "6. Quit"
LOCATE 23, 15: INPUT "Please enter the number of your choice"; CHOICE
SELECT CASE CHOICE
 CASE 1
  CALL CREATE
 CASE 2
  CALL PRINTDATA
  INPUT "Do you want to (C)orrect, (A)dd or (D)elete any data ?", MOD$
  CALL MODIFY(MOD$)
 CASE 3
  GOSUB MODEL
 CASE 4
  GOSUB SHELF
 CASE 5
  GOSUB STABILITY
 CASE 6
  GOTO FINAL
 CASE ELSE
  PRINT "Please try again!!"
 END SELECT

GOSUB MENU
'*******************************************************************************

MODEL:
CLS
PRINT "I am fitting the experimental data points in the following equations:"
PRINT "Henderson, Chen, Oswin, Halsey and GAB"
PRINT
FORMAT$ = "####.###    ####.###    ####.###   ####.###"
CALL HENDERSON(A0HE!(), A1HE!(), CORRHE!())
CALL CHEN(A0CH!(), A1CH!(), CORRCH!())
CALL OSWIN(A0OS!(), A1OS!(), CORROS!())
CALL HALSEY(A0HA!(), A1HA!(), CORRHA!())
CALL GAB(A0G!(), A1G!(), A2G!(), CORRG!())
CLS
PRINT TAB(15); "HENDERSON EQUATION COEFFICIENTS"
PRINT TAB(19); "Ao"; TAB(31); "A1"; TAB(42); "RMS"
PRINT "Component 1", TAB(15); USING FORMAT$; A0HE!(1); A1HE!(1); CORRHE!(1)
PRINT "Component 2", TAB(15); USING FORMAT$; A0HE!(2); A1HE!(2); CORRHE!(2)
PRINT TAB(15); "CHEN EQUATION COEFFICIENTS"
PRINT TAB(19); "Ao"; TAB(31); "A1"; TAB(42); "RMS"
PRINT "Component 1", TAB(15); USING FORMAT$; A0CH!(1); A1CH!(1); CORRCH!(1)
PRINT "Component 2", TAB(15); USING FORMAT$; A0CH!(2); A1CH!(2); CORRCH!(2)
PRINT TAB(15); "OSWIN EQUATION COEFFICIENTS"
PRINT TAB(19); "Ao"; TAB(31); "A1"; TAB(42); "RMS"
PRINT "Component 1", TAB(15); USING FORMAT$; A0OS!(1); A1OS!(1); CORROS!(1)
PRINT "Component 2", TAB(15); USING FORMAT$; A0OS!(2); A1OS!(2); CORROS!(2)
PRINT TAB(15); "HALSEY EQUATION COEFFICIENTS"
PRINT TAB(19); "Ao"; TAB(31); "A1"; TAB(42); "RMS"
```

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F

```
PRINT "Component 1", TAB(15); USING FORMAT$; A0HA!(1); A1HA!(1); CORRHA!(1)
PRINT "Component 2", TAB(15); USING FORMAT$; A0HA!(2); A1HA!(2); CORRHA!(2)
PRINT TAB(15); "GAB EQUATION COEFFICIENTS"
PRINT TAB(19); "Ao"; TAB(31); "A1"; TAB(42); "A2"; TAB(55); "RMS"
PRINT "Component 1", TAB(15); USING FORMAT$; A0G!(1); A1G!(1); A2G!(1); CORRG!(1)
PRINT "Component 2", TAB(15); USING FORMAT$; A0G!(2); A1G!(2); A2G!(2); CORRG!(2)
CALL PAUSA
PRINT
PRINT TAB(25); "Please input the isotherm equation to be used";
PRINT TAB(30); "(HE)NDERSON"
PRINT TAB(30); "(CH)EN"
PRINT TAB(30); "(OS)WIN"
PRINT TAB(30); "(HA)LSEY"
PRINT TAB(30); "(GAB)"
INPUT NISO$
GOSUB MENU
'*******************************************************************************

SHELF:

'INPUT PACKAGING, STORAGE ENVIRONMENT AND PRODUCTS DATA
CLS
PRINT "Please input packaging data"
INPUT "THICKNESS in u =", L
INPUT "PERMEABILITY COEFFICIENT in gu/m2 day mmHg =", P
INPUT "AREA in m2 =", A
PRINT : PRINT
PRINT "Please input storage environment data"
INPUT "STORAGE WATER ACTIVITY =", AWE
INPUT "VAPOR PRESSURE AT STORAGE TEMPERATURE in mmHg =", PS
PRINT : PRINT
PRINT "Please input products data"
INPUT "DRY WEIGHT OF COMPONENT 1 in g =", W(1)
INPUT "DRY WEIGHT OF COMPONENT 2 in g =", W(2)
INPUT "INITIAL MOISTURE CONTENT OF COMPONENT 1 in g/g =", MC0(1)
INPUT "INITIAL MOISTURE CONTENT OF COMPONENT 2 in g/g =", MC0(2)
INPUT "FINAL MOISTURE CONTENT OF COMPONENT 1 in g/g =", MCF(1)
INPUT "FINAL MOISTURE CONTENT OF COMPONENT 2 in g/g =", MCF(2)
PRINT : PRINT
'*************
'GET SORPTION ISOTHERM COEFFICIENTS
IF UCASE$(NISO$) = "HE" THEN
 FOR I = 1 TO 2
   A0!(I) = A0HE!(I)
   A1!(I) = A1HE!(I)
 NEXT I
END IF
IF UCASE$(NISO$) = "CH" THEN
 FOR I = 1 TO 2
   A0!(I) = A0CH!(I)
   A1!(I) = A1CH!(I)
 NEXT I
END IF
IF UCASE$(NISO$) = "OS" THEN
```

```
 FOR I = 1 TO 2
  A0!(I) = A0OS!(I)
  A1!(I) = A1OS!(I)
 NEXT I
END IF
IF UCASE$(NISO$) = "HA" THEN
 FOR I = 1 TO 2
  A0!(I) = A0HA!(I)
  A1!(I) = A1HA!(I)
 NEXT I
END IF
IF UCASE$(NISO$) = "GAB" THEN
 FOR I = 1 TO 2
  A0!(I) = A0G!(I)
  A1!(I) = A1G!(I)
  A2!(I) = A2G!(I)
 NEXT I
END IF
'**************
'CALCULATE SHELF - LIFE
'**********************************************************************************
PRINT "Please wait a moment .............."
PRINT
DIM MC!(2, 3000), AWI!(3000), DMC1#(3000), DMC2#(3000)
NIT = INT(ABS(MCF(1) - MC0(1)) / .00005)
IF NIT > 2999 THEN
 NIT = 2999
END IF
PRINT NISO$
PRINT "nit=", NIT
DMC1# = (MCF(1) - MC0(1)) / NIT
MC!(1, 1) = MC0(1)
MC!(1, NIT + 1) = MCF(1)
MC!(2, 1) = MC0(2)
AWI!(1) = FUNA#(NISO$, MC!(1, 1), A0!(1), A1!(1), A2!(1))
T = 0
FOR J = 2 TO NIT + 1
    X = 0
    MC!(1, J) = MC!(1, 1) + (J - 1) * DMC1#
    AWI!(J) = FUNA#(NISO$, MC!(1, J), A0!(1), A1!(1), A2!(1))
    IF UCASE$(NISO$) = "GAB" THEN
        DMC2#(J) = FUNM#(NISO$, AWI!(J), A0!(2), A1!(2), A2!(2)) - FUNM#(NISO$, AWI!(J - 1),
A0!(2), A1!(2), A2!(2))
    ELSE
        DMC2#(J) = DMC1# * FUNDM#(1, NISO$, AWI!(), MC!(1, J), A0!(), A1!(), A2!())
    END IF
    X = (W(1) * DMC1# + W(2) * DMC2#(J)) / (AWE - AWI!(J))
    T = T + X
NEXT J
TEMPO$ = "##### days"
MOIST$ = "#.#### g/g"
T = T * L / (P * A * PS)
PRINT "The time for component 1 to achieve final moisture content is"; USING TEMPO$; T
```

PR
+
C
D
F

```
PRINT "The final moisture content of component 2 is ="; USING MOIST$; FUNM#(NISO$, AWI!(NIT
+ 1), A0!(2), A1!(2), A2!(2))
CALL PAUSA
INPUT "The final moisture content of component 2 is higher than the critical (Y/N)", zxc$
IF UCASE$(zxc$) = "Y" THEN
 NIT = INT(ABS(MCF(2) - MC0(2)) / .00005)
 IF NIT > 2999 THEN
  NIT = 2999
 END IF
 PRINT "nit=", NIT
 DMC2# = (MCF(2) - MC0(2)) / NIT
 MC!(2, 1) = MC0(2)
 MC!(2, NIT + 1) = MCF(2)
 MC!(1, 1) = MC0(1)
 AWI!(1) = FUNA#(NISO$, MC!(2, 1), A0!(2), A1!(2), A2!(2))
 T2 = 0
 FOR J = 2 TO NIT + 1
    X = 0
    MC!(2, J) = MC!(2, 1) + (J - 1) * DMC2#
    AWI!(J) = FUNA#(NISO$, MC!(2, J), A0!(2), A1!(2), A2!(2))
    IF UCASE$(NISO$) = "GAB" THEN
        DMC1#(J) = FUNM#(NISO$, AWI!(J), A0!(1), A1!(1), A2!(1)) - FUNM#(NISO$, AWI!(J - 1),
A0!(1), A1!(1), A2!(1))
    ELSE
        DMC1#(J) = DMC2# * FUNDM#(2, NISO$, AWI!(), MC!(2, J), A0!(), A1!(), A2!())
    END IF
    X = (W(2) * DMC2# + W(1) * DMC1#(J)) / (AWE - AWI!(J))
    T2 = T2 + X
 NEXT J
 T2 = T2 * L / (P * A * PS)
 PRINT "The shelf life is"; USING TEMPO$; T2
 PRINT "The final moisture content of component 1 is ="; USING MOIST$; FUNM#(NISO$, AWI!(NIT
+ 1), A0!(1), A1!(1), A2!(1))
 CALL PAUSA
ELSE
 PRINT "The shelf life is"; USING TEMPO$; T
 PRINT "The final moisture content of component 2 is ="; USING MOIST$; FUNM#(NISO$, AWI!(NIT
+ 1), A0!(2), A1!(2), A2!(2))
 CALL PAUSA
END IF
GOSUB MENU

STABILITY:
'INPUT PACKAGING, STORAGE ENVIRONMENT AND PRODUCTS DATA
CLS
DIM M0!(2, 10)
PRINT "Please input packaging data"
INPUT "THICKNESS in u =", L
INPUT "PERMEABILITY COEFFICIENT in gu/m2 day mmHg =", P
INPUT "AREA in m2 =", A
PRINT : PRINT
PRINT "Please input storage environment data"
INPUT "STORAGE WATER ACTIVITY =", AWE
INPUT "VAPOR PRESSURE AT STORAGE TEMPERATURE in mmHg =", PS
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PRINT : PRINT
PRINT "Please input products data"
INPUT "DRY WEIGHT OF COMPONENT 1 in g =", W(1)
INPUT "DRY WEIGHT OF COMPONENT 2 in g =", W(2)
INPUT "INITIAL MOISTURE CONTENT OF COMPONENT 1 in g/g =", M0!(1, 0)
INPUT "INITIAL MOISTURE CONTENT OF COMPONENT 2 in g/g =", M0!(2, 0)
PRINT : PRINT
'**************
'GET SORPTION ISOTHERM COEFFICIENTS
IF UCASE$(NISO$) = "HE" THEN
 FOR I = 1 TO 2
  A0!(I) = A0HE!(I)
  A1!(I) = A1HE!(I)
 NEXT I
END IF
IF UCASE$(NISO$) = "CH" THEN
 FOR I = 1 TO 2
  A0!(I) = A0CH!(I)
  A1!(I) = A1CH!(I)
 NEXT I
END IF
IF UCASE$(NISO$) = "OS" THEN
 FOR I = 1 TO 2
  A0!(I) = A0OS!(I)
  A1!(I) = A1OS!(I)
 NEXT I
END IF
IF UCASE$(NISO$) = "HA" THEN
 FOR I = 1 TO 2
  A0!(I) = A0HA!(I)
  A1!(I) = A1HA!(I)
 NEXT I
END IF
IF UCASE$(NISO$) = "GAB" THEN
 FOR I = 1 TO 2
  A0!(I) = A0G!(I)
  A1!(I) = A1G!(I)
  A2!(I) = A2G!(I)
 NEXT I
END IF
'**************
'CALCULATE STORAGE STABILITY
'************************************************************************
DIM M!(1 TO 2, 0 TO 10, 1 TO 100), AW!(1 TO 100), DM1#(1 TO 100), DM2#(1 TO 100)
DIM U(0 TO 10), U1(0 TO 11, 1 TO 100), MF!(1, 0 TO 10)
INPUT "Time interval (days)=", TF
DT = TF / 10
U(0) = 0
U1(1, 1) = 0
M!(1, 0, 1) = M0!(1, 0)
AW!(1) = FUNA#(NISO$, M0!(1, 0), A0!(1), A1!(1), A2!(1))
CLS
PRINT NISO$: CALL PAUSA
PRINT
```

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TOMATO$ = "  ####          #.####          #.####"
PRINT TAB(20); "Storage Stability Data"
PRINT TAB(20); "======================"
PRINT TAB(10); "Time, days"; TAB(25); "MC of Component 1"; TAB(45); "MC of Component 2"
PRINT TAB(10); "----------"; TAB(25); "-----------------"; TAB(45); "-----------------"
FOR N = 1 TO 10
  U(N) = N * DT
  FOR J = 2 TO 100
    M!(1, N, J) = (J - 1) * .001 + M0!(1, N - 1)
    AW!(J) = FUNA#(NISO$, M!(1, N, J), A0!(1), A1!(1), A2!(1))
    DM1# = .001
    IF UCASE$(NISO$) = "GAB" THEN
      DM2#(J) = FUNM#(NISO$, AW!(J), A0!(2), A1!(2), A2!(2)) - FUNM#(NISO$, AW!(J - 1), A0!(2),
A1!(2), A2!(2))
    ELSE
      DM2#(J) = DM1# * FUNDM#(1, NISO$, AW!(), M!(1, N, J), A0!(), A1!(), A2!())
    END IF
    X = (W(1) * DM1# + W(2) * DM2#(J)) / (AWE - AW!(J))
    U1(N, J) = U1(N, J - 1) + X * L / (P * A * PS)
    IF U1(N, J) > U(N) THEN EXIT FOR
  NEXT J
  MF!(1, N) = M!(1, N, J)
  PRINT TAB(10); USING TOMATO$; U(N); MF!(1, N); FUNM#(NISO$, AW!(J), A0!(2), A1!(2),
A2!(2))
  M0!(1, N) = M!(1, N, J)
  AW!(1) = FUNA#(NISO$, M!(1, N, J), A0!(1), A1!(1), A2!(1))
  U1(N + 1, 1) = U1(N, J)
NEXT N
CALL PAUSA
GOSUB MENU

FINAL:
CLS
PRINT "BYE!!!!!": CALL PAUSA
END

SUB CHEN (A0CH!(), A1CH!(), CORRCH!())
DIM expdt AS Iso
DIM RH!(2, 20), MC!(2, 20), X!(2, 20), Y!(2, 20), SX!(2), SY!(2), SX2!(2), SXY!(2)
DIM XM!(2), YM!(2), CCCH!(2), N(2)
OPEN "iso1.dat" FOR RANDOM AS #1 LEN = LEN(expdt)
N(1) = 0
FOR K = 1 TO LOF(1) / LEN(expdt)
  GET #1, K, expdt
  RH!(1, K) = expdt.RH
  MC!(1, K) = expdt.MC
  N(1) = N(1) + 1
NEXT K
CLOSE #1

OPEN "iso2.dat" FOR RANDOM AS #1 LEN = LEN(expdt)
N(2) = 0
FOR K = 1 TO LOF(1) / LEN(expdt)
  GET #1, K, expdt
```

```
 RH!(2, K) = expdt.RH
 MC!(2, K) = expdt.MC
 N(2) = N(2) + 1
NEXT K
CLOSE #1

'********************************************************************************
'CALCULATE LINEAR REGRESSION
'********************************************************************************

SX!(I) = 0: SY!(I) = 0: SX2!(I) = 0: SXY!(I) = 0
FOR I = 1 TO 2
    FOR K = 1 TO N(I)
        X!(I, K) = MC!(I, K)
        Y!(I, K) = LOG(-LOG(RH!(I, K) / 100))
        SX!(I) = SX!(I) + X!(I, K)
        SY!(I) = SY!(I) + Y!(I, K)
        SX2!(I) = SX2!(I) + X!(I, K) * X!(I, K)
        SXY!(I) = SXY!(I) + X!(I, K) * Y!(I, K)
    NEXT K
XM!(I) = SX!(I) / N(I): YM!(I) = SY!(I) / N(I)
A1CH!(I) = (N(I) * SXY!(I) - SX!(I) * SY!(I)) / (N(I) * SX2!(I) - SX!(I) * SX!(I))
A0CH!(I) = YM!(I) - A1CH!(I) * XM!(I)

    CCCH!(I) = 0
    FOR K = 1 TO N(I)
        CCCH!(I) = CCCH!(I) + ((MC!(I, K) - ((Y!(I, K) - A0CH!(I)) / A1CH!(I))) / MC!(I, K)) ^ 2
    NEXT K
CORRCH!(I) = SQR(CCCH!(I) / N(I)) * 100
NEXT I

'********************************************************************************
'PRINT RESULTS OUTPUT
'********************************************************************************
FMAT$ = "   ##        ##.####      ##.####"
INPUT "Do you want to see the calculated moisture content with the Chen Equation (y/n) ? ", MNB$
PRINT
IF UCASE$(MNB$) = "Y" THEN
 FOR I = 1 TO 2
  CLS
  PRINT "Chen Equation"
  PRINT "----------"
  PRINT "COMPONENT ", I
  PRINT "Ao=", A0CH!(I)
  PRINT "A1=", A1CH!(I)
  PRINT
  PRINT TAB(15); "DATA POINT N.", "EXP MC", "CAL MC"
  PRINT TAB(15); "-------------", "-------", "------"
  FOR K = 1 TO N(I)
   PRINT TAB(15); USING FMAT$; K; MC!(I, K); (Y!(I, K) - A0CH!(I)) / A1CH!(I)
   NEXT K
   PRINT
   PRINT "RMS% =", CORRCH!(I)
   PRINT : PRINT
```

```
   CALL PAUSA
  NEXT I
END IF
END SUB

SUB CREATE
CLS
DIM expdt AS Iso
OPEN "iso1.dat" FOR RANDOM AS #1 LEN = LEN(expdt)
INPUT "Number of experimental points for component 1 ?", N1
FOR I = 1 TO N1
     INPUT "Relative humidity ="; expdt.RH
     INPUT "Moisture Content ="; expdt.MC
     PUT #1, I, expdt
NEXT I
CLOSE #1
OPEN "iso2.dat" FOR RANDOM AS #1 LEN = LEN(expdt)
INPUT "Number of experimental points for component 2 ?", N2
FOR I = 1 TO N2
     INPUT "Relative humidity ="; expdt.RH
     INPUT "Moisture Content ="; expdt.MC
     PUT #1, I, expdt
NEXT I
CLOSE #1

CALL PRINTDATA

END SUB

FUNCTION FUNA# (NISO$, MC!, A0!, A1!, A2!)
IF UCASE$(NISO$) = "HE" THEN
 FUNA# = 1 - EXP(-EXP(A0! + A1! * LOG(MC!)))
END IF
IF UCASE$(NISO$) = "CH" THEN
 FUNA# = EXP(-EXP(A0! + A1! * MC!))
END IF
IF UCASE$(NISO$) = "OS" THEN
 FUNA# = (EXP(A1! * LOG(MC!) + A0!)) / (1 + EXP(A1! * LOG(MC!) + A0!))
END IF
IF UCASE$(NISO$) = "HA" THEN
 FUNA# = EXP(-EXP(A0! + A1! * LOG(MC!)))
END IF
IF UCASE$(NISO$) = "GAB" THEN
 A = A2! * MC!: b = A1! * MC! - 1: c = A0! * MC!
 FUNA# = (-b - SQR(b ^ 2 - 4 * A * c)) / (2 * A)
END IF

END FUNCTION

FUNCTION FUNDM# (Q, NISO$, AWI!(), MC!, A0!(), A1!(), A2!())
IF Q = 1 THEN
 IF UCASE$(NISO$) = "HE" OR UCASE$(NISO$) = "OS" OR UCASE$(NISO$) = "HA" THEN
     FUNDM# = EXP((A0!(1) - A0!(2)) / A1!(2)) * (A1!(1) / A1!(2)) * MC! ^ (A1!(1) / A1!(2) - 1)
 ELSEIF UCASE$(NISO$) = "CH" THEN
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       FUNDM# = A1!(1) / A1!(2)
 END IF
ELSEIF Q = 2 THEN
 IF UCASE$(NISO$) = "HE" OR UCASE$(NISO$) = "OS" OR UCASE$(NISO$) = "HA" THEN
    FUNDM# = EXP((A0!(2) - A0!(1)) / A1!(1)) * (A1!(2) / A1!(1)) * MC! ^ (A1!(2) / A1!(1) - 1)
 ELSEIF UCASE$(NISO$) = "CH" THEN
       FUNDM# = A1!(2) / A1!(1)
 END IF
END IF
END FUNCTION

FUNCTION FUNM# (NISO$, AWI!, A0!, A1!, A2!)
IF UCASE$(NISO$) = "HE" THEN
 FUNM# = EXP((LOG(-LOG(1 - AWI!)) - A0!) / A1!)
END IF
IF UCASE$(NISO$) = "CH" THEN
 FUNM# = (LOG(-LOG(AWI!)) - A0!) / A1!
END IF
IF UCASE$(NISO$) = "OS" THEN
 FUNM# = (EXP(-A0! / A1!)) * (AWI! / (1 - AWI!)) ^ (1 / A1!)
END IF
IF UCASE$(NISO$) = "HA" THEN
 FUNM# = EXP((LOG(-LOG(AWI!)) - A0!) / A1!)
END IF
IF UCASE$(NISO$) = "GAB" THEN
 FUNM# = AWI! / (A2! * AWI! * AWI! + A1! * AWI! + A0!)
END IF


END FUNCTION

SUB GAB (A0G!(), A1G!(), A2G!(), CORRG!())
DIM expdt AS Iso
DIM RH!(2, 20), MC!(2, 20), X!(2, 20), Y!(2, 20), SX!(2), SY!(2), SX2!(2), SXY!(2)
DIM SX3!(2), SX4!(2), SX2Y!(2), F1!(2), F2!(2), F3!(2), F4!(2)
DIM XM!(2), YM!(2), CCG!(2), N(2)
OPEN "iso1.dat" FOR RANDOM AS #1 LEN = LEN(expdt)
N(1) = 0
FOR K = 1 TO LOF(1) / LEN(expdt)
 GET #1, K, expdt
 RH!(1, K) = expdt.RH
 MC!(1, K) = expdt.MC
 N(1) = N(1) + 1
NEXT K
CLOSE #1

OPEN "iso2.dat" FOR RANDOM AS #1 LEN = LEN(expdt)
N(2) = 0
FOR K = 1 TO LOF(1) / LEN(expdt)
 GET #1, K, expdt
 RH!(2, K) = expdt.RH
 MC!(2, K) = expdt.MC
 N(2) = N(2) + 1
NEXT K
```

```
CLOSE #1

'***************************************************************************
'CALCULATE QUADRATIC REGRESSION
'***************************************************************************

SX!(I) = 0: SX2!(I) = 0: SX3!(I) = 0: SX4!(I) = 0
SY!(I) = 0: SXY!(I) = 0: SX2Y!(I) = 0
FOR I = 1 TO 2
    FOR K = 1 TO N(I)
        X!(I, K) = RH!(I, K) / 100
        Y!(I, K) = (RH!(I, K) / 100) / MC!(I, K)
        SX!(I) = SX!(I) + X!(I, K)
        SX2!(I) = SX2!(I) + X!(I, K) * X!(I, K)
        SX3!(I) = SX3!(I) + X!(I, K) * X!(I, K) * X!(I, K)
        SX4!(I) = SX4!(I) + X!(I, K) * X!(I, K) * X!(I, K) * X!(I, K)
        SY!(I) = SY!(I) + Y!(I, K)
        SXY!(I) = SXY!(I) + X!(I, K) * Y!(I, K)
        SX2Y!(I) = SX2Y!(I) + X!(I, K) * X!(I, K) * Y!(I, K)
    NEXT K
F1!(I) = N(I) * SX2!(I) - SX!(I) * SX!(I)
F2!(I) = N(I) * SX3!(I) - SX!(I) * SX2!(I)
F3!(I) = F1!(I) * (N(I) * SX2Y!(I) - SY!(I) * SX2!(I))
F4!(I) = F2!(I) * (N(I) * SXY!(I) - SY!(I) * SX!(I))
A2G!(I) = (F3!(I) - F4!(I)) / (F1!(I) * (N(I) * SX4!(I) - SX2!(I) * SX2!(I)) - F2!(I) * F2!(I))
A1G!(I) = (N(I) * SXY!(I) - SX!(I) * SY!(I) - A2G!(I) * F2!(I)) / F1!(I)
A0G!(I) = (SY!(I) - A1G!(I) * SX!(I) - A2G!(I) * SX2!(I)) / N(I)

    CCG!(I) = 0
    FOR K = 1 TO N(I)
        CCG!(I) = CCG!(I) + ((MC!(I, K) - X!(I, K) / (A2G!(I) * X!(I, K) * X!(I, K) + A1G!(I) * X!(I,
K) + A0G!(I))) / MC!(I, K)) ^ 2
    NEXT K
CORRG!(I) = SQR(CCG!(I) / N(I)) * 100
NEXT I

'***************************************************************************
'PRINT RESULTS OUTPUT
'***************************************************************************
FMAT$ = "  ##      ##.####    ##.####"
INPUT "Do you want to see the calculated moisture content with the GAB Equation (y/n) ? ", MNB$
PRINT
IF UCASE$(MNB$) = "Y" THEN
 FOR I = 1 TO 2
  CLS
  PRINT "GAB Equation"
  PRINT "---------"
  PRINT "COMPONENT ", I
  PRINT "Ao=", A0G!(I)
  PRINT "A1=", A1G!(I)
  PRINT "A2=", A2G!(I)
  PRINT
  PRINT TAB(15); "DATA POINT N.", "EXP MC", "CAL MC"
  PRINT TAB(15); "-------------", "-------", "------"
```

```
  FOR K = 1 TO N(I)
    PRINT TAB(15); USING FMAT$; K; MC!(I, K); X!(I, K) / (A0G!(I) + A1G!(I) * X(I, K) + A2G!(I)
* X(I, K) * X(I, K))
    NEXT K
    PRINT
    PRINT "RMS% =", CORRG!(I)
    PRINT : PRINT
    CALL PAUSA
 NEXT I
END IF


END SUB

SUB HALSEY (A0HA!(), A1HA!(), CORRHA!())
DIM expdt AS Iso
DIM RH!(2, 20), MC!(2, 20), X!(2, 20), Y!(2, 20), SX!(2), SY!(2), SX2!(2), SXY!(2)
DIM XM!(2), YM!(2), CCHA!(2), N(2)
OPEN "iso1.dat" FOR RANDOM AS #1 LEN = LEN(expdt)
N(1) = 0
FOR K = 1 TO LOF(1) / LEN(expdt)
 GET #1, K, expdt
 RH!(1, K) = expdt.RH
 MC!(1, K) = expdt.MC
 N(1) = N(1) + 1
NEXT K
CLOSE #1

OPEN "iso2.dat" FOR RANDOM AS #1 LEN = LEN(expdt)
N(2) = 0
FOR K = 1 TO LOF(1) / LEN(expdt)
 GET #1, K, expdt
 RH!(2, K) = expdt.RH
 MC!(2, K) = expdt.MC
 N(2) = N(2) + 1
NEXT K
CLOSE #1

'******************************************************************************
'CALCULATE LINEAR REGRESSION
'******************************************************************************

SX!(I) = 0: SY!(I) = 0: SX2!(I) = 0: SXY!(I) = 0
FOR I = 1 TO 2
      FOR K = 1 TO N(I)
            X!(I, K) = LOG(MC!(I, K))
            Y!(I, K) = LOG(-LOG(RH!(I, K) / 100))
            SX!(I) = SX!(I) + X!(I, K)
            SY!(I) = SY!(I) + Y!(I, K)
            SX2!(I) = SX2!(I) + X!(I, K) * X!(I, K)
            SXY!(I) = SXY!(I) + X!(I, K) * Y!(I, K)
      NEXT K
XM!(I) = SX!(I) / N(I): YM!(I) = SY!(I) / N(I)
A1HA!(I) = (N(I) * SXY!(I) - SX!(I) * SY!(I)) / (N(I) * SX2!(I) - SX!(I) * SX!(I))
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A0HA!(I) = YM!(I) - A1HA!(I) * XM!(I)

    CCHA!(I) = 0
    FOR K = 1 TO N(I)
        CCHA!(I) = CCHA!(I) + ((MC!(I, K) - EXP((Y!(I, K) - A0HA!(I)) / A1HA!(I))) / MC!(I, K)) ^
2
    NEXT K
CORRHA!(I) = SQR(CCHA!(I) / N(I)) * 100
NEXT I

'*****************************************************************************
'PRINT RESULTS OUTPUT
'*****************************************************************************
FMAT$ = "  ##      ##.####    ##.####"
INPUT "Do you want to see the calculated moisture content with the Halsey Equation (y/n) ? ", MNB$
PRINT
IF UCASE$(MNB$) = "Y" THEN
 FOR I = 1 TO 2
  CLS
  PRINT "Halsey Equation"
  PRINT "------------"
  PRINT "COMPONENT ", I
  PRINT "Ao=", A0HA!(I)
  PRINT "A1=", A1HA!(I)
  PRINT
  PRINT TAB(15); "DATA POINT N.", "EXP MC", "CAL MC"
  PRINT TAB(15); "-------------", "-------", "------"
  FOR K = 1 TO N(I)
   PRINT TAB(15); USING FMAT$; K; MC!(I, K); EXP((Y!(I, K) - A0HA!(I)) / A1HA!(I))
   NEXT K
   PRINT
   PRINT "RMS% =", CORRHA!(I)
   PRINT : PRINT
   CALL PAUSA
 NEXT I
END IF
END SUB

SUB HENDERSON (A0HE!(), A1HE!(), CORRHE!())
DIM expdt AS Iso
DIM RH!(2, 20), MC!(2, 20), X!(2, 20), Y!(2, 20), SX!(2), SY!(2), SX2!(2), SXY!(2)
DIM XM!(2), YM!(2), CCHE!(2), N(2)
OPEN "iso1.dat" FOR RANDOM AS #1 LEN = LEN(expdt)
N(1) = 0
FOR K = 1 TO LOF(1) / LEN(expdt)
 GET #1, K, expdt
 RH!(1, K) = expdt.RH
 MC!(1, K) = expdt.MC
 N(1) = N(1) + 1
NEXT K
CLOSE #1

OPEN "iso2.dat" FOR RANDOM AS #1 LEN = LEN(expdt)
N(2) = 0
```

```
FOR K = 1 TO LOF(1) / LEN(expdt)
 GET #1, K, expdt
 RH!(2, K) = expdt.RH
 MC!(2, K) = expdt.MC
 N(2) = N(2) + 1
NEXT K
CLOSE #1

'*****************************************************************************
'CALCULATE LINEAR REGRESSION
'*****************************************************************************

SX!(I) = 0: SY!(I) = 0: SX2!(I) = 0: SXY!(I) = 0
FOR I = 1 TO 2
    FOR K = 1 TO N(I)
        X!(I, K) = LOG(MC!(I, K))
        Y!(I, K) = LOG(-LOG(1 - RH!(I, K) / 100))
        SX!(I) = SX!(I) + X!(I, K)
        SY!(I) = SY!(I) + Y!(I, K)
        SX2!(I) = SX2!(I) + X!(I, K) * X!(I, K)
        SXY!(I) = SXY!(I) + X!(I, K) * Y!(I, K)
    NEXT K

XM!(I) = SX!(I) / N(I): YM!(I) = SY!(I) / N(I)
A1HE!(I) = (N(I) * SXY!(I) - SX!(I) * SY!(I)) / (N(I) * SX2!(I) - SX!(I) * SX!(I))
A0HE!(I) = YM!(I) - A1HE!(I) * XM!(I)
CCHE!(I) = 0
    FOR K = 1 TO N(I)
        CCHE!(I) = CCHE!(I) + ((MC!(I, K) - EXP((Y!(I, K) - A0HE!(I)) / A1HE!(I))) / MC!(I, K)) ^
2
    NEXT K
CORRHE!(I) = 100 * SQR(CCHE!(I) / N(I))

NEXT I

'*****************************************************************************
'PRINT RESULTS OUTPUT
'*****************************************************************************
FMAT$ = "   ##       ##.####     ##.####"
INPUT "Do you want to see the calculated moisture content with the Henderson Equation (y/n) ? ", MNB$
PRINT
IF UCASE$(MNB$) = "Y" THEN
 FOR I = 1 TO 2
  CLS
  PRINT "Henderson Equation"
  PRINT "---------------"
  PRINT "COMPONENT ", I
  PRINT "Ao=", A0HE!(I)
  PRINT "A1=", A1HE!(I)
  PRINT
  PRINT TAB(15); "DATA POINT N.", "EXP MC", "CAL MC"
  PRINT TAB(15); "-------------", "-------", "------"
  FOR K = 1 TO N(I)
   PRINT TAB(15); USING FMAT$; K; MC!(I, K); EXP((Y!(I, K) - A0HE!(I)) / A1HE!(I))
```

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      NEXT K
      PRINT
      PRINT "RMS% =", CORRHE!(I)
      PRINT : PRINT
      CALL PAUSA
   NEXT I
END IF

END SUB

SUB MODIFY (MOD$)
DIM expdt AS Iso
'*****************************************************************************
FORMATO$ = "#    ##.#    ##.##"
IF UCASE$(MOD$) = "C" THEN
   INPUT "Do you want to correct data of component 1 ? (Y/N)", qw$
   IF UCASE$(qw$) = "Y" THEN
     OPEN "iso1.dat" FOR RANDOM AS #1 LEN = LEN(expdt)
     DO
        INPUT "Input the data point you want to correct", x1
        GET #1, x1, expdt
        INPUT "Relative humidity ="; expdt.RH
        INPUT "Moisture Content ="; expdt.MC
        PUT #1, x1, expdt
        INPUT "Do you wish to correct more data points ? (Y/N)"; ans$
     LOOP UNTIL UCASE$(ans$) = "N"
     CLOSE #1
   ELSEIF UCASE$(qw$) = "N" THEN
     PRINT "You'll correct data of component 2"
     OPEN "iso2.dat" FOR RANDOM AS #1 LEN = LEN(expdt)
     DO
        INPUT "Input the data point you want to correct", x2
        GET #1, x2, expdt
        INPUT "Relative humidity ="; expdt.RH
        INPUT "Moisture Content ="; expdt.MC
        PUT #1, x2, expdt
        INPUT "Do you wish to correct more data points ? (Y/N)"; ans$
     LOOP UNTIL UCASE$(ans$) = "N"
     CLOSE #1
   END IF
END IF


'*****************************************************************************

IF UCASE$(MOD$) = "A" THEN
   INPUT "Do you want to add data to component 1 ? (Y/N) ", Y$
     IF UCASE$(Y$) = "Y" THEN
       OPEN "iso1.dat" FOR RANDOM AS #1 LEN = LEN(expdt)
       I = LOF(1) / LEN(expdt)
       DO
         INPUT "Relative humidity ="; expdt.RH
         INPUT "Moisture Content ="; expdt.MC
         I = I + 1
```

```
        PUT #1, I, expdt
        INPUT "Do you wish to add more data points ? (Y/N)"; ans$
      LOOP UNTIL UCASE$(ans$) = "N"
      CLOSE #1
    ELSEIF UCASE$(Y$) = "N" THEN
      PRINT "You'll add data to component 2"
      OPEN "iso2.dat" FOR RANDOM AS #1 LEN = LEN(expdt)
      I = LOF(1) / LEN(expdt)
      DO
        INPUT "Relative humidity ="; expdt.RH
        INPUT "Moisture Content ="; expdt.MC
        I = I + 1
        PUT #1, I, expdt
        INPUT "Do you wish to add more data points ? (Y/N)"; ans$
      LOOP UNTIL UCASE$(ans$) = "N"
      CLOSE #1
    END IF
END IF
'**************************************************************************

IF UCASE$(MOD$) = "D" THEN
  INPUT "Do you want to delete data from component 1 ? (Y/N) ", Y$
    IF UCASE$(Y$) = "Y" THEN
      OPEN "iso1.dat" FOR RANDOM AS #1 LEN = LEN(expdt)
      OPEN "temp.dat" FOR RANDOM AS #2 LEN = LEN(expdt)
      DO
        INPUT "Input the data point you want to delete", ND
        FOR I = 1 TO ND - 1
          GET #1, I, expdt
          PUT #2, I, expdt
        NEXT I
        FOR I = ND + 1 TO LOF(1) / LEN(expdt)
           GET #1, I, expdt
           IX = I - 1
           PUT #2, IX, expdt
        NEXT I
        INPUT "Do you wish to delete more data points ? (Y/N)"; ans$
      LOOP UNTIL UCASE$(ans$) = "N"
      CLOSE #1
      CLOSE #2
      SHELL "DEL iso1.dat"
      SHELL "REN temp.dat iso1.dat"
    ELSEIF UCASE$(Y$) = "N" THEN
      PRINT "You'll delete data from component 2"
      OPEN "iso2.dat" FOR RANDOM AS #1 LEN = LEN(expdt)
      OPEN "temp.dat" FOR RANDOM AS #2 LEN = LEN(expdt)
      DO
        INPUT "Input the data point you want to delete", ND
        FOR I = 1 TO ND - 1
          GET #1, I, expdt
          PUT #2, I, expdt
        NEXT I
        FOR I = ND + 1 TO LOF(1) / LEN(expdt)
           GET #1, I, expdt
```

```
      IX = I - 1
      PUT #2, IX, expdt
     NEXT I
     INPUT "Do you wish to delete more data points ? (Y/N)"; ans$
   LOOP UNTIL UCASE$(ans$) = "N"
   CLOSE #1
   CLOSE #2
   SHELL "DEL iso2.dat"
   SHELL "REN temp.dat iso2.dat"
  END IF
END IF

'**************************************************************************

CALL PRINTDATA

END SUB

SUB OSWIN (A0OS!(), A1OS!(), CORROS!())
DIM expdt AS Iso
DIM RH!(2, 20), MC!(2, 20), X!(2, 20), Y!(2, 20), SX!(2), SY!(2), SX2!(2), SXY!(2)
DIM XM!(2), YM!(2), CCOS!(2), N(2)
OPEN "iso1.dat" FOR RANDOM AS #1 LEN = LEN(expdt)
N(1) = 0
FOR K = 1 TO LOF(1) / LEN(expdt)
 GET #1, K, expdt
 RH!(1, K) = expdt.RH
 MC!(1, K) = expdt.MC
 N(1) = N(1) + 1
NEXT K
CLOSE #1

OPEN "iso2.dat" FOR RANDOM AS #1 LEN = LEN(expdt)
N(2) = 0
FOR K = 1 TO LOF(1) / LEN(expdt)
 GET #1, K, expdt
 RH!(2, K) = expdt.RH
 MC!(2, K) = expdt.MC
 N(2) = N(2) + 1
NEXT K
CLOSE #1

'***************************************************************************
'CALCULATE LINEAR REGRESSION
'***************************************************************************

SX!(I) = 0: SY!(I) = 0: SX2!(I) = 0: SXY!(I) = 0
FOR I = 1 TO 2
    FOR K = 1 TO N(I)
        X!(I, K) = LOG(MC!(I, K))
        Y!(I, K) = LOG(RH!(I, K) / 100 / (1 - RH!(I, K) / 100))
        SX!(I) = SX!(I) + X!(I, K)
        SY!(I) = SY!(I) + Y!(I, K)
        SX2!(I) = SX2!(I) + X!(I, K) * X!(I, K)
```

```
        SXY!(I) = SXY!(I) + X!(I, K) * Y!(I, K)
    NEXT K

XM!(I) = SX!(I) / N(I): YM!(I) = SY!(I) / N(I)
A1OS!(I) = (N(I) * SXY!(I) - SX!(I) * SY!(I)) / (N(I) * SX2!(I) - SX!(I) * SX!(I))
A0OS!(I) = YM!(I) - A1OS!(I) * XM!(I)
    CCOS!(I) = 0
    FOR K = 1 TO N(I)
        CCOS!(I) = CCOS!(I) + ((MC!(I, K) - EXP((Y!(I, K) - A0OS!(I)) / A1OS!(I))) / MC!(I, K)) ^ 2
    NEXT K
CORROS!(I) = 100 * SQR(CCOS!(I) / N(I))
NEXT I

'**************************************************************************
'PRINT RESULTS OUTPUT
'**************************************************************************
FMAT$ = "  ##       ##.####     ##.####"
INPUT "Do you want to see the calculated moisture content with the Oswin Equation (y/n) ? ", MNB$
PRINT
IF UCASE$(MNB$) = "Y" THEN
 FOR I = 1 TO 2
  CLS
  PRINT "Oswin Equation"
  PRINT "-----------"
  PRINT "COMPONENT ", I
  PRINT "Ao=", A0OS!(I)
  PRINT "A1=", A1OS!(I)
  PRINT
  PRINT TAB(15); "DATA POINT N.", "EXP MC", "CAL MC"
  PRINT TAB(15); "-------------", "-------", "------"
  FOR K = 1 TO N(I)
   PRINT TAB(15); USING FMAT$; K; MC!(I, K); EXP((Y!(I, K) - A0OS!(I)) / A1OS!(I))
   NEXT K
   PRINT
   PRINT "RMS% =", CORROS!(I)
   PRINT : PRINT
   CALL PAUSA
 NEXT I
END IF

END SUB

SUB PAUSA
 DO
 LOOP UNTIL (INKEY$ <> "")
END SUB

SUB PRINTDATA
CLS
DIM expdt AS Iso
FORMATO$ = "##          ##.#          ##.####"
OPEN "iso1.dat" FOR RANDOM AS #1 LEN = LEN(expdt)
LOCATE 5, 15: PRINT "Sorption data of component 1"
LOCATE 6, 15: PRINT "----------------------------"
```

```
PRINT TAB(15); "n§"; TAB(25); "Rel.Humidity"; TAB(40); "Moist.Content"
FOR I = 1 TO LOF(1) / LEN(expdt)
GET #1, I, expdt
PRINT TAB(15); USING FORMATO$; I; expdt.RH; expdt.MC
NEXT I
CLOSE #1
CALL PAUSA

OPEN "iso2.dat" FOR RANDOM AS #1 LEN = LEN(expdt)
CLS
LOCATE 5, 15: PRINT "Sorption data of component 2"
LOCATE 6, 15: PRINT "----------------------------"
PRINT TAB(15); "n§"; TAB(25); "Rel.Humidity"; TAB(40); "Moist.Content"
FOR I = 1 TO LOF(1) / LEN(expdt)
GET #1, I, expdt
PRINT TAB(15); USING FORMATO$; I; expdt.RH; expdt.MC
NEXT I
CLOSE #1
CALL PAUSA

END SUB
```

APPENDIX C

COMPUTER SIMULATED RESULTS

Table C.1 - Components moisture content as a function of time for different components weight ratio. Simulated results using set of data A from Table 2

	Components Moisture Content, g/g					
	Run 1		Run 2		Run 3	
Time, days	Cereal	Raisin	Cereal	Raisin	Cereal	Raisin
0	0.0770	0.0900	0.0770	0.0900	0.0770	0.0900
30	0.0865	0.1153	0.0875	0.1179	0.0895	0.1231
60	0.0945	0.1362	0.0965	0.1414	0.0985	0.1467
90	0.1005	0.1520	0.1035	0.1600	0.1065	0.1680
120	0.1065	0.1680	0.1095	0.1761	0.1125	0.1843
150	0.1115	0.1816	0.1145	0.1898	0.1185	0.2009
180	0.1155	0.1926	0.1185	0.2009	0.1235	0.2150
210	0.1195	0.2037	0.1225	0.2122	0.1275	0.2266
240	0.1225	0.2122	0.1265	0.2237	0.1315	0.2383
270	0.1255	0.2208	0.1295	0.2324	0.1345	0.2472
300	0.1285	0.2295	0.1325	0.2412	0.1375	0.2562

Table C.2 - Components moisture content as a function of time for different storage water activities. Simulated results using set of data B from Table 2

	Components Moisture Content, g/g					
	Run 1		Run 2		Run 3	
Time, days	Cereal	Raisin	Cereal	Raisin	Cereal	Raisin
0	0.0770	0.0900	0.0770	0.0900	0.0770	0.0900
30	0.0875	0.1179	0.0865	0.1153	0.0855	0.1127
60	0.0965	0.1414	0.0935	0.1335	0.0915	0.1283
90	0.1035	0.1600	0.1005	0.1520	0.0975	0.1440
120	0.1095	0.1761	0.1055	0.1653	0.1015	0.1546
150	0.1145	0.1898	0.1095	0.1761	0.1055	0.1653
180	0.1185	0.2009	0.1135	0.1870	0.1085	0.1734
210	0.1225	0.2122	0.1175	0.1981	0.1115	0.1816
240	0.1265	0.2237	0.1205	0.2065	0.1145	0.1898
270	0.1295	0.2324	0.1235	0.2150	0.1165	0.1953
300	0.1325	0.2412	0.1255	0.2208	0.1185	0.2009

Table C.3 - Components moisture content as a function of time for different packaging barrier properties. Simulated results using set of data C from Table 2

	Components Moisture Content, g/g					
	Run 1		Run 2		Run 3	
Time, days	Cereal	Raisin	Cereal	Raisin	Cereal	Raisin
0	0.0770	0.0900	0.0770	0.0900	0.0770	0.0900
30	0.0935	0.1335	0.0875	0.1179	0.0855	0.1127
60	0.1055	0.1653	0.0965	0.1414	0.0935	0.1335
90	0.1145	0.1898	0.1035	0.1600	0.0995	0.1493
120	0.1215	0.2094	0.1095	0.1761	0.1055	0.1653
150	0.1275	0.2266	0.1145	0.1898	0.1105	0.1788
180	0.1325	0.2412	0.1185	0.2009	0.1145	0.1898
210	0.1365	0.2532	0.1225	0.2122	0.1185	0.2009
240	0.1405	0.2654	0.1265	0.2237	0.1215	0.2094
270	0.1435	0.2747	0.1295	0.2324	0.1245	0.2179
300	0.1465	0.2841	0.1325	0.2412	0.1275	0.2266

Table C.4 - Components moisture content as a function of time for different total weight to packaging area ratio. Simulated results using set of data D from Table 2

	Components Moisture Content, g/g					
	Run 1		Run 2		Run 3	
Time, days	Cereal	Raisin	Cereal	Raisin	Cereal	Raisin
0	0.0770	0.0900	0.0770	0.0900	0.0770	0.0900
30	0.0875	0.1179	0.0855	0.1127	0.0845	0.1101
60	0.0965	0.1414	0.0925	0.1309	0.0905	0.1257
90	0.1035	0.1600	0.0975	0.1440	0.0965	0.1414
120	0.1095	0.1761	0.1035	0.1600	0.1005	0.1520
150	0.1145	0.1898	0.1075	0.1707	0.1055	0.1653
180	0.1185	0.2009	0.1115	0.1816	0.1095	0.1761
210	0.1225	0.2122	0.1155	0.1926	0.1125	0.1843
240	0.1265	0.2237	0.1185	0.2009	0.1155	0.1926
270	0.1295	0.2324	0.1225	0.2122	0.1185	0.2009
300	0.1325	0.2412	0.1245	0.2179	0.1215	0.2094

APPENDIX D

PACKAGING MATERIALS CHARACTERIZATION

1. Film Permeability

Table D.1 - Materials water vapor transmission rate (g/m^2 day) at 25 °C. Infrared sensor method

Driving force	RH 100%	RH 74.3% (*)
OPP		
1	1.733	1.304
2	1.771	1.304
3	1.726	1.296
Average	1.743	1.301
St. Dev.	0.024	0.005
PE/barrier		
1	0.6965	0.5460
2	0.6919	0.5591
3	0.6991	0.5383
Average	0.6958	0.5478
St. Dev.	0.0036	0.0105
PE		
1	3.179	2.503
2	3.073	2.618
3	3.200	2.621
Average	3.151	2.581
St. Dev.	0.068	0.067

(*)
polyester water vapor transmission rate with water = 2.088 g/m^2 day
polyester water vapor transmission rate salt solution = 1.552 g/m^2 day
then ΔRH = 1.552 / 2.088 = .743

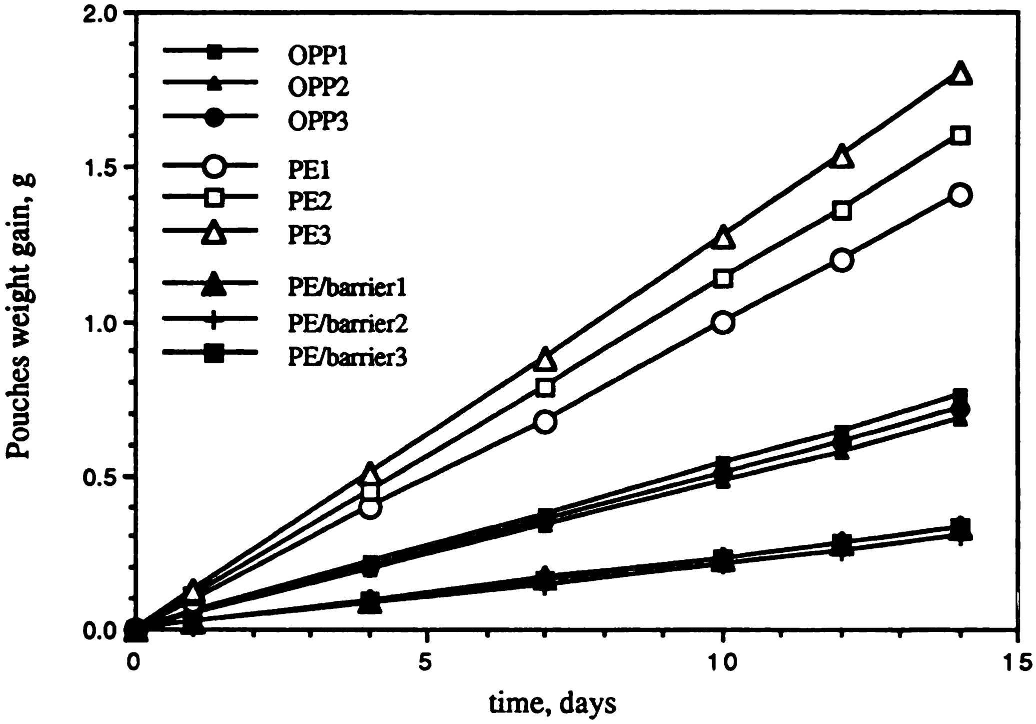

Figure D.1 - Pouches with desiccant weight gain over time for packaging permeance determination by the gravimetric method

Table D.2 - Experimental data for packaging permeance determination by the gravimetric method

Pouch Sample	Pouch Dimensions, cm	Slope, g/day	Correlation Coef.
OPP1	14.5 x 15.5	0.0540	0.9999
OPP2	15.0 x 14.0	0.0482	0.9999
OPP3	15.0 x 14.5	0.0510	0.9999
PE1	15.5 x 14.0	0.1004	0.9998
PE2	15.0 x 16.0	0.1144	0.9999
PE3	18.0 x 15.5	0.1284	0.9999
PE/barrier1	14.5 x 16.5	0.0236	0.9999
PE/barrier2	15.0 x 14.5	0,0214	0.9999
PE/barrier3	15.0 x 15.5	0,0232	0.9999

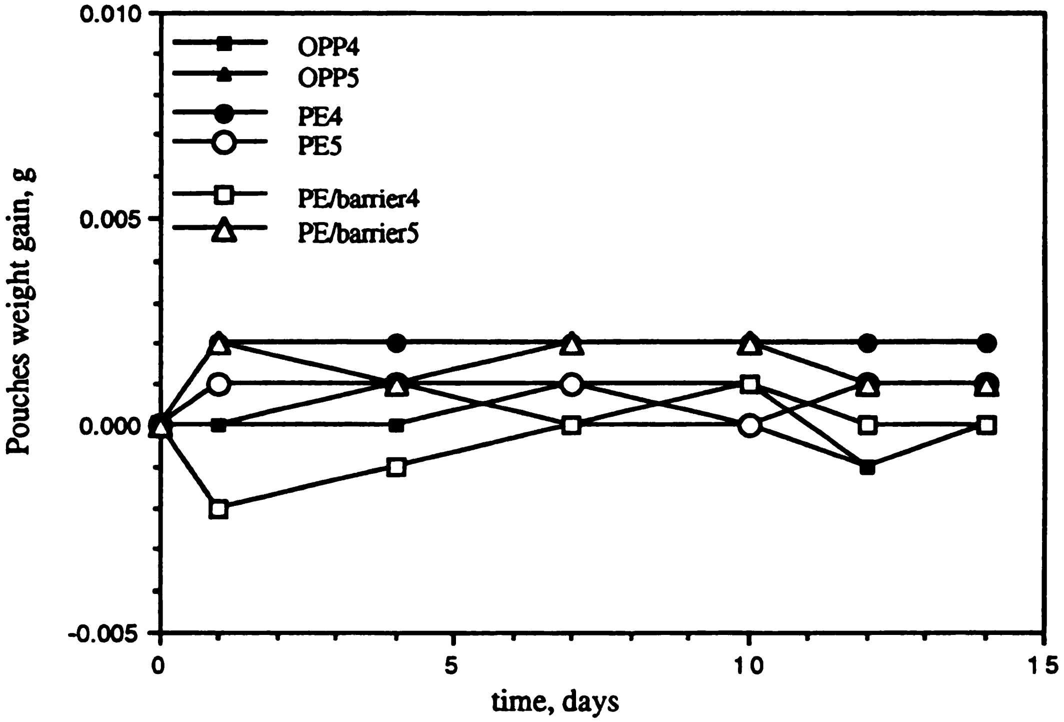

Figure D.2 - Empty pouches weight gain over time for packaging permeance determination by the gravimetric method

Table D.3 - Materials water vapor transmission rate (g/m^2 day) at 25 °C. Gravimetric method

Driving force	RH 72.8%
OPP	
1	1.201
2	1.149
3	1.172
Average	1.174
St. Dev.	0.026
PE/barrier	
1	0.4942
2	0.4921
3	0.5000
Average	0.4954
St. Dev.	0.0041
PE	
1	2.314
2	2.384
3	2.301
Average	2.333
St. Dev.	0.045

2. Materials Identification

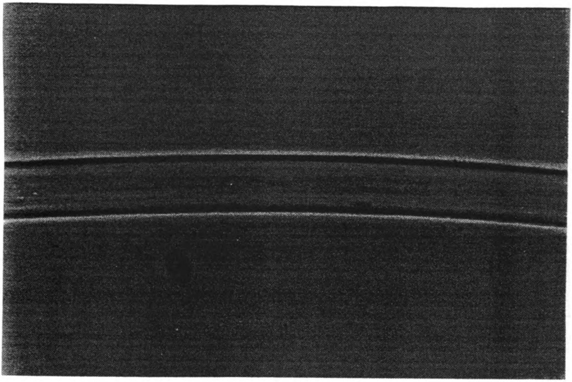

Figure D.3 - OPP film observed at microscope with phase contrast (x 560)

The outer layers were tentatively identified as PP-PE copolymers.

Total thickness: 25 µm

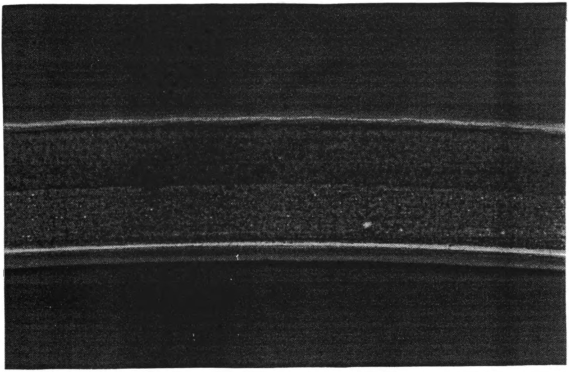

Figure D.4 - PE/ barrier film observed at microscope with phase contrast (x 560)

This material was found to be composed by two layers of PE, being one white pigmented, and one layer of a third material, possibly EVOH.

Total thickness: 65μm

First PE layer thickness: 30μm

Interior PE layer thickness: 25μm

Third layer thickness: 10μm

APPENDIX E

MOISTURE SORPTION ISOTHERM DATA

Table E.1 - Experimental Moisture Sorption Isotherm of Cereal, at 25 °C

Adsorption			Desorption		
RH, %	EMC, %	St.Dev.	RH, %	EMC, %	St.Dev.
9.6	2.572	0.094	9.2	2.759	0.095
13.6	2.980	0.059	13.3	3.189	0.043
24.7	4.482	0.046	23.5	4.679	0.178
33.5	5.769	0.046	32.7	6.082	0.103
45.5	7.313	0.142	44.0	7.471	0.166
53.6	8.631	0.064	52.8	8.847	0.124
65.6	11.158	0.074	63.7	10.990	0.047
75.9	16.192	0.004	73.5	14.980	0.058
81.3	21.586	0.110	78.2	20.813	0.222

Table E.2 - Experimental Moisture Sorption Isotherm of Powder Chocolate, at 25 °C

Adsorption			Desorption		
RH, %	EMC, %	St.Dev.	RH, %	EMC, %	St.Dev.
9.6	0.908	0.022	9.2	-	-
13.6	0.744	0.015	13.3	0.446	0.035
24.7	1.078	0.019	23.5	0.797	0.032
33.5	1.383	0.057	32.7	1.085	0.059
45.5	1.667	0.057	44.0	1.522	0.033
53.6	2.006	0.022	52.8	2.049	0.039
65.6	3.304	0.014	63.7	2.870	0.009
75.9	6.916	0.023	73.5	6.367	0.056
81.3	11.783	0.136	78.2	12.087	0.282

Table E.3 - Experimental Moisture Sorption Isotherm of Raisin, at 25 °C

Adsorption			Desorption		
RH, %	EMC, %	St.Dev.	RH, %	EMC, %	St.Dev.
9.5	-	-	9.5	11.112	0.064
13.3	-	-	13.3	11.106	0.207
24.6	6.426	0.031	24.6	11.382	0.109
32.8	8.463	0.111	32.8	12.265	0.044
44.5	13.185	0.140	44.5	15.688	0.120
53.4	17.840	0.081	53.4	20.386	0.102
64.5	25.955	0.243	64.5	28.152	0.010
74.4	42.204	0.205	74.4	-	-
79.2	52.081	0.188	79.2	-	-

APPENDIX F

DETAILED DATA OF VALIDATION EXPERIMENTS

Table F.1 - Initial weight of components and pouches weight (g) over time (days) for experiment 1

mixture 33/67		time, days	0	15	22	28	38	43	51	64	80
pouch	cereal, g	p.choc, g	pouch, g	pouch, g	pouch, g	pouch, g	pouch, g	pouch, g	pouch, g	pouch, g	pouch, g
1	8.452	18.991	29.405	30.097							
2	9.419	19.172	30.614	31.393							
7	9.155	18.901	30.030	30.869	31.073	31.202					
8	11.115	18.042	31.169	32.090	32.321	32.468					
13	9.981	21.266	33.263	34.129	34.347	34.480	34.668	34.742			
14	9.231	20.337	31.532	32.379	32.586	32.725	32.895	32.961			
19	10.997	21.275	34.274	35.177	35.407	35.554	35.748	35.821	35.934		
20	9.217	20.293	31.513	32.360	32.557	32.697	32.872	32.939	33.031		
25	9.448	20.784	32.220	32.966	33.173	33.311	33.475	33.537	33.641	33.780	
26	10.287	19.719	31.984	32.712	32.927	33.065	33.327	33.306	33.398	33.529	
31	8.575	20.282	30.799	31.560	31.752	31.869	32.044	32.110	32.210	32.337	32.445
32	9.615	19.909	31.430	32.414	32.633	32.768	32.916	32.970	33.043	33.141	33.239

Table F.1 (cont'd).

mixture 50/50		time, days	0	15	22	28	38	43	51	64	80
pouch	cereals, g	p.choc, g	pouch, g	pouch, g	pouch, g	pouch, g	pouch, g	pouch, g	pouch, g	pouch, g	pouch, g
3	14.981	13.264	30.076	30.827							
4	13.679	13.336	29.013	29.803							
9	12.848	12.735	27.575	28.469	28.695	28.834					
10	14.630	13.238	29.842	30.806	31.065	31.229					
15	15.488	16.685	34.163	35.135	35.412	35.595	35.818	35.906			
16	15.272	14.223	31.467	32.402	32.664	32.833	33.054	33.137			
21	13.829	12.916	28.732	29.634	29.874	30.027	30.225	30.298	30.406		
22	13.475	13.065	28.502	29.440	29.679	29.825	30.009	30.080	30.180		
27	14.269	12.803	29.077	29.831	30.081	30.202	30.400	30.467	30.553	30.689	
28	12.341	12.363	26.656	27.486	27.699	27.836	28.016	28.083	28.182	28.321	
33	14.328	13.549	29.889	30.712	30.923	31.073	31.256	31.321	31.427	31.581	31.716
34	14.697	12.226	28.902	29.730	29.968	30.122	30.318	30.387	30.500	30.652	30.875

Table F.1 (cont'd)

mixture 67/33		time, days	0	15	22	28	38	43	51	64	80
pouch	cereals, g	p.choc, g	pouch, g	pouch, g	pouch, g	pouch, g	pouch, g	pouch, g	pouch, g	pouch, g	pouch, g
5	17.752	9.286	29.045	29.921							
6	19.685	9.742	31.381	32.267							
11	18.025	10.505	30.565	31.507	31.809	32.004					
12	19.837	13.973	35.803	36.816	37.136	37.343					
17	17.580	9.017	28.574	29.546	29.820	30.003	30.235	30.321			
18	19.037	10.326	31.366	32.425	32.731	32.926	33.180	33.268			
23	20.277	10.816	33.085	34.061	34.361	34.564	34.821	34.920	35.061		
24	19.481	10.264	31.630	32.605	32.905	33.108	33.358	33.452	33.592		
29	17.905	8.750	28.613	29.365	29.617	29.811	30.059	30.141	30.252	30.438	
30	19.114	9.687	30.722	31.667	31.964	32.153	32.399	32.487	32.632	32.818	
35	18.452	9.451	29.894	30.730	31.026	31.194	31.424	31.514	31.647	31.831	31.988
36	19.299	10.095	31.329	32.277	32.550	32.754	32.997	33.087	33.233	33.408	33.569

Table F.1 (cont'd)

mixture 100/0		time, days	0	15	22	28	38	43	51	64	80
pouch	cereals, g	p.choc, g	pouch, g	pouch, g	pouch, g	pouch, g	pouch, g	pouch, g	pouch, g	pouch, g	pouch, g
49	18.062		20.030	20.860	21.105	21.251	21.432	21.496	21.590	21.723	21.848
50	18.680		20.675	21.577	21.824	21.996	22.193	22.271	22.369	22.523	22.646
51	20.859		22.809	23.643	23.898	24.060	24.292	24.384	24.505	24.674	24.833
52	20.395		22.362	23.105	23.374	23.558	23.797	23.881	24.007	24.178	24.334
53	19.109		21.060	21.963	22.222	22.310	22.605	22.687	22.790	22.941	23.069
mixture 0/100											
54		15.344	17.331	17.699	17.771	17.818	17.886	17.916	17.937	17.981	17.999
55		21.021	22.947	23.358	23.452	23.514	23.602	23.635	23.674	23.734	23.781
56		18.363	20.300	20.636	20.721	20.776	20.849	20.879	20.919	20.980	21.026
57		25.672	27.649	28.114	28.222	28.295	28.400	28.438	28.486	28.566	28.621
58		21.836	23.804	24.250	24.345	24.416	24.505	24.538	24.581	24.645	24.686

Table F.2 - Initial weight of components and pouches weight (g) over time (days) for experiment 2

mixture 50/50		time, days	0	7	14	21	28	40	50
pouch	cereals, g	p.choc, g	pouch, g	pouch, g	pouch, g	pouch, g	pouch, g	pouch, g	pouch, g
1	15.867	15.465	35.950	36.676					
2	15.124	15.075	34.742	35.513					
3	14.408	14.942	33.715	34.451	34.870				
4	14.332	15.355	33.994	34.775	35.196				
5	14.214	14.279	32.793	33.520	33.923	34.156			
6	14.668	14.612	33.370	34.127	34.569	34.803			
7	14.468	13.207	31.902	32.660	33.066	33.283	33.546		
8	14.879	15.027	34.348	35.056	35.442	35.705	35.976		
9	13.357	13.741	31.410	32.092	32.512	32.737	32.976	33.123	
10	13.891	12.847	30.886	31.564	31.954	32.188	32.449	32.583	
11	13.553	14.793	32.505	33.243	33.653	33.890	34.147	34.297	34.425
12	14.387	14.919	33.590	34.308	34.706	34.943	35.197	35.351	35.486

Table F.2 (cont'd).

mixture 100/0		time, days	0	7	14	21	28	40	50
pouch	cereals, g	p.choc, g	pouch, g	pouch, g	pouch, g	pouch, g	pouch, g	pouch, g	pouch, g
13	29.933		33.955	34.817	35.415	35.774	36.191	36.468	36.675
14	30.059		34.127	35.055	35.417	36.022	36.435	36.705	36.862
15	29.953		34.068	34.872	35.420	35.806	36.216	36.481	36.692
mixture 0/100									
16		28.422	32.650	33.131	33.339	33.468	33.620	33.696	33.765
17		29.447	33.370	33.870	34.085	34.209	34.358	34.443	34.518
18		28.908	33.127	33.600	33.799	33.923	34.067	34.157	34.228