MICROWAVE ASSISTED OSMOTIC DEHYDRATION OF APPLE CYLINDERS UNDER CONTINUOUS MEDIUM FLOW CONDITIONS FOR IMPROVING MOISTURE TRANSFER RATE AND PRODUCT QUALITY

By

Heping Li

Department of Food Science and Agricultural Chemistry
Macdonald Campus, McGill University
Montreal, Canada

June 2005

A thesis submitted to McGill University in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Library and
Archives Canada

Published Heritage
Branch

395 Wellington Street
Ottawa ON K1A 0N4
Canada

Bibliothèque et
Archives Canada

Direction du
Patrimoine de l'édition

395, rue Wellington
Ottawa ON K1A 0N4
Canada

Your file Votre référence
ISBN: 978-0-494-21670-5
Our file Notre référence
ISBN: 978-0-494-21670-5

NOTICE:
The author has granted a non-exclusive license allowing Library and Archives Canada to reproduce, publish, archive, preserve, conserve, communicate to the public by telecommunication or on the Internet, loan, distribute and sell theses worldwide, for commercial or non-commercial purposes, in microform, paper, electronic and/or any other formats.

The author retains copyright ownership and moral rights in this thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without the author's permission.

AVIS:
L'auteur a accordé une licence non exclusive permettant à la Bibliothèque et Archives Canada de reproduire, publier, archiver, sauvegarder, conserver, transmettre au public par télécommunication ou par l'Internet, prêter, distribuer et vendre des thèses partout dans le monde, à des fins commerciales ou autres, sur support microforme, papier, électronique et/ou autres formats.

L'auteur conserve la propriété du droit d'auteur et des droits moraux qui protège cette thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

In compliance with the Canadian Privacy Act some supporting forms may have been removed from this thesis.

While these forms may be included in the document page count, their removal does not represent any loss of content from the thesis.

Conformément à la loi canadienne sur la protection de la vie privée, quelques formulaires secondaires ont été enlevés de cette thèse.

Bien que ces formulaires aient inclus dans la pagination, il n'y aura aucun contenu manquant.

Canada

Suggested short title:

MICROWAVE ASSISTED OSMOTIC DEHYDRATION OF APPLES

ACKNOWLEDGMENTS

I would like to express my sincere gratitude to Dr. Hosahalli Subrayasastry Ramaswamy, my thesis supervisor for his intellect, guidance, advice, encouragement, kindness, patience, and financial support throughout this research. I particularly appreciate his depth knowledge and respect his characteristics. I would also like to extend my appreciation to McGill University for providing me opportunity to pursue my study.

I would like to thank Dr. Byong Lee, Dr. Inteaz Alli (former Chairman of the department), Dr. Benjamin Simpson and Dr. Michael Ngadi for their suggestions to the research project. Sincere thanks to all professors and staff of the Department of Food Science and Agricultural Chemistry for their support during my study, especially to Dr. Frederick R. van de Voort, Dr. Varoujan Yaylayan, Dr. Ashraf Ismail, Dr. Selim Kermasha for their guidance and support in my course studies and seminars, to Dr. William Marshall (Chairman of the department) for his kindness and support, and to Ms. Lise Stiebel, Ms Barbara Laplaine, and Mr. Ebrahim Noroozi for their extensive help and friendship.

I want to express my gratefulness to all friends in the food processing group for their friendship and assistance: Dr. Cuiren Chen, Dr. Pramod Pandey, Dr. Farideh Nourian, Dr. Esmaeil Riahi, Dr. Ahmod Jasim, Dr. Songming Zhu, Mr. Yangwen Shao, , Mr. Baboucarr Jobe, Ms. Hong Jin, Ms. Neda Maftoonazad, Mr. Yang Meng, Mr. Manguang Lin, Mr. Minli Chi, Mr. Hiremath Nikhil, Ms. Anuradha Gundurao, Mr. Shafi Zaman, and Mr. Dwivedi Mritunjay. I also appreciate the help and kindness from many friends at Macdonald Campus: Dr. Robert Cocciardi, Mr. Luke Haffenden, Ms. Ellen Kivtz, Ms Nada Houjaji, Ms Saira Prasher and others.

The financial support for the project from the Strategic Grants Program of the Natural Sciences and Engineering Research Council of Canada (NSERC) is gratefully acknowledged.

A heartfelt gratefulness is extended to my beloved parents and parents in law for their love and constant encouragement. Your patience and sacrifices made all this becomes truth. Special thanks to my brother and sisters, Mr. Yaoping Li, Ms. Shunli Li and Xiaoli Li, while I am away for many years, for taking care of my old parents.

This thesis is dedicated to my wife and best friend Dr. Xiangyang Sun, for her understanding, encouragement and support, to my lovely daughter Lauren Li for her understanding and patience. I owe them too much to be a husband and a father.

ABSTRACT

Microwave assisted osmotic dehydration (MWOD) under continuous medium flow conditions is a new process with good potential for quality optimization. It combines microwave process with osmotic dehydration and improves the mass transfer rate of osmotic dehydration process and product quality. The thesis describes the design and development of this process.

Preliminary studies on osmotic dehydration were carried out in two parts. First, the effects of processing time, temperature and solution concentration on mass transfer under conventional osmotic dehydration process were investigated and suitable ranges of parameters: 40-60°C, 40-60°Brix and 3h, for further osmotic dehydration kinetics study were identified. Then, the osmotic dehydration efficiency under continuous flow condition process was evaluated. For this, a continuous flow osmotic contactor was developed and found to be an efficient process in terms of osmotic dehydration of apple cylinders. Solids diffusivity (D_s) was lower in continuous flow osmotic dehydration process compared with conventional osmotic dehydration correspondents ($P<0.05$). Being a separate operation unit, the dehydration process and solution management can be done in a more efficient way in this process.

Following the preliminary studies, the osmotic contactor was relocated under a microwave oven so that heating and mass transfer operations could be facilitated by continuous microwave treatment providing a microwave assisted osmotic dehydration (MWOD) process. Compared with conventional osmotic dehydration (COD), moisture loss (ML%), solids gain (SG%) and mass transport coefficients (k_m and k_s) of MWOD were improved, the average k_m was increased 80% and the average k_s was decreased 20%, respectively. Moreover, product rehydration property and color profile were improved. Microwave heating had an important effect on water transfer during the osmotic dehydration. Application of microwave heating to osmotic dehydration process facilitated in increasing moisture loss from the sample and simultaneously restricted the product's solute gain. Higher moisture loss in mass transfers area helped to control and strongly counters the solids gain.

Modeling of the mass transfer phenomenon is necessary to optimize osmotic dehydration processes to have a high product quality at minimum energy costs. To explain the simultaneous mass-flow in an osmo-dehydration process, evaluation of equilibrium kinetics is important. Pseudo-equilibrium (practical equilibrium) and dynamic period data are necessary for estimating the time of osmotic process, and ultimate mass transport of the solutes and water, and hence these data were gathered.

The effect of osmotic dehydration treatment on sample subsequent air drying behavior and product quality parameters were investigated. Compared with control samples, osmostically treated samples moisture diffusivity during subsequent air drying process was reduced over same moisture content range: from $1.18*10^{-9}m^2/s$ to $0.77*10^{-9}$–$1.07*10^{-9}\ m^2/s$. Drying rates of MWOD pretreated samples varied depending on treatment conditions. MWOD pretreatment shifted product's color profile to those that can be achieved under freeze drying conditions.

Sorption isotherms induced by osmotic dehydration were studied, using a gravimetric-static method, and fitted to GAB model. Adsorption isotherms of products were affected by drying method and osmotic dehydration pretreatment conditions. Adsorption isotherms of osmo-air dried apple cylinders followed type II isotherms (Sigma shaped curve). Monolayer (M_m) values of the osmo-air dried products were reduced. Sorption isotherms of osmotically treated-air dried products were shifted from the control isotherms.

Overall, this work has demonstrated potential of microwave heating for improving moisture transfer during osmotic dehydration and microwave osmotic treatment on subsequent air drying and resulting product quality, as well as the importance of equilibrium kinetics study in process modeling.

RÉSUMÉ

Le processus osmotique de la déshydratation aidé par micro-onde (MWOD) sous des conditions moyennes d'écoulement continu est un nouveau processus avec un bon potentiel pour optimisation de la qualité. Il combine le processus de micro-onde avec le processus osmotique de déshydratation et améliore le taux de transfert de masse du processus osmotique de déshydratation. La these suivante décrit le design et le développement de ce processus.

Des études préliminaires sur la déshydratation osmotique ont été effectuées en deux parties. En premier lieu, les effets de la durée de la transformation, de la température et de la concentration de solution sur le transfert de masse du processus osmotique conventionnel de déshydratation ont été étudiés et des gammes convenables des paramètres (40-60°C, 40-60°Brix et 3hrs) ont été choisies pour une étude plus avancée de la cinétique du processus osmotique de déshydratation. Ensuite, l'efficacité de la déshydratation osmotique d'un processus d'écoulement continu a été évaluée. Pour cela, un conjoncteur osmotique d'écoulement continu a été développé pour avoir un processus efficace de déshydratation osmotique pour des échantillons de cylindres de pomme. Le coefficient de diffusion de matières solides (D_s) du processus de déshydratation osmotique d'écoulement continu était inférieur comparé à sa valeur correspondante pendant le processus de déshydratation osmotique conventionnel ($P<0.05$). Étant une unité séparée d'opération, le processus de déshydratation et sa gestion peut être effectuée d'une manière plus efficace dans ce processus.

Par la suite des études préliminaires, le conjoncteur osmotique a été replacé sous le four à micro-ondes pour que les opérations de thermalisation et du transfert de la masse pourraient être facilitées par le traitement continu de micro-onde fournissant un processus osmotique de la déshydratation aidé par micro-onde (MWOD). Comparé à la déshydratation osmotique conventionnelle (MORUE), la perte d'humidité (ML%), l'augmentation de matières solides (SG%) et les coefficients de transport de masse (k_m and k_s) du MWOD ont été améliorés; le k_m moyen a augmenté de 80% et le k_s moyen a baissé de 20% respectivement. De plus, la propriété de réhydratation des produits et le profil de couleur ont été améliorés. Le chauffage par micro-ondes a eu un effet important

sur le transfert de l'eau pendant la déshydratation osmotique. L'application du chauffage par micro-ondes au processus osmotique de déshydratation a augmenté la perte d'humidité de l'échantillon et a limité la prise de solides par le produit. La perte d'humidité dans la zone de transfert de masse a aidé contrôler et fortement contrebalancer le gain de matières solides.

Modeler le phénomène de transfert de masse est nécessaire pour optimiser les processus osmotiques de déshydratation pour avoir un produit de qualité élevée à des coûts d'énergie bas. Pour expliquer l'écoulement de masses simultané dans un processus d'osmo-déshydratation, l'évaluation de l'équilibre de la cinétique est importante. Le pseudoéquilibre (équilibre pratique) et les données des périodes dynamiques sont nécessaires pour estimer la durée du processus osmotique et le transport de masse final des corps dissous et de l'eau et donc, c'est de cette manière que les données ont été recueillies.

L'effet de la déshydratation osmotique sur le comportement subséquent de l'échantillon quand séché à l'air et sur les paramètres de qualité du produit ont été étudiés. Comparé aux échantillons contrôles, la diffusivité d'humidité pendant le séchage subséquent à l'air des échantillons ayant subi l'osmose, a été réduite pour une même étendue de teneur d'humidité : de $1.18*10^{-9} m^2/s$ à $0.77*10^{-9}$–$1.07*10^{-9} m^2/s$. Les taux de séchage des échantillons préalablement traités au MWOD ont changé selon la variation des conditions du traitement. Le prétraitement MWOD d'un produit change son profil de couleur comparé à celui obtenu quand le produit est lyophilisé.

Des isothermes de sorption induites par la déshydratation osmotique ont été étudiées,en utilisant une méthode statique gravimétrique et adaptées au modèle GAB. Les isothermes d'adsorption des produits ont été affectées par la méthode de séchage et la variation des conditions de prétraitement de la déshydratation osmotique. L'isotherme d'adsorption des échantillons de cylindres de pommes séchés à l'air osmotique ont suivi le type II d'isothermes (courbe sigma). Les valeurs mono-couche (M_m) des produits séchés à l'air osmotique ont été réduites. Les isothermes de sorption des produits ayant subi un traitement osmotique-séchage à l'air ont décalé des isothermes contrôles.

De façon générale, ce travail a démontré le potentiel de chauffage par micro-ondes pour améliorer le transfert d'humidité pendant la déshydratation osmotique et pendant le traitement osmotique par micro-ondes et leurs influences sur le séchage à l'air subséquent et sur la qualité du produit résultante ainsi que sur l'importance de l'étude d'équilibre de cinétique dans le processus de modelage.

CONTRIBUTIONS TO KNOWLEDGE

The major contributions of this research were enriching scientific knowledge on osmotic dehydration research and its application, and the development of microwave assisted osmotic dehydration (MWOD) technique. The specific contributions include the following aspects:

- Using classical diffusion model, finite apple cylinders mass transfer coefficients were calculated and good results were obtained on the mass transfer during osmotic dehydration process. Although the researches on mass diffusion of several other shapes have been well documented, little information has been reported for finite cylinders geometry.
- MWOD is a new concept in osmotic dehydration (OD) and is first developed in this study. It combines microwave process with OD and improves the moisture transfer rate of osmotic dehydration process. Compared with conventional osmotic dehydration process, the moisture loss (*ML%*) of MWOD treated sample was increased, whereas the solid gain (*SG%*) of the sample was reduced. Moreover, the rehydration property and color of the sample were highly improved. The technique provides a new way to study osmotic dehydration principle of food materials in liquid environment. In terms of practical applications, it reduces the osmotic dehydration time, improves the product quality characteristics. This finding is new in literature.
- The combined MWOD-air dried products total color difference (ΔE) was closer to or better than that of freeze dried product. MWOD treatment reduced product color damages during subsequent air-drying process compared with sample only air-dried without MWOD pretreatment. This finding is new in literature.
- Equilibrium osmotic dehydration kinetics study was highlighted. To explain the simultaneous mass-flow in an osmo-dehydration process, evaluation of equilibrium kinetics is important. The osmotic dehydration process was first characterized by equilibrium, pseudo-equilibrium and dynamic periods in this study. Pseudo-equilibrium (practical equilibrium) kinetics study was suggested

instead of theoretical equilibrium kinetics study. It is different from those equilibrium kinetics reported in literature.

- The effect of osmotic dehydration treatment on subsequent air drying behavior was investigated. Compared with control samples, osmotically treated samples had lower moisture diffusivity during subsequent air drying process. Drying rates of MWOD pretreated samples varied depending on pretreated conditions variation. The results obtained were different from those from theoretical calculation method reported in literature.
- Adsorption isotherms of product were affected by drying method and osmotic dehydration pretreatment conditions. Adsorption isotherm of osmo-air dried apple cylinders followed type II isotherms (Sigma shaped curve). Monolayer moisture content (M_m) of the osmo-air dried product was reduced. Sorption isotherms of osmotic dehydrated-air dried product were shifted from control isotherms. This is important for practical applications, but available information in this aspect is rather limited.

LIST OF PUBLICATIONS AND PRESENTATIONS

Part of this thesis has been or will be published in refereed scientific publications:

Li, H.& Ramaswamy, H.S. 2005a. Osmotic dehydration of apple cylinders: I. Conventional batch processing conditions. Drying Technology Journal. (submitted).

Li, H.& Ramaswamy, H.S. 2005b. Osmotic dehydration of apple cylinders: II. Continuous medium flow conditions. Drying Technology Journal. (submitted).

Li, H.& Ramaswamy, H.S. 2005c. Osmotic dehydration of apple cylinders: III. Continuous medium flow Microwave heating conditions. Drying Technology Journal (submitted).

Li, H.& Ramaswamy, H.S. 2005. Mass transfer equilibrium consideration in osmotic dehydration. Journal of Food Engineering (submitted).

Li, H.& Ramaswamy, H.S. 2005.Osmotic dehydration treated apple cylinders convective air drying: drying rate and quality characteristics. Journal of Food Science (in preparation).

Li, H.& Ramaswamy, H.S. 2005. Sorption isotherm changes induced by osmotic dehydration of apple cylinders in different conditions. Lebensmitted-Wissenschaft und Technologie (Food Science and Technology) (in preparation).

Li, H.& Ramaswamy, H.S. 2005. Microwave Drying in Food Dehydration Handbook, ed. Farid, M. Dekker (In press)

Li, H.& Ramaswamy, H.S. 2004. Continuous flow osmotic dehydration of apples in a microwave environment. International Workshop and Symposium on Industrial Drying: Symposium. P: 119-133.

Li, H.& Ramaswamy, H.S. 2004. Equilibrium consideration in osmotic dehydration. International Workshop and Symposium on Industrial Drying: Workshop. P: 90-103.

Part of this thesis has been presented or will be presented in scientific conferences:

Li, H. & Ramaswamy, H.S. 2002. Osmotic drying kinetics of apple slices under continuous flow conditions. NABEC meeting, Quebec city, Quebec, Canada, July 16-19, 2002.

Li, H. & Ramaswamy, H.S. 2003. Equilibrium considerations in osmotic drying models. CSAE/SCGR Annual Meeting, Montreal, QC, Canada, July 6-9, 2003.

Li, H. & Ramaswamy, H.S. 2003. Continuous flow microwave osmotic combination drying of apple slices. IFT Annual Conference, Chicago, Illinois, USA, July 12-16, 2003.

Li, H. & Ramaswamy, H.S. 2003. Osmotic dehydration kinetics of apple cylinders under continuous flow conventional and microwave heating condition. AIChe Annual Meeting. San Francisco, CA. USA. 2003. Nov.16-21.

Li, H., Kivtz, E. & Ramaswamy, H.S. 2004. Solid-liquid consideration in osmotic drying. IFT Annual Conference, Las Vegas, NA, USA, July 12-16, 2004.

Li, H. Gundurao, A. & Ramaswamy, H.S. 2004. Evaluation of microwave assisted osmotic dehydration effects on apply cylinders color changes during conventional air drying. ASAE/CSAE Annual International Meeting, Ottawa, ON, Canada, August 1-4, 2004.

Li, H. & Ramaswamy, H.S. 2005. Sorption changes induced by osmotic dehydration of apple cylinders in different conditions. IFT Annual Conference, New Orleans, LA. USA, July 17-19, 2005

Li, H. & Ramaswamy, H.S. 2005. Solid penetration trend investigation during osmotic equilibration. Journée scientifique et technique en GÉNIE AGROALIMENTAIRE. Mar. 25. 2005 Saint Hatythine, Quebec, Canada

Li, H. & Ramaswamy, H.S. 2005. Study of deviation from diffusion controlled solid penetration in osmotic drying of apple slices. IADC-2005. Aug. 20. Montreal. Canada

CONTRIBUTIONS OF AUTHORS

The research has resulted in several publications and presentations. Two authors have been involved in the thesis and their contributions to the various articles are as follows:

Heping Li is the Ph.D. candidate who planed and conducted all experiments, in consultation with his supervisor, gathered and analyzed the results, and drafted all manuscripts for scientific publication.

Dr. H.S. Ramaswamy is the thesis supervisor, under whose guidance the research was carried out, and who assisted the candidate in planning and conducting the research as well as in correcting, editing and reviewing the manuscripts.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Page

NOMENCLATURE

Chapter 3

b_o b_i b_{ii} b_{ij}	represent constant coefficients in model
Bi	Biot number, is formulated for mass transfer as: $Bi = kr/D\rho_s$
C	Mass concentration
d	Significant dimension, such as the radius of a cylinder or sphere, or thickness of slab
D	Diffusion coefficient (m^2/s)
D_w D_s	Diffusion coefficients of water and soluble solids, respectively (m^2/s).
Fo	Fourier No.= Dt/a^2
J_0, J_1	Bessel function of order zero and one, respectively
k	Convective mass transfer coefficient (m^2/s kg)
l	Half thickness of a plate (m)
M	Dimensionless mass ratios under transient conditions
M_{mfc}	Unsteady mass concentration in a finite cylinder at final (dimensionless)
M_{mc} M_{mp}	Mass average concentration ratios for an infinite cylinder and slab, respectively (dimensionless)
M_{mfcw} M_{mfcs}	Moisture loss ratio and solids gain ratio at final, respectively (dimensionless)
M_o M_t M_e	Sample mass at initial time, time t and equilibrium, respectively (kg)
MLR_i	Moisture loss rate between time t_i and t_{i-1}, h^{-1}
SGR_i	Solids gain rate between time t_i and t_{i-1}, h^{-1}
ML_i ML_{i-1}	The fraction moisture loss at time t_i and time t_{i-1}, respectively
ML_o ML_t ML_∞	The fraction moisture loss at at initial time, time t and equilibrium, respectively
r	radius of the cylinder (m)
SG_i	The fraction solids gain at time t_i
SG_i	The fraction solids gain at time $t_{i-1}{}^1$
T_m	Time to get the sample moisture loss to a 25%, h

T_s	Time to get the sample solids gain to a 5%, h
T_w	Time to get the sample weight reduction to a 20%, h
R_c R_p	characteristic functions of Biot number for infinite cylinder and slab, respectively
S_c S_p	characteristic functions of Biot number for infinite cylinder and slab, respectively
SG_o SG_t SG_∞	The fraction of solids gain at initial time, time t and equilibrium, respectively
s_o s_t s_e	Sample solids fraction at initial time, time t and equilibrium, respectively (kg/kg wet base)
t	Contact time (s)
V	Volume (m^3)
x	Distance from the plane of the slab with the highest concentration water and the lowest concentration sugar (m)
x_o x_t x_e	Sample moisture fraction at initial time, time t and equilibrium, respectively (kg/kg wet base)
x_i x_j	represent independent variables in model
y	response in model

Abbreviations

MLR	Moisture loss rate
ML	Moisture loss
SGR	Solid gain rate
SG	Solid gain
WR	Weight reduction

Greek symbols

β_n	The nth positive root of characteristic equation $\beta t \tan \beta = Bi$
γ_n	The nth positive root of characteristic equation $\gamma J_1(\gamma) = BiJ_o(\gamma)$
ρ_s	density of bone dry apple (kg/m^3)

Chapter 4

D_c	Diameter of container (m)

Greek symbols

υ	average velocity of solution (m/s)
ρ	density of the solution (kg/m^3)
μ	viscosity of the solution (mPa/s)

Chapter 5

k_m k_s	moisture transport coefficient and soluble solids transport coefficient, respectively (dimensionless)
A	parameter coefficient (dimensionless)
B	parameter coefficient (dimensionless)
C	solution concentration (°Brix)
T	solution temperature (°C)
x_m x_s	parameter related to temperature estimated by experimental data for moisture and solid respectively (dimensionless)
y_m y_s	parameter related to solution concentration estimated by experimental data for moisture and solid respectively (dimensionless)

Abbreviations

COD	Conventional osmotic dehydration
CFOD	continuous flow osmotic dehydration
MWOD	Microwave assisted osmotic dehydration

Chapter 6

K	function of time and rate of moisture loss or solids gain (dimensionless)
MS	fraction of water that can diffuse out, but remains in the food at time *t* (dimensionless)
M_d	after certain osmotic dehydration treatment, the solid mass of the sample
N	number of experimental data points
s s_1 s_2	constants related to the rate of moisture loss, weight reduction and soluble solids gain, respectively (dimensionless)
V_e V_c	value got by experimental result and model predicted result, respectively

Abbreviations

RMS	root mean square
MC	moisture content (wb)
SC	solids content (wb)

Chapter 7

L L_o	lightness of sample and standard, respectively (dimensionless)
a a_o	chromaticity coordinates (red to green) of sample and standard, respectively
b b_o	chromaticity coordinates (yellow to blue) of sample and standard, respectively
D	diffusion coefficient (m^2/s)
ΔE	total color difference
m_o m_t m_e	moisture content of the sample at initial time, time t and equilibrium, respectively (kg/kg, DB)

Chapter 8

m	the equilibrium moisture content in kg water/kg dry solids
M_m	the monolayer moisture content (in kg water/kg dry solids)
c	the Guggenheim constant related to heat of sorption for the first layer (dimensionless)
g	constant related to the heat of sorption for multilayer water (dimensionless)
a_w	water activity
Q	regression constant
P_m	mean relative modulus

CHAPTER 1

INTRODUCTION

Being a partial dehydration or concentration step with low energy consumption, osmotic dehydration (OD) is used as a pretreatment proceeding other drying processes or freezing for improving fruit products quality. The driving force comes from chemical potential difference between the interface of the sample and the solution. Depending on process conditions, water loss of the sample can extend to 70% of its initial weight, but usually goes up to 30-50% of its initial weight for practical application, and solids gain can reach 5-25% of its initial weight. The process could be described by at least two simultaneous mass transfer phenomena: water moves from the biological tissue to the solution, and solutes migrate into the sample tissue. The selective permeability of water is probably due to the semi-permeable characteristics of biological materials and water physicochemical property specialty.

OD techniques have been widely used in fruit preservation as they present many advantages over the traditional drying. Fruits are not submitted to high temperatures, minimizing sensory attribute changes, such as color, aroma, flavor and texture, and preserving nutritional values of the fresh fruit: vitamins, minerals, etc. (Fito et al., 1995; García-Martínez et al., 2002). On the other hand, food structure is not so much affected because water elimination dose not involve phase change that is usually present in the process of drying and freezing (Pinnavaia et al., 1988; Giangiacomo et al., 1994).

Over the last few decades, factors that influence the osmotic dehydration process have been studied extensively. Apart from the influence of solid structure, mass transfer depends on operating variables, such as osmotic temperature, time duration, solute concentration and composition of the solution (i.e. solute molecular weight and nature, presence of ions), pressure, and the product: solution ratio (Raoult-Wack et al.,1994). Overall, studies on osmotic dehydration have mainly focused on the effect of operating variables on osmotic dehydration or modeling of water loss and solid gain, and less on osmotic solution management and osmotic dehydration effects on subsequent processing and product quality.

Since the rate of mass transfer during osmotic dehydration is relatively slow, a number of techniques have been tried to improve mass transfer rate. These techniques include: the application of a partial vacuum (Fito 1994; Shi et al., 1995; Rastogi & Raghavarao, 1996), freeze/thaw effects (Lazarides and Mavroudis, 1995), ultra high hydrostatic pressure (Rastogi & Niranjan, 1998; Rastogi et al., 2000), high intensity electrical field pulses (Rastogi et al., 1999; Taiwo et al., 2003; Ade-Omowaye et al., 2003), supercritical carbon dioxide (Tedjo et al., 2002) to the material prior to osmotic dehydration treatment; using centrifugal force (Azuara et al., 1996), ultrasound (Simal et al., 1998) and microwave (Li and Ramaswamy, 2003) during the osmotic dehydration process. According to the improvement mechanism, these processes may fall into following categories:

- Increased the permeability of cell structure: application of high hydrostatic pressure, pulsed electrical field (PEF), supercritical carbon dioxide (CO_2) treatments and freeze/thaw effects. All these effects may increase the permeability of plant cells. However, with the permeability increasing, solids gain increases as well (Lazarides and Mavroudis, 1995; Tedjo et al., 2002).
- Improved sample cell internal pressure: application of ultrasound and microwave heating during osmotic dehydration process. Simal et al. (1998) reported that application of sonication to osmotic dehydration of porous fruit increased mass transfer rates in comparison with the osmotic process carried out under dynamic conditions. Our study (2003) reported microwave assisted osmotic dehydration (MWOD) increased moisture loss while reduced sample solids gain in comparison with without using microwave heating during osmotic dehydration process.
- Increased solution and sample contact surface: vacuum treatment related osmotic dehydration. Fito (1994) reported that vacuum treatment increased the osmotic mass transfer and explained this on the basis of pressure gradient and capillary flow. The reduction in external pressure causes the expansion and escape of sample internal gas. When the pressure is restored, the pores can be occupied by osmotic solution, thus increasing the available mass transfer surface area.

- Other process: using centrifugal force during osmotic dehydration process. Azuara et al. (1996) reported that centrifugation enhanced water loss by 15% while considerably retarding the solid uptake (by about 80%).

Microwave assisted osmotic dehydration (MWOD) is osmotic dehydration process under microwave field to fulfill osmotic dehydration process. Microwave drying employs a completely different mechanism for heating. Because of the internal heat generated by microwave field, there is an internal pressure gradient, which may effectively push the water to the surface. The synergistic effect of increased internal pressure and external osmotic stress may enhance the mass transfer of osmotic dehydration process.

The main objectives of this research were to study osmotic dehydration applied under microwave heating to increase moisture transfer of osmotic dehydration and to investigate the effect of microwave assisted osmotic dehydration process on subsequent drying process and related product quality. The specific objectives were:

1. To study the effect of temperature and concentration on osmotic dehydration kinetics in the conventional batch mode and to study osmotic dehydration kinetics of apple cylinders under continuous flow conditions;
2. To develop microwave assisted osmotic dehydration process;
3. To study osmotic dehydration equilibrium kinetics;
4. To investigate MWOD treatment effects on sample convective air drying behavior;
5. To investigate MWOD treatment effects on product quality parameter influences.

Based on above research objectives, studies were carried out as indicated in the following flowchart (Figure 1.1).

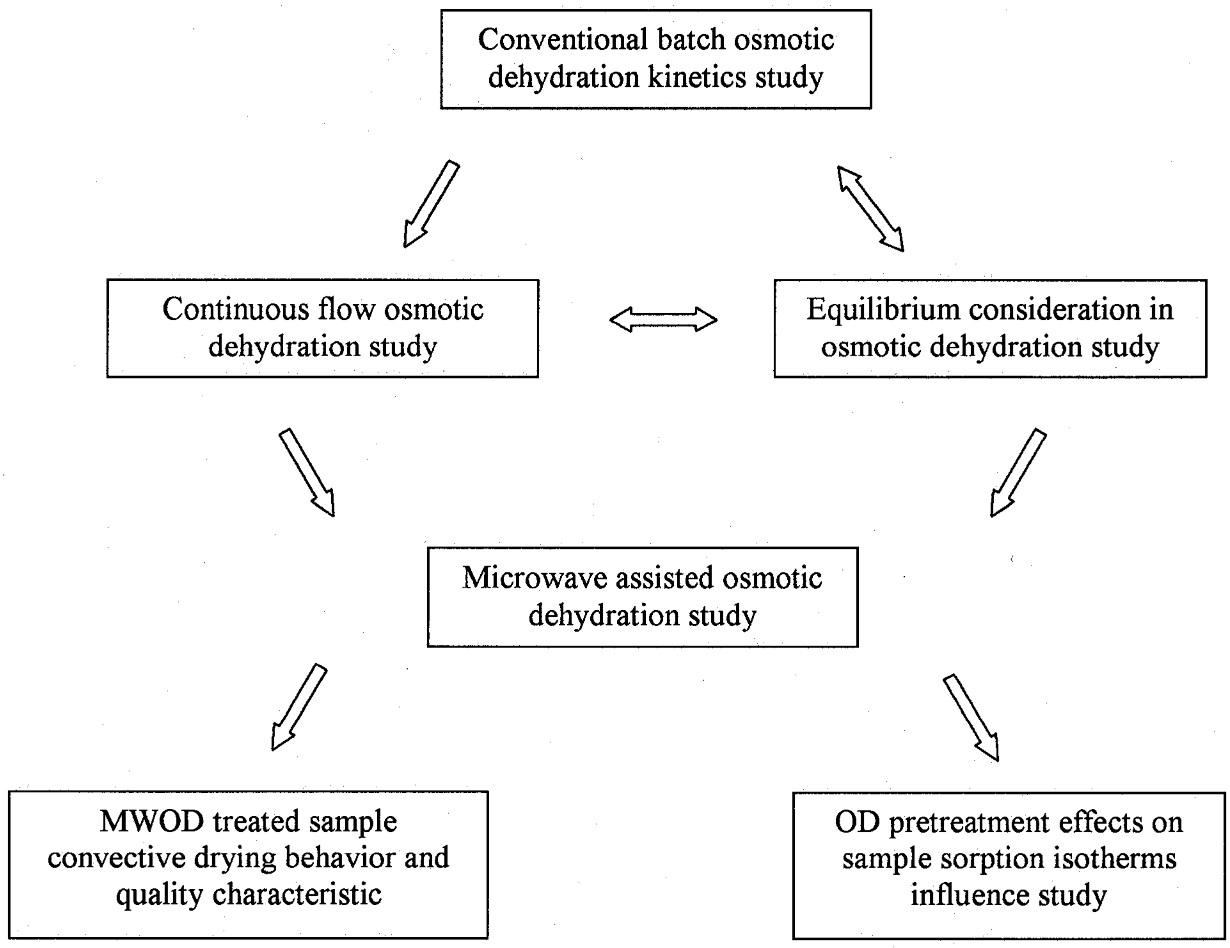


Figure 1.1 Flowchart of this research work

CHAPTER 2

LITERATURE REVIEW

The use of microwave to improve mass transfer rate during osmotic dehydration process is a totally new research field. The aim of this review chapter is to address the available scientific information in literature related to this thesis research, mainly osmotic dehydration, air drying and microwave drying and applications.

2.1 Osmotic dehydration

2.1.1 Introduction

Osmotic dehydration (OD) can be described as a partial dehydration of fruits and other materials through the process of osmosis, which involves immersing samples for a given period time in a solution-often sugar solution with a water activity (a_w) lower than that of the foodstuff. It gives rise to two major simultaneous counter-current flows: an important water flow into the solution and solute into the food, which are both due to the water and solute activity gradients across the interface of the sample and the solution. Leaching of natural solutes within the tissue also occurs but is probably quantitatively negligible. The process of OD, sometimes is also called dewatering-impregnation soaking (Raoult-Wack, 1994), involves removing up to 50% of the initial weight of moisture in the food (Ponting et al., 1966), with minimal solute uptake from the solution (5-25% per 100 g of fresh sample). Compared with conventional drying methods, two major characteristics of OD process make them different. First, the soaking process achieves a twofold transformation of the product by effecting both a dewatering and a formulation effect. Second, the soaking process does not generally produce a stable product; further steps such as: drying, freezing, pasteurization, canning, frying and/or the addition of preservative agents are needed (Raoult-Wack, 1994).

The demand for healthy, natural and tasty processed fruits continuously increases, not only for finished products, but also for ingredients to be included in complex foods such as ice cream, cereals, dairy, confectionary and bakery products. Over the last few decades, wide prospects for OD have arisen as a pre-treatment in combined techniques. These processes use a sequence of technological steps to achieve controlled changes of the original properties of the raw material (Torreggiani et al., 1993). While some treatments such as freezing have primarily stabilizing effects, other steps such as partial dehydration, particularly OD allows structural, nutritional, sensory and other functional properties of the raw material to be modified. Osmotic dehydration has been successfully used in conjunction with air drying (Ponting et al., 1966; Islam & Flink, 1982; Lerici et al., 1985); dehydrofreezing (Biswal et al., 1991; Torreggiani et al., 1993), vacuum drying (Ponting, 1973), fluidized bed drying (Kim & Toledo, 1987), convective air drying (Grabowski et al., 1994) and microwave convective drying (Torringa et al., 2001) on a laboratory and pilot scale. The applications of osmotic dehydration are shown in Figure 2.1 (Torreggaini, 1993).

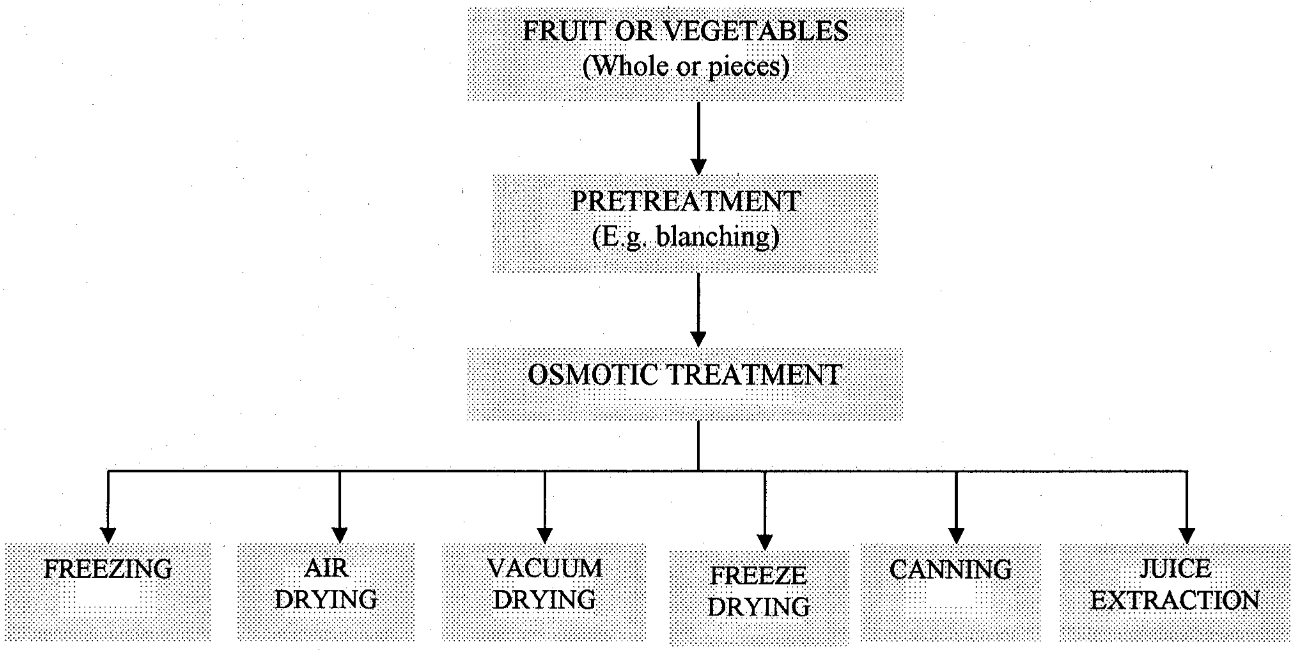


Figure 2.1 Applications of osmotic dehydration in fruit and vegetable processing (Torreggiani, 1993)

2.1.2 Principle of osmotic dehydration

Osmosis is the movement of water across a differentially permeable membrane from a solution at a high water potential to one at a low water potential. This process occurs when a plant tissue or cell is immersed in a hypertonic solution (a solution with a higher osmotic pressure than that of the plant tissues), e.g. sucrose, glycerol, salt and mixed osmotic agent solutions. Food preservation by osmotic dehydration is therefore based on the simultaneous counter-current diffusion of water from the plant materials into the solution outside the sample and solute absorbed into the sample from the solution (Figure 2.2). Small quantities of solute in the cells (e.g. organic acids, minerals, salts, sugars etc.) also leach into the solution. The resulting osmotic dehydrated product has a lower water activity and a higher solute content than the fresh product.

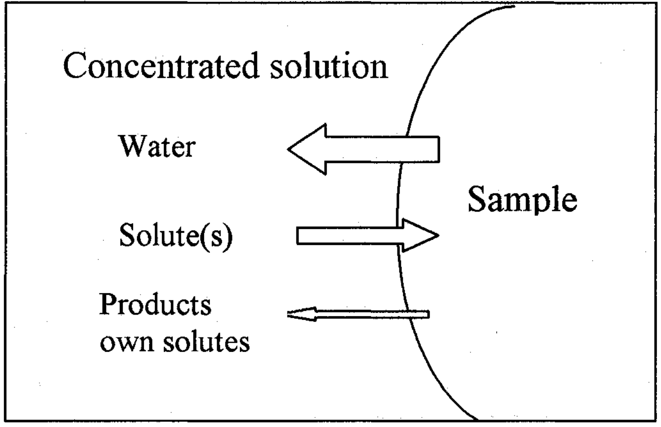


Fig. 2.2 Mass transfer in osmotic dehydration process

2.1.2.1 Plant cell

Cell is the smallest biological unit having those attributes characteristic of living matter. It includes a unique chemical composition, metabolism, growth, reproduction and organization. A plant cell can be simply pictured as a unit consisting of two main components: cell wall and the protoplast (Figure 2.3). Cellulose is the main component of the cell wall. Its content is between 62-90% and depends strongly on the stage of maturity. Other components include pectins, hemicellulose, polymeric substances and mineral compounds. The cell wall is perforated and the channels are filled with thin strands of protoplasm, assuring the contact between protoplasts of neighboring cells. These strands of protoplasm are called plasmodesmata. The diameter of the strands is 20-

70 nm and the average contact area can be estimated as 0.2 m^2/m^2 of the cell wall (Nobel, 1970). The protoplast is composed of protoplasm enclosed in a membrane called plasmalemma, vacuoles, and other structural elements such as the nucleus, plastids, and so on. The plasmalemma is a protein-lipid layer that regulates the contact between the protoplast and the environment. It is 7.5-10 nm thick (Nobel, 1970), permeable to water, and selectively permeable to other substances. Protoplasm is a colloidal solution of proteins and lipoproteins in water. The vacuole is suspended in protoplasm and is enclosed in a membrane called the tonoplast. It contains a solution of minerals, sugars, and other organic compounds in water.

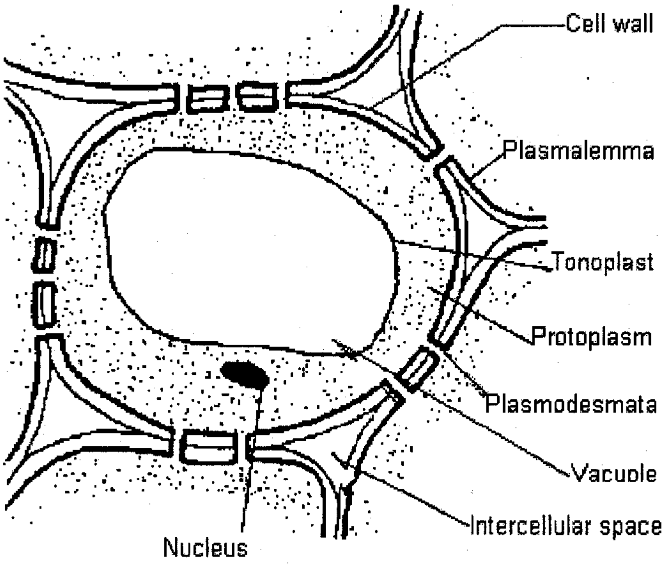


Figure 2.3 A plant cell (simplified)

Most cells have dimensions between 10 and 100 μm. Depending on their function they are loosely or closely packed in a tissue. Usually, parenchyma cells are loosely arranged in the tissue and intercellular spaces are formed. It is estimated that the volume occupied by cell walls and intercellular spaces accounts for 7-10% of the tissue volume (Nobel, 1970). Intercellular spaces form a continuous system of channels that is filled with air.

2.1.2.2 Osmotic potential and water activity

The driving force for the spontaneous diffusion of uncharged molecules into or out of plant cells is the concentration gradient across the plasmalemma (Nobel, 1970). From a thermodynamic viewpoint, the driving force propelling transport of water from one point to another in plant tissue is the difference in chemical potential of water in the two regions. The influence of the amount of a particular species "j" on its chemical potential is dependent on the activity of that species, "a_j." The activity of that species is then related to its concentration, "c_j", by its activity coefficient, "y_j":

$$a_j = y_j c_j \tag{2.1}$$

The activity coefficient is a correction factor, which quantifies deviations from ideal behavior since the thermodynamic activity of a species is less than its concentration.

The presence of solutes in an aqueous solution tends to decrease the activity of water (a_w) and increase its chemical potential. It also leads to an osmotic pressure, π, in the solution. The osmotic pressure and water activity are related as follows:

$$\pi = -\frac{RT}{V_w}\ln(a_w) \tag{2.2}$$

where: R = universal gas constant; T = absolute temperature, K; V_w = molar volume and a_w = water activity. For dilute solutions:

$$Ln(a_w) \cong -\frac{\sum_j n_j}{n_w} \tag{2.3}$$

where: n_j is the number of moles of solute j and n_w is the number of moles of water in the system.

Upon substituting equation (2.3) into (2.2), a relationship between the concentration of species j (c_j) and osmotic potential or pressure is obtained.

$$\pi = RT\sum_j \frac{n_j}{V_w n_w} = RT\sum_j c_j \tag{2.4}$$

where: $V_w n_w$ is the total amount of water in the system, $n_j/V_w n_w$ is the concentration of species j and the summations are over all solutes.

2.1.2.3 Transport of water in a plant tissue

Osmotic dehydration occurs on a piece of material and not only on a single cell. Hence, it should be assumed that the piece contains in all kinds of plant tissues. As a rule a skin removed from the raw material; therefore, epidermal cells and cuticle are absent in most cases. A piece of fruit or vegetable thus will contain parenchymatous and vascular tissue and intercellular spaces, as well.

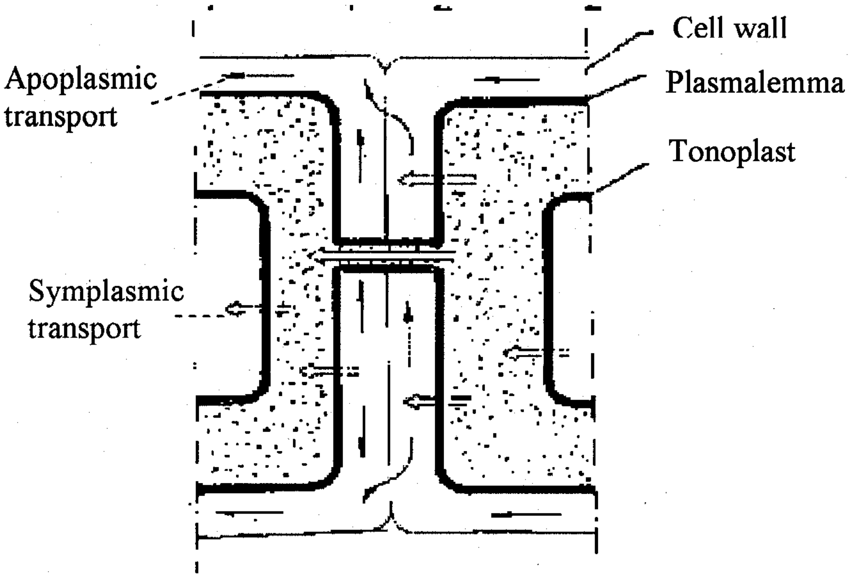


Figure 2.4 Apoplasmic and symplasmic transport of water

All vascular plants contain two potential avenues for transport of substances: symplamic and apoplasmic. Since cell walls are interconnected in the tissue, a continuous matrix capable of transporting water and small molecules is formed. This continuum is called the *apoplast*. Plasmalemma is the next barrier to the mass transfer in the tissue. In a majority of cells, protoplasm of neighboring cells is interconnected through plasmodesmata and another continuous network is formed. The system of protoplasts and connecting plasmodesmata is widely known as *symplast*. Since plasmodesmata permit the passage of solutes, they undoubtedly permit the passage of water also. Classic theory of water transport in plants assumed the movement of water from the vacuole of one cell to the vacuole of the neighboring cell; the driving force was the difference in water chemical potential. Two ways water is transported in a plant have been recognized: *apoplasmic* and *sympalsic* (Figure 2.4)

The apoplast is exterior to the cell membrane and can be visualized as a diffusion of molecules in the cell wall and the intercellular spaces between cells. The symplast is interior to the plasmalemma and is characterized by a movement of molecules from one cell to another through small channels. Finally, the transmembrane transport is an exchange between the protoplast and the free space, which comprises the intercellular space and the cell wall. It is obvious that the rate of swelling or shrinking of a plant tissue immersed in an osmotic solution will depend on extracellular solute diffusion in, intracellular water diffusion out and cell membrane permeation if we consider that there is no particular relation between cells. The behavior of the whole tissue is then the same as the behavior of a single cell. However, an alternative process is also possible when taking into account the relation between cells. A change in the concentration of the osmoticum is sensed by the first cell and induces a flow of solvent from cell to cell through the symplast. Whether the apoplastic or the symplastic pathway is more predominant in plant tissue varies for different plant tissues.

2.1.2.4 Plasmolysis

A solution in a vacuole has an osmotic pressure that pushes protoplasm and plasmalemma toward the cell wall. The protoplast is tightly pressed to the cell wall and the cell is in a turgor state. The difference between the osmotic pressure in the cell and in its surroundings is called turgor pressure. If the cell and the surroundings have the same osmotic pressure then turgor pressure is zero and the system is in thermodynamic equilibrium. Osmotic pressure of the surroundings lower than that of the cell causes

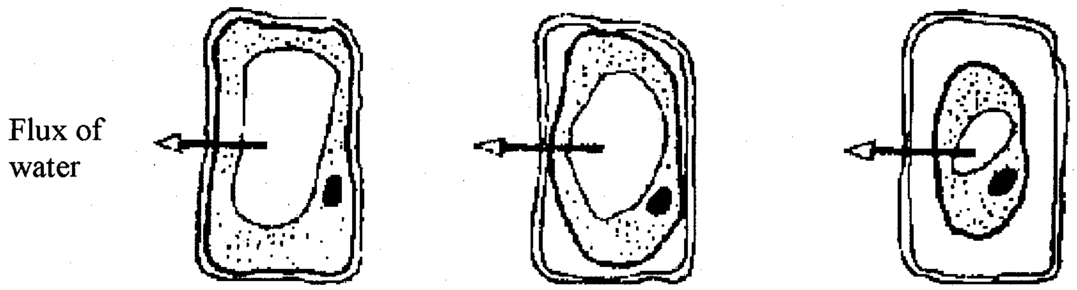


Figure 2.5 Plasmolysis

transfer of external water into the cell. The cell swells, but the rigid cell wall limits the extent of swelling. A cell placed in a hypertonic solution (osmotic pressure higher than that of the cell) will lose water. The dehydration of a protoplast causes decrease of its volume and in consequence, detachment of plasmalemma from the cell wall. This process is called plasmolysis (Fig 2.5). The extent at which the cells will plasmolysis is a function of the concentration of the osmotic solution. If the plasmolyzed cell remains in certain plasmolyzing solution, it may recover from plasmolysis. The recovery will depend on the ability of the dissolved solute in the external plasmolyzing solution to penetrate through the protoplasmic layer and into the vacuole, the more rapidly the solute permeates into the vacuole, the more rapidly will deplasmolysis take place, i.e. plasmolysis with an ethanol solution (Le Maguer, 1988). Plasmolysis is a phenomenon occurring in all plant cells.

Combining all these mechanisms, water diffusing out and solute moving into the tissue during osmotic dehydration process.

2.1.3 Osmotic dehydration study

2.1.3.1 Factors influencing osmotic dehydration

Over the last few decades, the factors that influence the osmotic dehydration process have been studied extensively. Apart from the influence of solid structure, mass transfer depends on operating variables: such as osmotic temperature, time duration, solute concentration, composition of the solution (i.e. solute molecular weight and nature, presence of ions), pressure, and the product: solution ratio. (Raoult-Wack et al.,1994). The factors influencing osmotic dehydration are briefly reviewed below:

2.1.3.1.1 Temperature

Osmotic diffusion is a temperature-dependent phenomenon. Higher process temperatures generally promote faster water loss through swelling and plasticizing of cell membranes, faster water diffusion within the product and better mass (water) transfer characteristics on the surface due to lower viscosity of the osmotic medium (Lazarides et al., 1995). Conway et al. (1983) reported that for every 10°C increase in temperature, there was a corresponding 5% increase in the percentage final moisture loss from the produce. Yang and Le Maguer (1992) compared the dehydration kinetics of strawberries in sucrose solution at 25°C and 50°C. The authors noted that higher temperatures during dehydration resulted in a significant weight loss and sugar gain. Acceleration of water loss without modification of sugar gain when temperature is increased, has also been observed by many authors (Ponting, 1966; Islam & Flink, 1982). However there is a temperature limit, perhaps 60°C, above which the cell membrane of the plant tissue is damaged (Marcotte, 1988). Ponting et al. (1966) and Videv et al. (1990) noted that temperatures above 50°C caused internal browning and loss of fruity flavor in apple slices. Bakalis et al. (1994) observed that temperature had a positive effect on moisture diffusivity in apples within a range of 24°C to 38°C. Nieuwenhuijzen et al. (2001) reported different sizes apple slices moisture loss and solids gain generally increased with increasing temperature of osmotic solution. The best processing temperature depends on the food, for example for green beans (Biswal et al., 1991), 40°C is too high, and a temperature 20°C gives better results.

2.1.3.1.2 Time

The rate of moisture loss and solid gain is highest within the first hour of osmosis followed by drastically lower rates for the rest of the time. On average, moisture loss rates drops to ca 20% of the initial rate during the first hour of dehydration and kept decreasing at a much slower rate to nearly level off at ca 10% of the initial rate within 3 h. Solid gain rates show a similar decrease trend. The rate of solid gain drops to ca 25% of the initial rate within the first hour and leveled off at ca 15% of the initial rate within 3 h of dehydration (Farkas et al.,1969; Raout-Wack et al., 1992; Lazarides et al., 1995a and Kowalska et al., 2001).

Rapid loss of water in the beginning is due to the large osmotic driving force between the dilute sap of the fresh fruit and the surrounding hypertonic solution. On the other hand, rapid drop of the water loss rate within the first hour seems to result from a serious disturbance of the initial osmotic concentration difference due to superficial sugar uptake. Hawkes and Flink (1978) also observed that solute uptake behavior occurred very early in the dehydration process and increased very slowly as dehydration progressed. Lerici et al. (1985), in their study on osmotic dehydration of apples, noted that in the first 2h of the process, water diffused out of the apples with little or no loss of the soluble solid constituents. Lerici et al. (1985) further noted that the most important mass transfer of water and solids occurred in the first hour of the osmotic dehydration process.

Afterwards the fruit solution system tended to equilibrium. Torreggiani et al. (1988) studied the effect of different contact times on the water loss and solids gain kinetics of cherries in sugar solution. The authors noted that there were no significant differences in the chemical and sensory characteristics of cherries subjected to contact times of 2 to 6h. They further observed that fruit dehydration and sugars exchange with the osmotic solution occurred during the first 2h of the process.

2.1.3.1.3 Osmotic solution to fruit ratio

The ratio of osmotic solution to fruit expresses the mass of solution required per unit mass of treated food. On an industrial scale, the ratio must be as low as possible to restrict plant size and the costs of solution regeneration. However, the use of a low ratio leads to significant changes in the solution composition. Most laboratory and pilot plant studies are carried out using a large excess of solution so as to ensure negligible variation in the solution composition, which makes the interpretation and modeling easier. The weight ratio of solution to product is generally in the range 20-30.

2.1.3.1.4 Agitation during osmotic dehydration

In early works (Ponting et al., 1966), the effect of agitation was studied by comparison of agitated and non-agitated treatments. It was reported that agitated samples exhibited greater weight loss than non-agitated ones and thus agitation was found to be another process parameter. Raoult-Wack et al. (1989) studied the effect of agitation on both water loss and solid gain and reported: agitation of the osmotic solution resulted in higher mass transfer coefficient values for solutions of higher concentration and higher viscosity. Agitation has a good influence on weight loss (especially for the concentrated solutions) and on the exchange speed. The agitation ensures that the concentrated solutions are renewed around the particle and therefore, a concentration difference favorable to mass transfer is recreated. As a corollary, dilution of the boundary layer increases solute gain-since agitation provide lower sugar gain (Raoult-Wack et al., 1989). In some cases, intermittent agitation or short time duration may be sufficient.

2.1.3.1.5 Nature of the fruit

Water loss and solid gain are mainly controlled by the raw material characteristic (Torreggiani et al., 1987; 1993), certainly influenced by the possible pre-treatments. The great variability observed among the different fruits is mostly related to the tissue compactness (Giangiacomo et al, 1987), initial insoluble and soluble solid content (Lenart & Flink, 1984a, b), intercellular spaces, presence of gas, ratio between the different pectin fractions (water soluble pectin and protopectin) (Forni et al., 1986) and gelification level of pectin (Moy et al., 1987) of the fruit. Ponting et al. (1966) reported that osmotic dehydration is not suitable for citrus fruits and tomatoes because of their excessive loss of juice during the process. Fruits that are very porous e.g. pineapples are better suited to vacuum treatment during osmotic dehydration (Shi & Maupoey, 1993).

2.1.3.1.6 Size and shape of fruit

The higher the ratio of surface area to volume, the higher is the osmotic dehydration rates. Islam and Flink (1982) reported that the size and geometry of the food had some influences on the extent of final solute concentration, especially during short dehydration times, and at such times, dehydration was primarily a transport phenomenon related to surface area. According to Nieuwenhuijzen et al. (2001), moisture loss and solids gain increased as particle size decreased under same processing conditions.

2.1.3.1.7 Type of Osmotic Agent

The choice of the solute and its concentration depends upon several factors. The organoleptic evaluation of the final product is considered as one of the most important factors. Another factor is the cost of this solute. The solubility of the substance in water is also crucial for its effect on the maximum possible concentration in the osmotic solution. The lowering capacity of the compound on water activity will affect the driving force responsible for the mass transport. The solutes are the inorganic salts: calcium chloride, sodium chloride, monohydroxyl ethanol and the polyhydroxyl organics such as sucrose, lactose, maltodextrin, and high fructose corn syrup. The properties of the solutes as well as their sensory effects on the final product are summarized below.

2.1.3.1.7.1 Sucrose

Carbohydrates have been a part of the human diet since antiquity. In addition to sweetness, they provide valuable functions in food systems, which include structure, mouth-feel, texture and flavor enhancement. Before the development of the sugar refining industry, sweetening agents were largely limited to fruits, honey, maple syrups, and etc.

Sucrose suppresses bitter, acid and salty tastes, but the sweet taste of sucrose is not much suppressed except at high concentration of the other tastes (Goodshall, 1990). This ability of sucrose to suppress other basic tastes, especially bitter and sour tastes is responsible for much of sugar's ability to 'smooth' the flavor of foods. Sucrose effectively decreases the acidity of sour compounds, for example, the sourness of citric acid undergoes an exponential decrease with increased sucrose concentration (Hoppe, 1981). Furthermore, sucrose moderates the 'unpleasantness' of acids (Frank and Archambo, 1986).

Sucrose is known for its good water activity depressing properties, playing in this case a role of preservative or foods sensitive to bacterial spoilage. The sucrose in solution generates a high osmotic pressure and hence a reduced water activity, which is an important factor in food preservation. High concentration of sugars decreases the water activity, leaving insufficient water available to sustain viable microorganisms. The antioxidant properties of sucrose, because it prevents the deterioration of flavor in canned fruit and of rancidity in cookies, have been attributed to its ability to lower water activity (Mathlouthi & Reiser, 1996).

2.1.3.1.7.2 Lactose, high fructose corn syrup and maltodextrin:

Lactose and maltodextrin, because of their low levels of sweetness, are desirable osmotic agents for food materials requiring less sweetening. Nevertheless, lactose cannot be used alone because of its low solubility. It has a solubility limit of about 25% and, in dry systems, forms a caked layer around the fruit piece that prevents further transport of water from the sample (Hawkes and Flink, 1978). The increasing availability of lactose as increasing quantities of cheese whey are recovered may make it an economical partial substitute for sucrose in both dry and aqueous media. Maltodextrin can also be used as a partial substitute for sucrose. The rate of penetration into the fruit pieces was faster with high fructose corn syrup than sucrose. However, taste panel evaluations indicated that overall sucrose solution was preferred as an osmotic medium over HFCS (Le Maguer, 1988).

2.1.3.1.7.3 Calcium Chloride:

Ponting et al. (1972 a) reported that calcium treatment of apples was the logical and historical method for increasing firmness. The effect of a calcium dip was effective in preserving texture over an extended storage period, as well as having a synergistic effect with ascorbic acid or sulfur dioxide in preventing browning. However, Ponting and Jackson (1972 b) observed that it should be used in small quantity below 0.5% otherwise it was found to cause bitterness.

2.1.3.1.7.4 Sodium chloride:

For products osmo-dehydrated with sodium chloride, drying can be completed to the required water activity at higher final moisture content than that achieved when sucrose is used (Islam and Flink, 1982). This is attributed to the small size of the salt ions, which enables them to easily diffuse through the cell membrane resulting in a high solids gain. The solids uptake reduces the osmotic potential of individual cell membranes and thereby reduces the water loss. Hawkes and Flink (1978) noted that a 25% sodium chloride solution was the best osmotic agent because of its high molar concentration which increased even more because the ability of sodium chloride to ionize in solution. However, in order to have an acceptable product from a sensory viewpoint, the salt concentration of the osmotic agent should not exceed 10%. The saltiness of sodium chloride limits its usage in fruit processing. Using a mixture of sodium chloride and sucrose resulted in higher rates of osmotic dehydration than if sucrose were used alone (Hawkes and Flink, 1978).

2.1.3.1.7.5 Ethanol

Ethanol has been used in order to decrease the viscosity and the freezing point of the osmotic in the dehydrocooling process as suggested by Le Maguer and Biswal (1984) and in the freezing process using an aqueous media as proposed by Cipoletti et al. (1977). In order to block the aftertaste, pre-dipping in a sucrose solution followed by freezing in the aqueous freezant of 15% NaCl and 15% ethanol got satisfactory results.

In summary, sucrose or sodium chloride has been mostly used for osmotic dehydration, but any very soluble solute or solvent that is miscible with water can be used (e.g. dextrose, starch syrup, ethanol, polyols). For instance, impregnation is favored by low molecular weight solutes, whereas the dewatering effect is enhanced by high molecular weight solutes. Therefore, the use of blends comprising two or more solutes has been proposed, which may provide the advantages of both solutes (Raoult-Wack, 1994).

2.1.3.2 Modeling the Osmotic Dehydration Process

The importance of modeling osmotic dehydration process was found on the need to optimize osmotic dehydration and subsequent drying processes, to have the highest possible quality at minimum energy costs. The unusual features come from the interaction between the solution and material of biological origin. Two basic approaches can be used to model osmotic processes (Salvatori et al., 1998). One macroscopic approach assumes that the tissue is homogeneous and the modeling is carried out on the cumulated properties of cell walls, cell membranes and cell vacuoles. The other (microscopic approach) recognizes the heterogeneous properties of the tissue and is based on cell microstructure.

2.1.3.2.1 Macroscopic approach

Macroscopic analysis has been carried out by diffusion, square root of time, irreversible thermodynamics and other approaches. Existing models mostly based on the assumption that the mass transfer can be described by a fickian model in unsteady state (Fick's "second laws"). This allows the estimation of the diffusion coefficients for both water loss and solid gain individually or simultaneously. The mass transfer is assumed to be unidirectional and the interactions of the other components on the diffusion of the solute are negligible.

$$\frac{\partial C_i}{\partial \theta} = \frac{\partial}{\partial z} D_i \frac{\partial C_i}{\partial z} \tag{2.5}$$

Crank (1975) presented a detailed theoretical description of the diffusion process. Analytical solutions of the equation are available for idealized geometries, i.e. spheres, infinite cylinders, infinite slabs, and semi-infinite medium. For these analytical solutions of the unsteady state diffusion model to exactly apply, it is necessary either to keep external solution concentration constant or to have a fixed volume of solution. The resistance at the surface of the solid is assumed to be negligible compared to the internal diffusion resistance in the solid.

Biswal et al. (1991) used a rate parameter to model osmotic dehydration of green bean as a function of solution concentration and process temperature. The parameter was calculated from the slope of the straight line obtained from bean moisture loss and solid gain vs square root of time. A similar empirical model was used by Shi et al. (1995) for studying the influence of vacuum treatment on mass transfer during osmotic dehydration of fruits; by Pokharkar and Prasad (1998) for studying mass transfer during osmotic dehydration of banana slices and by Salvatori and Alzamora (2000) for process variables effects on apple slices.

From a modeling point of view, irreversible thermodynamics have been applied to the study of diffusion in gels and foods (Djelveh et al., 1989), and a general model based on irreversible thermodynamics augments and the mechanics of continuous media has been tested to take the elastic behavior of the material into account (Mrani, 1993). Both cases have resulted in a better understanding of the involved factors (Djelveh et al., 1988; Djelveh and Gros, 1989)

Azuara et al. (1992) developed a model based on mass balances of water and sugar to predict the kinetics of water loss and solids gain during osmotic dehydration. The model was developed to have the flexibility to facilitate its application to different geometric shapes. It was tested using published data on apples, beef and pineapples and, was used to predict the values of water loss and solids gain beyond the range actually studied. Correlation coefficients obtained for all cases studied were close to 0.99. The model was then related to Fick's second law of unsteady state one-dimensional diffusion through a thin slab in order to calculate the apparent diffusion coefficients for each condition.

Raoult-Wack et al. (1994) developed a bi-compartment model to simulate the mass transfer kinetics as well as the average water and solute concentration levels in a model food cube, agar (Figure 2.6). The model was designed as a representation of the model food cube with two concentric cubic compartments. The mass transfer of both water and solutes was then considered to occur between the inner and outer compartment of the model food, as well as between the outer compartment of the model food and the osmotic solution. The authors reported that information about the inner concentration in each compartment would be useful in optimization of osmotic dehydration and the subsequent drying processes e.g., air drying, with respect to product quality and energy savings. Furthermore, by taking into account the internal movement of water and solute within the foodstuff, the model would accurately predict the effects of any abrupt changes in the external conditions (temperature, concentration of osmotic solution) that occurred during osmotic dehydration. This so-called bi-compartmental model made it possible to obtain an accurate simulation of mass transfer kinetics as well as the average water and solute concentration levels which were representative of each compartment as a function of time.

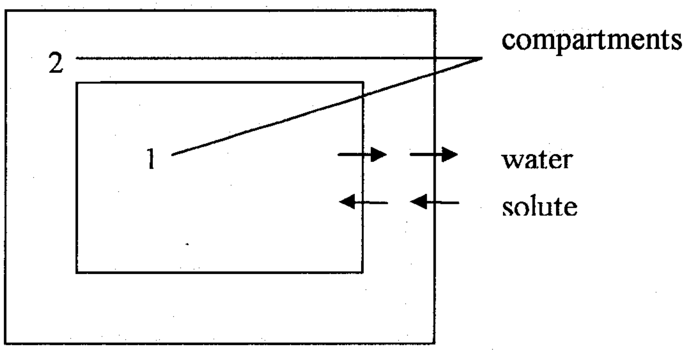


Figure 2.6 Schematic diagram of water and solute transfer in the in the compartment model (Raoult-Wack et al., 1994)

Correlative models were proposed, either to compute the time required for a given weight reduction as function of the processing temperature and of the solution concentration (Farkas and Lazar, 1969) or to estimate the dehydration parameters and the water activity of the products as functions of the solution concentration and of the product quantity/solution quantity mass ratio (Lenart and Flink, 1984). Rastogi and Raghavaro (1996) proposed a mathematical model based on osmotic pressure to investigate the vacuum effects during osmotic dehydration; Nsonzi and Ramaswamy (1998) studied osmotic dehydration kinetics of blueberry and further modeled moisture diffusivity (D_m) and soluble solids diffusivity (D_s) with quadratic functions of temperature and concentration. Panagiotou et al. (1998) developed an empirical model based on first order kinetic equation to predict water loss and solid gain during osmotic dehydration of fruits. The usefulness of these correlations is limited to the operating conditions and to the studied products.

A major limit of all these models is that the obtained transport coefficients in fact are global. They do enable neither to dissociate the respective contributions of each mass transfer, nor to take into account the probable interactions between water and solute flows. Their usefulness is then limited as far as technological control of the process is expected. But once the coefficients have been obtained in a well-defined range of temperature and concentration by experimental design, they can be used to predict and optimize parameters relevant to the process.

2.1.3.2.2 Microscopic approach

Cellular structure modeling is extremely challenging since it attempts to take into account the internal changes that take place as the solute penetrates the material. Models involving irreversible process thermodynamics (Toupin, 1986; Marcotte, 1988) have also been developed in order to integrate the contribution of each component i.e. osmotic solution and water to the osmotic dehydration process, as well as to account for the natural tissue action e.g. shrinkage that occurs during osmotic dehydration. Toupin (1986) developed a model for mass transport phenomena in plant materials based on irreversible process thermodynamics. In the model, the diffusion of the impermeable and permeable species in the matrix as well as shrinkage of the tissue was taken into account. The model included terms to describe the cell and tissue properties e.g. plasmalemma occupied by the plasmodesmata, critical cell volume. In the model, many of the parameters were estimated and adjusted because of lack of data.

Marcotte (1988) developed a microscopic model for dehydration of potato tissue in sucrose solutions of different concentrations. The bulk diffusion within the extracellular space was described using relations associated with the extended form of Fick's second law. The transmembrane and the symplastic transport mechanisms, which were considered to be the major transport mechanisms with respect to osmotic dehydration, were modeled based on the theory of irreversible thermodynamics. As with Toupin (1986), the model included terms for the diameter of the cell volume, total diameter of the cell, tortuosity, area of exchange of the plasmalemma, among others. The model was used to predict total cell volumes, extracellular volume and the cellular volumes. It was showed that the model was able to describe the mass transport phenomena of potato tissue undergoing osmotic dehydration in sucrose solution. Although these approaches were theoretically satisfying, they did not lend themselves to easy implementation. Instead they required a lot important numbers of parameters that were not available for the most part in the literature.

In summary, Fick's law of unsteady state diffusion gives a good correlation between the experimental and predicted values of water loss and solids gain (Conway et al., 1983; Beristain et al., 1990). Fick's second law and the analytical solutions given in Crank (1975) have found general acceptance and wide usage in modeling the kinetics of water loss and solids gain during osmotic dehydration of different foods with different shapes (Hawkes and Flink, 1979; Conway et al., 1983; Beristain et al., 1990; Biswal and Borzghemr, 1991, 1992; Yang & Le Magure, 1992; Mauro & Menegalli, 1995; Lazarides & Mavroudis, 1996).

2.1.3.3 Osmotic solution management

The implementation of osmotic processing of plant or animal materials in concentrated solutions presents a critical factor due to the management of the concentrated sugar/salt solutions (Rosa and Giroux, 2001). During osmotic treatment of fruit and vegetables, the solution was diluted and its dewatering potential was reduced; aromas, pigments, acids, proteins and pulp fragments were leached into the solution. All these transferred materials lead to chemical, chemical-physical and sensory changes in the solution after utilization.

2.1.3.3.1 Concentration restoring and solution recycling

Restoring of solute concentration is the first main problem in managing the osmotic solution. Technological processes to restore the concentration may include both phase and non-phase changing processes:

- Evaporation (atmosphere at high temperature; under vacuum at moderate temperature).
- Solute addition (no phase change).
- Membrane concentration (no phase change).
- Cryoconcentration.

2.1.3.3.2 Microbial control of the solution

Microbial targets have to be individualized for different foods to be processed in order to assure the safety and to save the solution from overheating. The necessity of microbial assessment during and at the end of the process allows optimizing the heat treatment.

Different sources of contamination can affect the microbial stability of the used solutions. During the processing of fruit and vegetables with a pH ≤ 4.5, yeast, moulds and lactic bacteria are the most frequent micro-organisms released from the products to the solution. In this situation pathogenic bacteria are not able to grow. Depending on the environmental process conditions, the microbial load after several osmotic treatments (OT) cycles can range from 2×10^2 CFU ml^{-1} (Valdez-Fragoso, 1998) to high levels of yeast and fungi after 15th cycle (Valdez-Fragoso, 1998), and to 10^5 CFU ml^{-1} after 8 h of continuous treatment (Dalla Rosa et al., 1995). Furthermore, microbial contamination from the environment can occur if the process technology is carried out without any air filtering systems.

Some experiments have been carried out to establish the possibility to submit sugar solutions to the thermal treatments. Results showed that the main problem occurring after heat treatment is related to non-enzymatic browning such as caramelisation as well as Maillard reaction since some amino acids or proteins have been extracted from the food.

Individualisation of CCP and implementation of HACCP methodology for process control becomes a need when the OT process is carried out in order to produce minimally processed foods and any subsequent process is not set up to obtain the final stabilization of the product (Singh & Oliveira, 1994; Leistner & Gorris, 1995).

2.1.3.3.3 Osmotic solution end-point determination

End-point of the use of the solution has to be determined according to different factors:

- Type of food being processed;
- Sequence of the food to be processed;
- Type of filtration used in the process;
- Type of re-concentration technology;
- Presence or absence of sanitation step (pasteurization).

Analytical determinations should be performed along the process line to monitor the solution condition. Some of the most common determinations are: soluble concentration (by refractive index); electric conductivity (by potentiometric evaluation); optical density (by spectrophotometric analysis) and tristimulus color (using CIE scale). All these evaluation can be easily carried out with automatic probes placed in-line. It is concluded that monitoring the microbiological quality of syrups is essential if they are to be used for OD; variations in color and turbidity and values for acidity, electrical conductivity and contents of reducing sugars may be used to monitor syrup deterioration (Valdez-Fragoso et al., 1998).

2.1.3.3.4 Possible utilization of spent solutions

When the end-point is reached and the previously proposed methods of purification are not applicable, the solution has to be taken out from the process and then different possibilities could be suggested for other food preparations:

- Syrup for fruit canning (also fruit treated by OT);
- Jams;
- Mixing with fruit juices;
- Diluting with water and addition of carbon dioxide to obtain fruit soft drinks;
- Use of the osmotic solution in the canned product;
- Possible use of the secondary by-products for the production of natural flavorings (Shukla, 1991).

Some other applications have been proposed, such as bee feeding or animal feed after increasing protein content. Spent solutions if not used as outlined above have to be discharged as wastewater; the main problem is related to the high BOD_5 of the concentrated solution.

In summary, it is generally recognized that the reuse of concentrated solutions for osmotic drying must be clearly understood to ensure the economical viability of the process itself. On the basis of specific researches on concentrated solution used in OD, it is possible to affirm that the re-use for several times (at least 20 cycles) of the same recycled solutions from the engineering point of view (Rasa and Giroux, 2001).

2.1.4 Related techniques to improve OD mass transfer

The driving force for the diffusion of water from the tissue into the solution is provided by the higher osmotic pressure of the hypertonic solution. The rate of mass transfer during osmotic dehydration is generally low. A number of techniques have been tried to improve mass transfer rate. These techniques include: application of partial vacuum (Fito, 1994; Rastogi & Raghavarao, 1996), subjecting food material to ultra high hydrostatic pressure (Rastogi & Niranjan, 1998), high intensity electrical field pulses (Rastogi et al., 1999), with supercritical carbon dioxide treatment (Tedjo et al., 2002) prior to osmotic dehydration processing; and using centrifugal force (Azuara et al., 1996), applying ultrasound (Simal et al., 1998) and microwave (Li & Ramaswamy 2003) during osmotic dehydration process.

2.1.4.1 Application of vacuum during osmotic dehydration

Mass transfer during osmotic dehydration under vacuum has been reported to be quicker than under ambient pressure (Fito, 1994; Rastogi & Raghavarao, 1996). The reduction in pressure causes the expansion and escape of gas occluded in the pores. When the pressure is restored, the pores can be occupied by osmotic solution, increasing the available mass transfer surface area. The effect of vacuum application during osmotic dehydration was explained on the basis of the diffusion osmotic transport parameter, mass transfer coefficient and interfacial area. The vacuum applied only affects the rate at which the equilibrium is achieved and not the equilibrium moisture content.

Conducting the osmotic process under vacuum conditions resulted in fruit pieces with higher solids content. During the processing, a porous product consists of exchanging the internal liquid gas or liquid occluded in open pores for an external liquid phase, due to the action of hydrodynamic mechanisms (HDM) promoted by pressure changes (Fito, 1994; Fito & Pastor, 1994; Fito et al., 2001). The operation is carried out in two steps after the product immersion in the tank containing the liquid phase. In the first step, vacuum pressure (p_1:50-100 mbar) is imposed on the system for a short time (t_1) in the closed tank, thus promoting the expansion and outflow of the product internal gas. The releasing of the gas takes the product pore filled with liquid. In the second step the atmospheric pressure (p_2) is restored in the tank for a time (t_2) and compression leads to a great volume reduction of the remaining gas in the pores and so to the subsequent in flow of the external liquid in the porous structure. Compression can also reduce the pore size depending on the mechanical resistance of the solid matrix.

2.1.4.2 Application of high hydrostatic pressure

Application of high pressures causes permeabilization of the cell structure (Dornenburg & Knorr, 1993; Eshtaghi et al., 1994; Rastogi et al., 1994). This phenomenon has been exploited to enhance mass transfer rates during osmotic dehydration of pineapple (Rastogi & Niranjan, 1998). The application of high pressure damages the cell wall structure, leaving the cells more permeable, which leads to significant changes in the tissue architecture resulting in increased mass transfer rates during osmotic dehydration as compared to untreated samples. The experimentally determined diffusivity values, based on a Fickian model, were found to increase 4-fold for water and 2-fold for sugar in the pressure range investigated (100-800 MPa) (Rastogi et al., 2002).

2.1.4.3 Application of pulsed electric field

High intensity electrical pulsed field treatment has been reported to increase the permeability of plant cells (Geulen et al., 1994; Knorr et al., 1994; Knorr & Angersbach, 1998). High intensity electrical pulsed field (0.22-1.60 kV/cm) pretreatment was also shown for the first time to accelerate osmotic dehydration. The rise in effective diffusion coefficient can also be attributed to an increase in cell wall permeability, facilitating transport of water and solute. High electrical pulsed field treatment-induced cell damage results in softening of tissue. This in turn results in the loss of turgor pressure leading to reduction in compressive strength.

2.1.4.4 Application of supercritical carbon dioxide

Supercritical fluid using CO_2 has emerged as an attractive unit operation for the processing of food and biological materials. The critical point of CO_2 gas is at 304.17 k and 7.38 MPa. Supercritical carbon dioxide processing as a separation technique for lipophilic compounds, inactivation of microorganisms as well as reduction of enzyme activities has been reported (Sankar, 1989; Tedjo et al., 2000). The combination of pressure and temperature as process parameters makes it possible to vary the solvent power of the medium within certain ranges as desired without having to change the composition of the solvent (Rizvi et al., 1994). Water loss by supercritical carbon dioxide treated samples was lower than for the other sample. During application of supercritical carbon dioxide, gas diffused into the sample that caused lower water loss. These results indicate that solid uptake during OD may not necessarily be a function of permeabilized cells alone but may also depend on the type of chemical and structure changes caused by the pretreatment as suggested by Rastogi and Ranghavarao (1994).

2.1.4.5 Application of ultrasound during osmotic dehydration

The mechanical and physical effects of sound can be used to enhance many processes where diffusion takes place (Floroous & Liang, 1994). Acoustic streaming will affect the thickness of the boundary layer, which exists between stirred fluid and solid. Cavitation, a phenomenon produced by sonication, consists of the formation of bubbles in the liquid, which can explosively collapse and generate localized pressure fluctuations. Diffusion across the boundary between the suspended solid and liquid is substantially accelerated in an ultrasonic field. Pressure and the frequency are the two main factors to take into consideration. No increase in diffusion rates when the maximum value of intensity is achieved due to violent cavitation that produces an extreme turbulence or vapor locks at the interface. The mechanism of ultrasonic frequency on diffusion has not been elucidated.

2.1.4.6 Application of centrifugal force during osmotic dehydration

Azuara et al. (1996) applied centrifugal force during osmotic dehydration and found, centrifugation (64 g) enhanced mass transfer (water loss) by 15% while considerably retarding the solid uptake (by about 80%). Further work was needed to investigate the effect of variable such as: rotational speed, temperature and concentration of osmotic solution, type of solute or their mix and size, as well as shape of the foodstuff.

2.1.4.7 Application of microwave heating during osmotic dehydration

Microwave heating has been traditionally recognized to provide rapid heating conditions. MW process can be expected to benefit osmotic drying as well. Microwave heating employs a completely different mechanism (detailed information about **MW** is presented in **Section 2.4.2**). Because of internal heat generated by microwave field, there is an internal pressure gradient, which effectively pumps water to the surface of sample. Combining the osmotic pressure difference with microwave pumping effect, moisture transfer during osmotic dehydration will be accelerated. Experimental results showed that solids gain during osmotic dehydration by the samples was always lower when microwave heating applied to the system; in the meantime moisture loss during osmotic dehydration process was increased. Moisture loss in mass transfer area might control and strongly counter-act solids gain in MWOD. The overall ratio of ML/SG was higher in MWOD than in COD.

As summarized in the above sections, significant advances have been made in enhancing rates of mass transfer. However, there is ample scope for further research and development in this area. For instance, high pressure and high electric pulsed field are employed as pretreatment methods. The effects of high pressure and high electric pulsed field on microstructure of different kinds of food material need a detailed study (Rastogi et al., 2002). Similarly, acoustic and microwave field technology have a considerable scope for this purpose by studying the effect of frequency, amplitude and the power of fields on the rate of mass transfer and the influence on products quality characteristics.

2.2 Conventional air drying

2.2.1 Introduction

Drying is a process in which water is removed to halt or slow down the growth of spoilage microorganisms, as well as the occurrence of biological and chemical reactions. Drying technology has evolved from the simple use of solar energy to current technology that includes, among others, kiln drying, tray drying, tunnel drying, spray drying, drum drying, freeze dehydration, osmotic dehydration, extrusion, fluidization, and the use of microwaves, radio frequency (RF), refractance window, and hurdle technology (Vega-Mercado et al., 2001).

Solids drying involve two fundamental and simultaneous process of heat being transferred to evaporate liquid and mass being transferred as liquid within the solid and vapor from the surface (Porter, 1973). The factors that influence the rates of these processes determine the drying rate. Therefore, a study on the drying of a solid may be based on the internal mechanism of liquid flow or on the effect of the external conditions of temperature, humidity and airflow.

2.2.2 Drying rates and related affect factor

Of all the conditions that affect the drying rate at which a moist or wet material can be dried, the most fundamental is the physical and chemical structure of the material (Van Arsdel and Brown, 1973). The amount of dry solids in a product also influences the drying rate because the rate is expressed on a dry solids basis. The drying rate of product with lower solids content is higher than the drying rate of the product with higher solids content.

2.2.2.1 Product composition:

Differences in the composition of the material influence the drying rates of foods. Van Arsdel and Brown (1973) observed that in the high moisture range, blanched materials dried more rapidly than unblanched materials. The authors attributed this occurrence to the tissue damage resulting from blanching which made the cell membranes of the product freely permeable to water. In another study on the influence of the sugar content of potatoes on drying rates, Van Arsdel and Brown (1973) reported that the sugar content did not influence the drying rate of potatoes down to moisture content of about 0.30 kg/kg dry solid. However, at lower moisture contents (0.30-0.075 kg/kg dry solids), the drying rates decreased with increasing sugar content. The drying times were therefore longer. Similar observations were found by Sankat et al. (1996) in their study on the air drying behavior of fresh and osmotically dehydrated banana slices and Marousis et al. (1989) in their study on the effect of sugars on water diffusivity in starch.

2.2.2.2 Disposition of the sample related to drying rate

A large surface area favors a high drying rate: increasing the drying surface area per unit of total space occupied enhances drying rates. In the later drying stages, the thickness of the solid substance through which the water must diffuse becomes the controlling factors. Drying times are therefore reduced if the size of pieces is reduced. In drying, special designs are sometimes employed in order to increase the amount of through-flow and thereby the drying rates, especially for heavily loaded trays.

2.2.2.3 Product loading

Van Arsdel (1951) reported that increasing the tray loading reduces the rate of drying during the early stages of drying. As drying progresses, the rates become more nearly equal for heavily loaded and lightly loaded trays. For heavily load trays, product shrinkage increases the open-air structure through which air can circulate freely as it does for lightly loaded trays. Similar adverse effects also occur for soft materials, which mash together during the spreading operation or bottom layers that crush together under their own weight. Evaporation occurs almost exclusively from the top layer of the sample pieces so that the initial rate of loss of weight from a heavily loaded tray is not much greater than from a lightly loaded tray.

2.2.2.4 Wet-bulb depressing

The wet-bulb depression, which is the difference between the dry-bulb and wet-bulb air temperature, is the most important factor correlated with the drying rate (Carrier, 1921). If this depression is zero the air is saturated and no drying occurs. Van Arsdel and Brown (1973) reported that in the early drying stages, the internal transfer of water occurs readily and the surface resistance to evaporation almost exclusively controls the drying rate. In the later drying stages, the internal resistance to moisture flow mainly controls the rate, such that an increase in external drying potential by increasing the wet-bulb depression has little effect.

2.2.2.5 Air quality

Except that moisture content of air, air temperature and air velocity are both important factors related to drying process. The higher temperature, the greater drying rate under same moisture level; the internal redistribution of moisture is enhanced by the rise in material temperature as well. At low moisture contents, Van Arsdel (1951) reported the drying rate was substantially independent of air velocity. The author also noted at high moisture contents, there were differences between the drying rates of samples dried with air at high velocity and at low velocities.

2.2.3 Diffusion model for air drying

Fruit drying is mostly in the falling rate period (Saravacos and Charm, 1962), during which water is transferred by diffusion from the interior to the surface. It is assumed that liquid flow conforms to Fick's second law of diffusion (equation 2.6) and the mathematical solutions can be used to solve the equation, as explained earlier.

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \tag{2.6}$$

where: C is the concentration of diffusion substance, x the space coordinate measured normal to the section, and D is called the diffusion coefficient.

In spite of the limitations of the diffusion model based on Fick's law of unsteady state diffusion, good correlations have been obtained between predicted and experimental results when the diffusion model has been used to characterize the drying behavior of potatoes (Saravacos and Charm, 1962), shrimp (Ramaswamy et al., 1982), apple puree (Bains et al., 1989) and bananas (Sankat et al., 1996).

2.2.4 Drying process related some quality parameters

2.2.4.1 Color

Color is an important quality attribute in a food to most consumers. It is an index of the inherent good qualities of a food. The association of color with acceptability of food is universal. Among the natural color compounds, carotenoids and chlorophylls are distributed in fruits and vegetables. Preservation of these pigments during dehydration is important to make the fruit and vegetable product attractive and acceptable.

One obstacle in the dehydration is the discoloration due to browning. Browning in foods is of two types: enzymatic and nonenzymatic. In the former, the enzyme polyphenol oxidase catalyzes the oxidation of mono and ortho diphenols to form quinines that cyclize, undergo further oxidation, and condense to form brown pigments (melanins). Nonenzymatic browning (NEB), also known as Maillard reaction, describes a group of diverse reactions between amino groups and active carbonyl groups leading eventually to the formation of insoluble, brown, polymeric pigments, collectively known as melanoidin pigments. The rate of browning is also dependent on the moisture content of the material. In the intermediate moisture content of 15-20%, the browning rate reaches a maximum; at higher and lower moisture content levels, the browning rate is relatively low. It is also influenced by the type of reactant sugars and amines, pH, temperature, and a_w.

The addition of sulfites during the predrying step is the only effective means available at present of controlling NEB in the dried fruit and vegetable product. Nevertheless, as a result of adverse reactions in sensitive individuals, the Food and Drug Administration issued a regulation prohibiting the use of sulfites have been added and are detected at 10 ppm (FDA, 1986). In this respect, processes e.g. osmotic dehydration that minimize quality degradation during air drying were investigated (Ponting et al., 1966; Hawkes & Flink, 1978; Islam & Flink, 1982; Kim & Toledo, 1987; Rahman & Lamb, 1991; Grabowski & Mujumdar, 1992; Grabowski et al., 1994; Sankat et al., 1996; Li & Ramaswamy, 2004).

2.2.4.2 Sorption isotherms

All food materials display a characteristic vapor pressure at constant moisture content and temperature. The moisture in food always tends to approach the equilibrium with the temperature and vapor pressure of its surrounding gaseous atmosphere. If the conditions of the surrounding atmosphere are not changed for a sufficiently long time (theoretically for infinitely long time), the equilibrium at which the vapor pressure and temperature of the food material and its surrounding are the same, is established. At equilibrium no further change in the moisture content of the food occurs.

The interactions between the moisture in the surroundings and in the food are usually tidied in the systems in equilibrium. A sorption isotherm, which represents these interactions macroscopically (Multon, 1988), is a graph between EMC (as ordinate) and ERH or a_w (as abscissa) for any given temperature. A typical isotherm for food materials is sigmoid in shape. A sorption isotherm is conventionally divided into three successive parts. The first part of the isotherm in the low humidity range which falls approximately between $a_w = 0$ and $a_w = 0.2$, is concave to the a_w axis. The polar groups, especially those of carbohydrates and proteins, create an electrostatic force field at the surface of the molecule, which is responsible for adsorption of water molecules in the food. The first part of the isotherm represents the "monolayer" where the water molecules are strongly bound to the polar groups (primary adsorption sites) by high-energy hydrogen bonds. These water molecules posses a specific and rigid orientation, their mobility and chances of taking part in any biochemical reaction are practically zero (Multon, 1988). The water molecules in the monolayer may be considered to form an integral part of the solid phase, which displays none of the functional properties of pure water (Troller and Christian, 1978). A steep slope in the sorption curve in this zone generally indicates a high concentration of hydrophilic sites in the substrate.

The second part of the isotherm which is almost linear and which falls approximately between $a_w = 0.2$ and $a_w = 0.65$ corresponds to the binding of several layers of water molecules super-imposed on the previous layers, to which they are attached by hydrogen bonds of decreasing energies. The binding may also occur at polar sites, which were previously buried but became accessible upon subsequent swelling. The water molecules in these layers have decreasing binding energies and their mobility remains limited. Their chances of taking part in biochemical reactions can only be very restricted (Multon, 1988).

The third part of the isotherm, for a_w greater than 0.65 and almost asymptotic to a_w of 1.0, represents the water retained by capillarity, solution formation and osmosis. As the accumulation of water molecules in micropores precedes the molecules become associated in liquid phase under tension. The liquid phase obeys the laws of capillarity. As a_w progressively increases, other pores of increasing size are filled in their turn. Low molecular weight compounds may then dissolve in the liquid phase. If there are semi-permeable walls within the food structure, osmosis comes into effect. Water held in food by these mechanisms is much larger than what might have been possible only by adsorption. A steep gradient in this part of the curve indicates high substrate porosity, large concentration of solutes and/or the presence of semi permeable walls. The binding energy and degree of mobility of water in the third part is almost equal to that of the pure water and the water in this zone can participate in biochemical reactions. Most of the foods deteriorating reactions or processes including growth of microorganisms take place in this zone because of the availability of moisture.

2.2.4.3 Isotherm equations

Numerous attempts have been made to model the sorption phenomena. It is one thing to find a mathematical equation which may fit the typical sigmoid shaped isotherm curve and quite another to actually model the physical-chemical sorption phenomena. The problem in characterizing the physical and chemical properties of food constitutes, the complexity of their interaction with water and the effect of water on their internal structure makes it extremely difficult to accurately model the physico-chemical sorption phenomena in mathematical form. Several scientists have made attempts in this direction to find a theoretical isotherm equation. Using the kinetic approach Brunauer et al. (1938) derived the BET equation, which was a multilayer homogeneous isotherm equation. Anderson (1946) modified the BET equation and the modified equation was later known as GAB equation.

None of the theoretical equations derived so far describe the complete sorption phenomena. Van den Berg and Bruin (1981) complied 77 mathematical equations, including theoretical equations to describe isotherms of various products. Young and

Corwell (1962) remarked that a theoretical equation that may account for the complete sorption phenomena will be too complex and will have too many parameters to be of any use. It is recognized that it may not be possible to simultaneously evaluate more than four parameters with a reasonable accuracy and an isotherm equation should not have more than four parameters (van den berg, 1985).

2.2.4.3.1 BET equation

Taking the classical monolayer gas adsorption model of Langmuir (1918) as the starting point, Brunauer et al. (1938) developed a model for multiplayer molecular adsorption of vapor on solid surfaces. The equation is:

$$\frac{M}{M_m}=\frac{C*a_w}{(1-a_w)(1-a_w+C*a_w)} \tag{2.7}$$

It is a correct first approach to model the adsorption of water by food solids (van den Berg, 1985). The model assumes homogenous sorption whereas the water sorption in food materials is heterogeneous (van den Berg and Bruin, 1981). The model also assumes that heat of sorption of second and successive layers is equal to the heat of liquefaction (Brunauer et al., 1938). The model is consistent with the water interactions in the first two parts of the typical sigmoid shaped isotherm curve but does not remain consistent in the third part due to underlying simplifying assumptions (Multon, 1988). The model gives satisfactory results in a_w range from 0.01 to 0.50 (Brooker et al., 1974).

2.2.4.3.2 GAB equation

The GAB equation was first proposed as modification of BET equation by Anderson (1946). The modification involved multiplication of the water activity in the BET equation by a constant that is less than one. The constant was interpreted to mean that the heat of adsorption in the second to ninth layers is less than the heat of liquefaction. It has been recognized as the most satisfactory theoretical isotherm equation. GAB equation takes into account the biological structures, which are responsible capillarity phenomena.

$$\frac{M}{M_m}=\frac{C*K*a_w}{(1-K*a_w)(1-K*a_w+C*K*a_w)} \tag{2.8}$$

2.3 Microwave drying and application

2.3.1 Introduction

Drying has become an important procedure in almost all areas of industrial processing. When using conventional driers, with hot air or infrared, the speed of drying is limited by the rate at which water or solvent diffuses from the interior to surface from which it is evaporated. The diffusion occurs by capillarity, the longer or more difficult the diffusion path, the slower the drying. Increasing the ambient temperature, which increases the evaporation of water on the surface faster, can sometimes speed up drying. However, the drying may still be limited by the rate at which the interior water can reach the surface. It is usually not a good idea to try to dry too quickly, since this may result in the surface to over-dry, causing case hardening or blocking the interior water from reaching the surface quickly enough. Also, as drying progresses, the path for diffusion of the interior water becomes longer and more difficult, and the drying rate usually slows dramatically, as shown in Figure 2.7. All drying curves look alike and usually two-thirds or more time is required to remove the last one third or less of the water (Schiffmann, 1987, 2002).

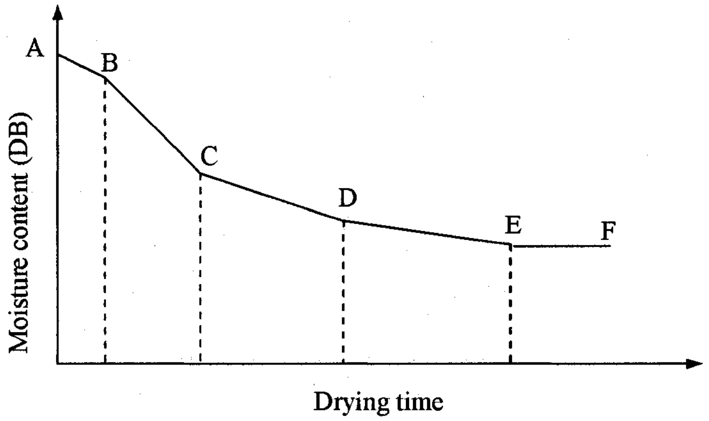


Figure 2.7 Typical moisture drying curve, showing moisture content vs. time in the dryer and the various stages in the drying process.

AB: initial adjustment; BC: constant rate period; CD: First falling rate period; DE: second falling state; EF: equilibrium moisture content.

Microwave drying employs a completely different mechanism. Because of the internal heat generated by microwave field, there is an internal pressure gradient, which effectively pumps water to the surface. The usual means of applying microwaves to a drying process is at the end of the falling rate period (Figure 2.8), in which case this is referred to as finish drying. A good example of this is the finish drying of chips and cookies. Microwaves can also be applied throughout the drying process at low power levels to "boost drying" by constantly pumping water to the drying surface. This technique is used for the microwave drying of pasta. There is also the possibility of applying microwave heating prior to hot air drying, thereby preheating the product to the drying temperature. This has been tried with cake batters (Schiffmann, 1987).

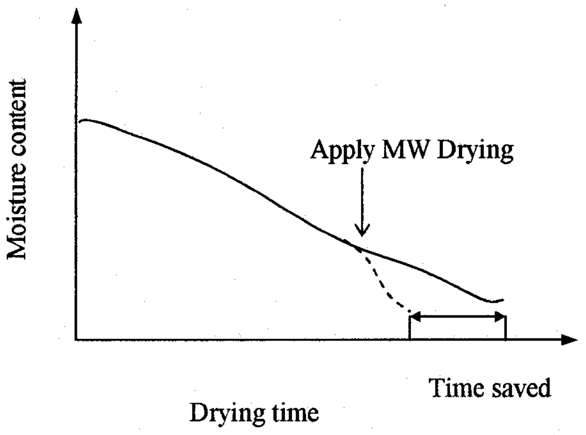


Figure 2.8 Microwave finish drying. Conventional hot air drying employed first and microwave energy is added near the end of the falling rate period to rapidly remove the last traces of moisture.

2.3.2 Microwave theory and characteristics

Microwaves are part of the electromagnetic spectrum (Figure 2.9) and are located between 300 MHz and 300 GHz. Microwave wavelengths range from 1 mm to 1 m. The terms "dielectric" and "microwave" are used inter-changeably and in somewhat confusing manners and must be defined. The term "dielectric heating" can be applied logically to all electromagnetic frequencies up to and including at least the infrared spectrum. The lower frequency systems operated at frequencies through at least two bands: HF (3-30 MHz) and VHF (30-300 MHz). Thus, the names high frequency (HF), dielectric, radio frequency and microwave (MW) heating can often be used interchangeably. However, it is generally accepted that dielectric heating is done at frequencies between 1 and 100 MHz, whereas microwave heating occurs between 300 MHz and 300 GHz (Schiffmann, 1987; Dibben, 2002). Microwave heating is defined as the heating of a substance by the electromagnetic energy operating in that frequency range.

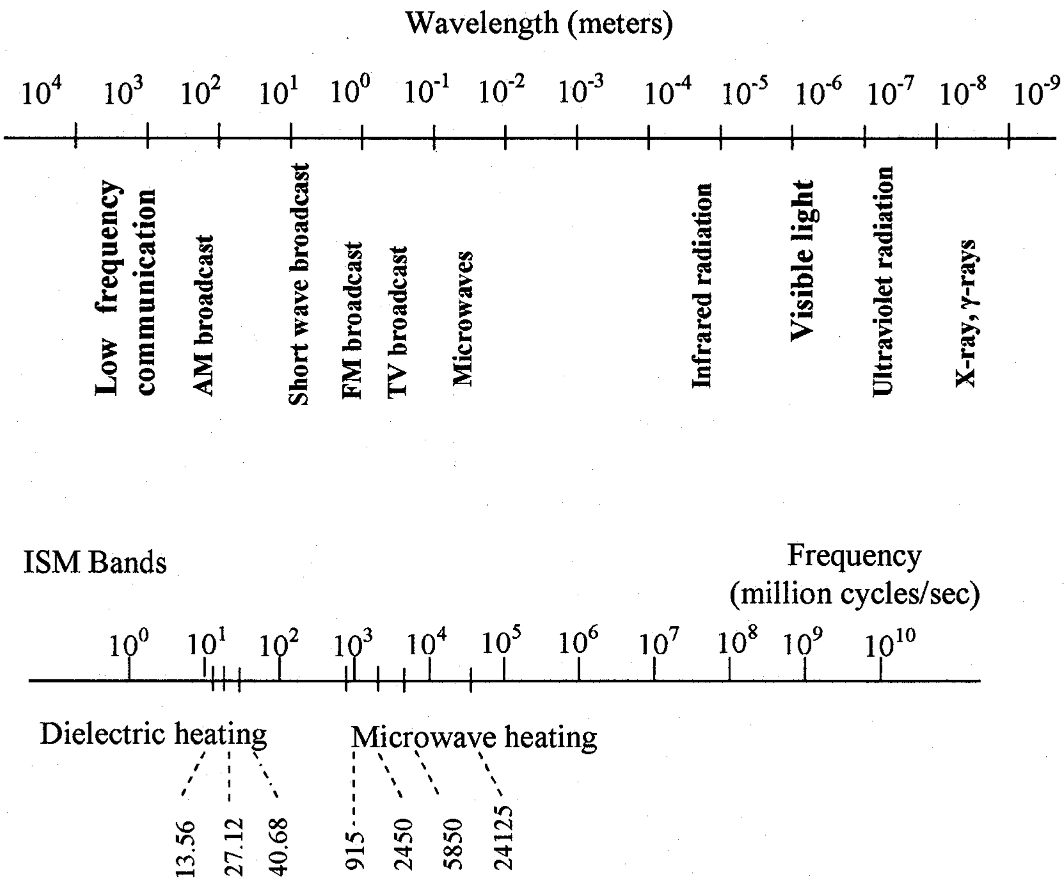


Figure 2.9 Electromagnetic spectrum

The close proximity of microwaves to radio and TV waves posses a potential problem of interference between these waves. Only selected microwave or high frequencies are allowed for heating in industrial, scientific, and medical applications, the ISM frequencies. Specific frequencies (915 MHz, 2450 MHz, 5800 MHz and 24,125 MHz) have been authorized for usage. The most popular frequencies used in North America are 915 MHz and 2450 MHz. 915 MHz is generally used for industrial food processing applications while 2450 MHz is widely used for domestic applications

(Ryynänen, 2002). More specific industrial, scientific and medical (ISM) bands established by international agreement are shown in Table 1 (Metaxas and Meridith, 1983).

Table 2.1 Some of the ISM allocated frequency bands

Frequency MHz	Area permitted
433.92	Austria, Netherlands, Portugal, Germany, Switzerland, Great Britain
896	Great Britain
915	North and south America
2375	Albania, Bulgaria, Hungary, Romania, Czechoslovakia, Russia
2450	Worldwide except where 2375 MHz is used
5800	Worldwide
24125	Worldwide

All bodies above absolute zero temperature emit electromagnetic waves. All electromagnetic waves are characterized by their wavelength and frequency, and an illustration of a plane monochromatic electromagnetic wave is shown in Figure 2.10. Microwave is analogous to light in that it can be transmitted and reflected. Being an electromagnetic wave, microwaves have electric field (E, V/m) and a magnetic field (H, A/m), acting perpendicular to each other. They also show mono-chromaticity and are highly polarized. In free space the propagating wave has a velocity (C_0) of about 3.0 x 10^8 m/s, and this is the maximum speed at which energy can travel. Frequency (f) and wavelength (λ) are linked by equation (2.9):

$$c = \lambda \bullet f \tag{2.9}$$

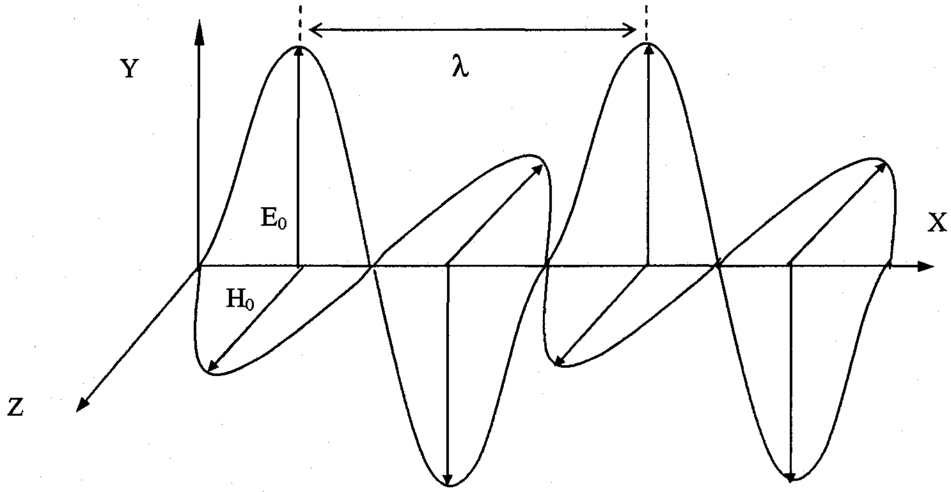


Figure 2.10 Diagrammatic illustration of a plane electromagnetic wave. E and H represent the electrical and magnetic components of the wave; E_0 and H_0 are their respective amplitudes

2.3.3 Microwave heating mechanisms

Microwaves themselves do not represent heat, but the absorbed energy is converted into heat inside the product. There are many factors affecting how food is heated in a microwave field and this makes the heating mechanism very complicated to understand. When a microwaveable product is to be developed, the fundamental mechanisms of microwave heating and the interaction of microwaves with materials should be understood (Dibben, 2002).

The heating of foods by microwave energy is accomplished by the absorption of microwave energy both by dipolar water molecules and ionic components of the food. Thus, both the water content and the dissolved ion content (often salt) are dominating factors in the microwave heating of foods. When the dipolar water molecule is subjected to a microwave field, with the field rapidly changing its direction, the dipole tries to align itself with the field direction. There is a time lag, as some response time is required for the water molecule to overcome the inertia and the intermolecular forces in the water. The electric field thus provides energy for the water molecule to rotate into alignment. The energy is then lost to the random thermal motion of the water and results in a temperature rise. When ionized compounds are subjected to a microwave field, they randomly collide with non-ionized groups in an electric field. The kinetic energy of these ions is transmitted into heat during the collisions.

The most obvious direct effect of microwave heating is embodied in the volumetric heating that will quickly raise the temperature and alter the temperature profile depending on the moisture profile in the drying material. Microwaves are absorbed by polar molecules and other ionic compounds but are reflected by metals while glass and plastic allow the microwaves to pass through them. Materials are roughly divided into three kinds according to their interaction with electromagnetic fields: ***transparent, reflecting*** and ***absorbing*** (Figure 2.11).

Transparent materials, such as air, quartz glass and water-free ceramic bodies, allow the waves to pass through unhindered, as glass does with light (Figure 2.11a). In the microwave field, these materials do not heat. ***Reflecting*** materials, such as metals or graphite, ideally permit no rays to penetrate them. The waves hit the surface and are thrown back almost unchanged into space (Figure 2.11b). These materials also remain cold in the microwave field. ***Absorbing*** materials, such as foods, fresh wood and moist ceramic bodies, are able to absorb microwave energy and convert it into heat (Figure 2.11c). How deeply the rays penetrate the interior varies, depending on the material and its specific dielectric properties. If a material consists of several components, and at least one component is a good absorber, then it can be heated well.

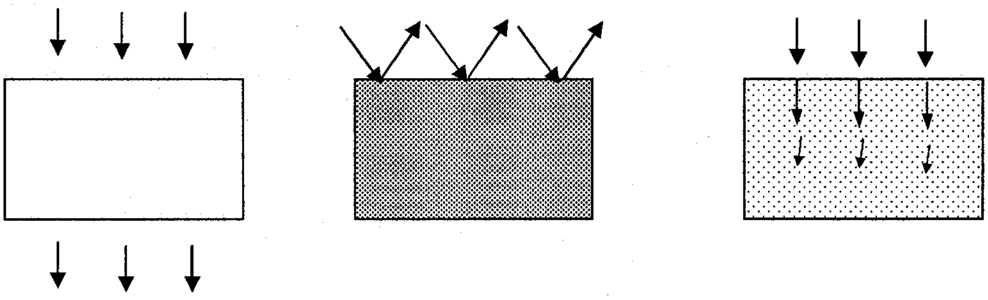


Figure 2.11a

Figure 2.11b

Figure 2.11c

Figure 2.11 Materials interaction with electromagnetic field

There are several energy conversion mechanisms by which heat is generated by microwaves. These include: ionic conduction, dipole rotation (entire molecule quantized, twisted or bent), interface polarization, ferroelectric hysterisis, electric domain wall resonance, electro-restriction, phiezoelectricity, nuclear magnetic resonance, ferro and ferri-magnetic resonance. For microwave heating in foods, only ionic conduction and dipolar rotation are of primary interest (Schiffmann, 1987; Owusu-Ansah, 1991).

2.3.3.1 Ionic conduction

Ionized compounds randomly collide with non-ionized groups when subjected to an electric field. The kinetic energy of these ions is transmitted as heat during such collisions. The heating rate due to ionic conduction can be expressed as (Schiffmann, 1987; Owusu-Ansah, 1991):

$$\frac{P_\mu}{V_\mu} = E^2 qn\mu \tag{2.10}$$

where: E= electric field

P_μ = power

V_μ= volume of material

q = the electric charge on each of the ions

μ = level of mobility of the ions

n = the number of charges

The conductivity (σ_1) may be expressed as:

$$\sigma_1=qn\mu \tag{2.11}$$

For materials containing different types of ions in a specific volume, the total conductivity is the sum of the individual conductivities of each ion.

2.3.3.2 Dipole rotation

Dipole rotation is dependant on frequency (time) and temperature. When two opposite charges are separated by a distance, they constitute an electric dipole. Molecules with non-zero permanent electric dipole moments are called polar molecules. Non-polar molecules may obtain a dipole moment in an electric field as a result of the distortion of their electronic distributions and nuclear positions. The energy transfer mechanism will be efficient only if the time between the changes of direction of the electric field is so short that the dipolar molecule aggregates can barely follow the changes. If the time is long (frequency low) the alignment will be the good and the energy transfer is low. If the time is short (frequency high), the aggregates will not move much between field reversals, and energy transfer rate will again be low. Since the statistical number of water molecules that are bound together by hydrogen bonding will decrease with increasing temperature, so the inertia and energy release will be reduced with temperature increasing as well. For dipole rotational heating the conductivity (σ_0) and the heating rate could respectively be expressed by the following equations (2.12) and (2.13) (Schiffmann, 1987; Owusu-Ansah, 1991)

$$\sigma_0 = 2\pi f\varepsilon \tan\delta \tag{2.12}$$

where f is the frequency of the field.

The heating rate for dipolar rotation is

$$\frac{P_v}{V_v} = kE^2 f\varepsilon \tan\delta \quad \text{or} \quad \frac{P_v}{V_v} = kE^2 f\varepsilon' \tag{2.13}$$

where P_v = power

V_v= volume of material

k = constant dependent upon the units of measurement used

E = electric field strength, in volts per unit distance

f = frequency

ε = relative dielectric constant

$\tan\delta$ = loss tangent or dissipation factor

ε' = loss factor

The heat generated in a given medium depends primarily on three variables: the intensity of applied field, its frequency, and the dielectric loss factor of the medium. Water is a particularly lossy medium and most solid portions of the materials to be heated have molecules that are not so lossy, hence drying is one of the most prevalent applications of dielectric heating. Food systems generally have high dielectric constants due to its high water content. They also have relatively high loss tangents (0.1-1.0) that make them good materials for microwave attenuation (Owusu-Ansah, 1991).

2.3.4 Microwave drying

Microwave drying is based on the absorption of microwave radiation by the water molecules in the sample. This results in heat generation that leads to vaporization of water and volatile components. The preferred frequency for drying processes is 2.45 GHz at a wavelength of 122.4 mm. At this level, microwaves cause the molecules of suitable materials to vibrate, and this vibration creates intermolecular heat that causes the water within the material to evaporate. The method is not suitable for samples with very low or no moisture.

2.3.4.1 Factors affecting microwave drying

Dehydration and heating of foods are the major application areas for microwave heating, especially for granular materials and larger, regularly shaped pieces of food. However, it is not economical to use microwave heating for the complete drying of high moisture of foods, but rather as a complement to conventional heating to greatly accelerate the later stages of the process. Evaporation of water from the surface during the constant rate period of drying is best done by air convection or radiation. The constant rate period can be extended by balancing the internal moisture transport, intensified by deep microwave heating, to surface evaporation in an optimal way so that case hardening and shrinkage are prevented, while significantly reducing drying time and processing costs (Funebo and Ohlsson, 1998). The following related factors are summarized while considering microwave drying.

2.3.4.1.1 Penetration depth

The penetration depth is conveniently used in various applications of microwaves in food industry. The microwave penetration of products is determined by factors such as electrical and compositional properties of the material. Assuming microwaves impinge on a hypothetical large surface of a piece of plane (Figure 2.12), in general, some amount of the incident wave is reflected, some progressively attenuated and thus decreased in magnitude as it penetrates into the plane. If the power of the incident wave is represented as P_i, the reflected power represented as P_f and the residual power at a distance of m from the surface is represented as P_m, then the attenuated power (P_a) can be represented as follows:

$$P_a = P_i - (P_f + P_m) \tag{2.14}$$

For food material $\sqrt{\varepsilon}$ is so large that at 2450MHz the wavelengths are small. If the incident wave is perpendicular to the surface of the material then the reflected power relative to the incident power may be approximately represented as (Risman, 1988; Owusu-Ansah, 1991):

$$\frac{P_f}{P_i} = \frac{(1-\sqrt{\varepsilon})^2}{(1+\sqrt{\varepsilon})} \tag{2.15}$$

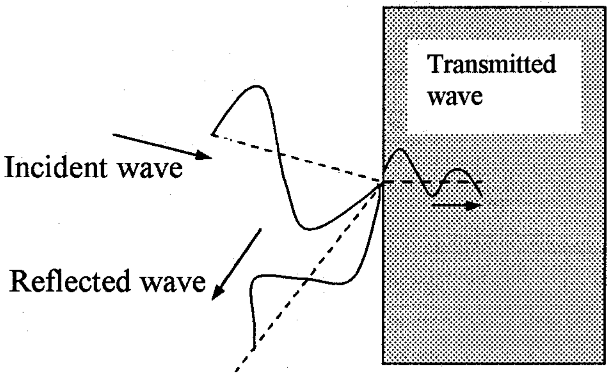


Figure 2.12 Distribution of microwave incident on a Plane surface

To gain a practical understanding of the meaning of the values of the dielectric properties, a penetration depth can be calculated from the dielectric properties. Theoretically, the penetration depth d_p (or power penetration depth) is defined as the depth below a large plane surface of a substance at which the power density of a perpendicularly impinging, forward propagating plane electromagnetic wave has decayed by 1/e (1/e is about 37 %). If tan δ is smaller than about 0.5, the following simplified formula gives 97% to 100% of the correct value (Ohlsson, 1989; Risman, 1991):

$$d_p = \frac{\lambda_0 \sqrt{\varepsilon}}{2\pi\varepsilon'} \tag{2.16}$$

where λ_0 = free space wavelength.

The absorbed power density near the surface of an infinite inhomogeneous plane is approximately proportional to ε' when ε does not vary very much. If tan δ is greater than 0.5, the more exact formula should be used (Risman, 1988):

$$d_p = \frac{\lambda_0}{2\pi\sqrt{2}} \left(\varepsilon[\sqrt{1+(\varepsilon'/\varepsilon)^2} - 1]\right)^{-1/2} \tag{2.17}$$

When a dielectric material is introduced into an AC current containing a capacitor, the angular lead of the current over the voltage is reduced from the 90° exhibited for ideal capacitors (Owusu-Ansah, 1991). This reduction in angular lead of the current over the voltage is known as the loss tangent (tan δ). The tan δ provides indications on the penetration depth and is related to the half-power penetration depth D_{50} by the following equation (2.18, 2.19) (Schiffmann, 1987).

$$D_{50} = \frac{0.189\lambda_0}{\sqrt{\varepsilon}\sqrt{\sqrt{1+\tan^2\delta}-1}} \tag{2.18}$$

for small tan δ<<1,

$$D_{50} = \frac{0.269\lambda_0}{\sqrt{\varepsilon}\tan\delta} \tag{2.19}$$

From these equations it is obvious that materials with high dielectric constants and loss tangents will have smaller depths of penetration than those with lower values. These parameters dictate the efficiency or even the propensity for microwave attenuation in materials and indicate that, depending on factors such as composition, temperature or moisture content of the material, microwave heating in a material could be a surface phenomenon rather than the conventional misconception of internal heating (Owusu-Ansah, 1991).

2.3.4.1.2 Dielectric properties

The dielectric properties describe how materials interact with electromagnetic radiation. The relative permittivity ε is a measure of the polarizing effect from an external field, i.e., how easily the medium is polarized. The absolute permittivity in vacuum is ε_0 and it is determined by the speed of light (c_0) and the magnetic constant (μ_0), which are linked by equation (2.20) (Ryynänen, 1995, 2002):

$$c_0^2\mu_0\varepsilon_0 = 1 \tag{2.20}$$

The numerical value for ε_0 is $8.854\text{x}10^{-12}$ F/m. In other media (solid, liquid and gaseous), the permittivity has higher values and it is usually expressed relative to the value in vacuum (Nafors and Vainikainen, 1989):

$$\varepsilon_{abs} = \varepsilon_r \times \varepsilon_0 \tag{2.21}$$

where ε_{abs} is absolute permittivity of a material and ε_r is relative permittivity of a material. It is often recommended that the subscript r, which stands for relative, be eliminated. The high frequency and microwave fields are sinusoidal time-dependent (time-harmonic) and common practice is to use complex notation to express the time dependence (Nafors and Vainikainen, 1989). Therefore, the permittivity will also be a complex quantity with real and imaginary components (Risman, 1991, 1994). The equation for complex permittivity (ε^*) is:

$$\varepsilon^* = \varepsilon - j\varepsilon' \tag{2.22}$$

where $j = \sqrt{-1}$ and the real part is called the dielectric constant, ε, which signifies reversible interactions. The imaginary part, the loss factor ε', describes lossy interactions.

The imaginary component is related to various absorption mechanisms of energy dissipation and is always positive and usually much smaller than ε. It is approximately proportional to the attenuation of a propagating wave. The substance is microwave lossless if $\varepsilon' = 0$ (Nafors and Vainikainen, 1989; Mudgett, 1995). The ratio of ε' to ε is called the (dielectric) loss tangent ($\tan \delta$). This factor measures the amount of energy dissipated when a material is subjected to an alternating current. The relative dielectric loss factor (ε') is related to the dielectric constant (ε) as shown in equation (2.23).

$$\varepsilon' = \varepsilon \tan \delta \tag{2.23}$$

The dielectric constant predominantly provides indication on the reflection properties and wavelength in the material and is related to the wavelength in the material as follows:

$$\lambda = \frac{\lambda_0}{\sqrt{\varepsilon}} \tag{2.24}$$

where: λ = wavelength in material

λ_0 = wavelength in free space

The dielectric properties of food products are determined by their chemical composition and, to a much lesser extent, by their physical structure. The influence of water and salt (or ash) content depends to a large extent on the manner in which they are bound or restricted in their movement by the other food components. This complicates the prediction of the dielectric properties of a mixture, based on data for single ingredients (Mudgett, 1995). There have been some attempts to predict dielectric properties of foods (Calay, et al., 1995; Datta, et al., 1995). They found that although significant data exist in the literature, there was much variability due to different measuring techniques, variations in composition, etc. (Schiffmann, 1987; Ryynänen, 2002).

The dielectric properties of some foods can be found in the literature (Tinga and Nelson, 1973; Stuchly and Stuchly, 1980; Kent, 1987; Thuery, 1992; Datta et al., 1995) and in databases. The most common food products have a loss factor of less than 25 and permittivity (dielectric constant) between 30 and 80, which implies a penetration depth of 0.8 to 1.5 cm. However, literature data is mostly limited to food ingredients and their components. For complex foods the dielectric properties must be measured or estimated (Ohlsson, 1989; Buffler and Stanford, 1991; Calay et al., 1995).

Generally, the dielectric properties of a material are dependent on various factors such as temperature, physical structure, frequency, and chemical composition. Materials with high dielectric loss factors are termed loss materials and these attenuate microwaves. Dielectric properties are considered in the context of the behavior of materials during dielectrically enhanced drying.

2.3.4.1.3 Moisture content

Moisture exists in materials in different forms. In drying practice, non-hygroscopic materials contain a significant amount of free water but little bound water, while hygroscopic materials have a significant level of bound water. Free water retained in the void space of the porous material exerts an equilibrium vapor pressure as defined by the Claperyon equation. Bound water is retained in such a way that it exerts less than its equilibrium vapor pressure. Bound water has less rotational freedom and absorbs less energy from the field, resulting in lower values for ε'. Thus, typically ε' and ε are both lower in absolute value for materials containing less free moisture and exhibit a more gradual rise with increasing bound moisture content (Schiffmann, 1987; Ryynänen, 2002). Substantial increases in the loss factor are observed only when significant free water is present in the material. For pure water, ε' decreases rapidly with increasing temperature (Schiffmann, 2002).

To et al. (1974) measured the dielectric properties for beef and turkey products at 300, 915 and 2450 MHz and concluded that moisture content is important, but at the same time both ash and protein content can also affect dielectric properties. Carbohydrates do not show appreciable dipole polarization at microwave frequencies. For fats and oils, both ε and ε' are very low (Bengtsson and Risman, 1971). Both ε and ε' are low also for flours at microwave frequencies as long as water content is low (Kent, 1987). Vegetables have quite high permittivity in accordance with their high water content (Bengtsson and Risman, 1971). For dried vegetables, ε and ε' are low as the water content is low.

Salts dissolved in aqueous solutions act as conductors in an electromagnetic field. They simultaneously depress the permittivity and elevate the dielectric loss factor compared to the behavior of pure water. The depression of ε results from the binding of free water molecules by counter-ions of dissolved salts, and the elevation of ε' results from the addition of conductive charge carriers (dissolved salts). Both ε and ε' depend on the concentration of the aqueous ionic solution. The major effect of undissolved structural or colloidal organic solids is to exclude more dielectrically active materials (mainly water) from the total volume, thus depressing the permittivity. The properties of undissolved food solids, and also fats and oils, are similar to those of ice at temperatures near the freezing point and they are relatively independent of frequency and temperature (Bengtsson and Risman, 1971; Mudgett, 1995).

The permittivity of aqueous solutions or mixtures is decreased by two mechanisms: the replacement of water by a substance with a lower permittivity and the binding of water molecules. When the size of non-homogeneities (particles, grains) is much smaller than the wavelength, the effective permittivity of the mixture depends only on the shape of the non-homogeneities, not on their size. Attempts to predict the dielectric behavior in the microwave range of both polar - polar or polar - non-polar mixtures have not been successful. This is due to the complexity in deriving expressions for the local electric field that account accurately for the dipole-dipole and dipole-induced dipole interactions (Bertolini et al., 1983).

Because the relaxation is due to the mobility of the molecules, bound molecules have a lower relaxation frequency than free water molecules. The static permittivity for the most tightly bound molecules has about the same value as ice (Risman, 1988; Nafors and Vainikainen, 1989). Many frozen products may be viewed as homogeneous mixtures of solids (mostly ice) and aqueous ions. Since the dielectric properties of ice and water are widely different at microwave frequencies, both ε and ε' increase strongly with rising temperature during the thawing of high water content materials, which includes most foods. After thawing, the values again decrease with increasing temperature (Bengtsson and Risman, 1971).

In addition, heating characteristics also vary with particle size, homogeneity, and distribution. For example, laminated or fibrous structures have higher ε than do granular ones. The effects of pH are not believed to be significant per se (Ohlsson et al., 1974; Nafors and Vainikainen, 1989). The large differences in both dielectric and thermal properties between frozen and thawed foods can cause difficulties in thawing.

2.3.4.1.4 Temperature effects

In a microwave or high frequency field, the dipoles try to follow the rapidly changing field. The dipoles are not completely oriented due to the disorienting effect of thermal motion. This phenomenon is strongly temperature dependent; with rising temperature the thermal agitation becomes more vigorous. Elevations in temperature raise the mobility of ions in solution as well as the rotational and vibrational energies.

Although ε varies with water content, temperature has only a minor effect. The dielectric constant is not strongly affected by temperature in liquids; for water at 25°C it is 77, while at 95°C it is 52 (Ryynänen, 2002). The loss factor of distilled water decreases from 1.2 to 0.36 at 1 GHz and from 12 to 2.44 at 3 GHz as the temperature increases from 25°C to 95°C. For nonhygroscopic materials, as the temperature rises, the loss factor decreases. Near room temperature, the ionic conductivity of an electrolytic solution increases approximately 1.5 to 2% per Celsius degree (Schiffmann, 2002). Hygroscopic materials may be affected differently. If there is a large enough bound moisture, the loss factor of the material exhibits an increase with increasing temperature. The loss factor of the solid portion is seldom significant, but for some materials, such as nylon and acrylics, an increase in loss factor at elevated temperatures may result in thermal "runaway", i.e., producing an unstable increase in heating rate which ultimately culminates in destruction of the structure. Therefore, it is important to define the operating conditions in dielectrically enhanced drying of these materials, especially at low moisture contents.

Preface to Chapter 3

Osmotic dehydration (OD) is a partial drying process for fruits, vegetables and other biological samples when immersed in a hypertonic solution. The driving force comes from the water and solute activity gradients across the interface of the sample and the solution. Mass transfer rate during osmotic dehydration depends on many factors such as: concentration, temperature, composition of the osmotic solution, immersion time, nature of the fruit and their geometry, solution agitation etc. (Roult-Wack, 1994). For developing food-processing technology based on OD process, it is important to understand OD kinetics so as to set the desired dehydration or impregnation levels during the process. In this study, kinetic parameters weight reduction (WR), moisture loss (ML), solids gain (SG), moisture loss rate (MLR) and solids gain rate (SGR) were investigated during osmotic dehydration process. Ratio of ML/SG, times to reach certain weight reduction (T_w), moisture loss (T_m) and solids gain (T_s) were used to evaluate osmotic dehydration (OD) efficiency.

A conventional diffusion model involving a finite cylinder was also used for moisture loss and solids gain, and the associated diffusion coefficients were computed. This work would partially fulfill the first objective of this thesis, and provide background for better understanding the following chapters.

Part of this research has been presented in some conferences and/or being prepared for publication in scientific journals detailed earlier. The experimental work and data analysis were carried out by the candidate under the supervision of professor Dr. H.S. Ramaswamy.

CHAPTER 3

OSMOTIC DEHYDRATION OF APPLE CYLINDERS UNDER CONVENTIONAL BATCH PROCESSING CONDITIONS

Abstract

Osmotic drying was carried out, with cylindrical samples of apple cut to a diameter to length ratio of 1:1, in a well agitated large tank containing the osmotic solution at the desired temperature. The solution to fruit volume ratio was kept greater than 30. A modified central composite rotatable design (CCRD) was used with five levels of sucrose concentrations (34-63 °Brix) and five temperatures (34-66°C). Kinetic parameters: weight reduction (WR), moisture loss (ML), solids gain (SG), moisture loss rate (MLR) and solids gain rate (SGR), were considered. A polynomial regression model was developed to relate moisture loss and solids gain to process variables. A conventional diffusion model involving a finite cylinder was also used for moisture loss and solids gain, and the associated diffusion coefficients were computed. Results indicated that higher concentration and temperature gave higher MLR and higher SGR. Ratio of ML/SG could describe osmotic dehydration (OD) efficiency. The calculated moisture diffusivity ranged from 8.20×10^{-10} to 24.26×10^{-10} m^2/s and the solute diffusivity ranged from 7.82×10^{-10} to 37.24×10^{-10} m^2/s. Suitable ranges of main parameters were identified for OD kinetics further study.

3.1 Introduction

Water is partly removed by osmotic dehydration (OD) when immersing fruits or vegetables in a hypertonic solution. The driving force comes from the water and solute activity gradients across the interface of the sample and the solution. Mass transfer rate during osmotic dehydration depends on many factors such as: concentration, temperature, composition of the osmotic solution, immersion time, nature of the fruit and their geometry, solution agitation etc. (Roult-Wack, 1994). For developing food-processing technology based on OD process, it is important to understand OD kinetics so as to set the desired dehydration or impregnation levels during the process.

The influence of main process variables *e.g.* the concentration and composition of osmotic solution, temperature, process time, effect of agitation, solution/sample ratio on the mass transfer mechanism and the product quality have been studied extensively (Ponting, et al., 1966; Farkas and Lazar 1969; Islam and Flink 1982; Conway, et al., 1983; Lenart and Lewicki 1990; Rastogi & Raghavarao 1994; Lazarides, et al., 1995, a & b; Nsonzi and Ramaswamy 1998; Nieuwenhuijzen, et al., 2001; Genina-Soto, et al., 2001; Kowalska and Lenart, 2001; Ramaswamy and Nieuwenhuijzen, 2002). Among these variables, the concentration and temperature of the osmotic solution, and contact time of the sample with osmotic solution are the most important factors that affect the osmotic dehydration process. A higher solution concentration, a higher temperature and longer contact time increase the water loss and solids gain. The rate of mass transfer can be predicted using unsteady state diffusion model (Fick's second law). Crank (1975) has made a detailed theoretical description of the diffusion process. Analytical solutions of the equation are available for idealized geometric, i.e. spheres, infinite cylinders, infinite slabs, and semi-infinite medium. This allowed the estimation of the diffusion coefficients for both water loss and solid gain individually or simultaneously. However, only limited research has been carried out on finite apple cylinders under typical osmotic dehydration conditions that describe mass transfer phenomenon. Conventional diffusion modeling of the osmotic process would require data on mass transfer properties of the material in contact with the osmotic solution (Biswal and Le Maguer 1989; Marcotte, et al., 1991).

The objective of the study was to determine the influence of process temperature, solution concentration and contact time on mass transfer of water and sucrose during the osmotic dehydration of apple cylinders, in order to develop a comparative database and for selecting suitable conditions for further testing of osmotic dehydration methods (continuous flow and microwave assisted systems detailed in other chapters).

3.2 Materials and methods

3.2.1 Materials

Apples (Idared variety) of uniform size and ripeness, was obtained from the local farm of the campus and commercial sucrose (sugar) was obtained from a local supermarket. The fruits were stored refrigerated at 2°C-5°C and at 95% relative humidity until used for experiments. After cutting calyx end and pedicel end, apple cylindroids were cut vertical to their axis and five cylinders of 2.0 cm in diameter, 2.0 cm in height were prepared from each fruit.

3.2.2 Osmotic dehydration procedure

Osmotic dehydration was carried out using five different solutions: 34, 40, 50, 60 and 63°Brix; and five temperatures 34, 40, 50, 60 and 66°C. Higher concentration posed difficulty for thorough mixing of the solution and for achieving satisfactory mass transfer characteristics because of the dramatic increase in viscosity of the osmotic medium; lower concentration were not suitable because of the reduction in dehydration driving force between the external solution and the internal solution of the sample. Also, higher temperatures could not be used without severe negative side effects, i.e. tissue softening, enzymatic browning and loss of aroma. On the other hand, lower temperatures would again prohibit thorough mixing and satisfactory mass transfer characteristics because of the temperature related increase in viscosity of the osmotic medium. The fruit-syrup mass ratio (R) was kept high (1:30) and circulated with two high speed paddle mixers. At the end of 0.25, 0.5, 1, 1.5, 2, 2.5, 3, 4.5 and 5.5 h immersion, samples were removed from the solution, quickly rinsed, gently blotted dry with a paper towel to remove adhering osmotic solution and then analyzed. All experiments were performed at least in triplicate and average values were reported.

3.2.3 Analyses

The sugar concentration was measured with a portable refractometer (ATAGO, Japan) at 20°C. Moisture content of fresh and osmotically treated apple cylinders were determined by an oven method. The moisture content and total solids were measured gravimetrically on apple cylinders after different contact times. For measuring solids content, sample were air dried in a convection oven at 105°C for 24h.

3.2.4 Weight reduction, moisture loss and solids gain

The weight reduction, moisture loss and solids gain were calculated based on the general balance of concentration driven mass transfer between the liquid and solid phases:

$$\%WR = 100\frac{M_o - M_t}{M_o} \qquad (3.1)$$

$$\%ML = 100\frac{(M_0x_0 - M_tx_t)}{M_0} \tag{3.2}$$

$$\%SG = 100\frac{(M_ts_t - M_0s_0)}{M_0} \tag{3.3}$$

where: M_0 and M_t are the sample mass (kg) at time 0 and time t; x_0 and x_t are the moisture fractions (kg/kg wet basis) at time 0 and time t; s_0 and s_t are the solid fractions (kg/kg wet basis) at time 0 and time t. These equations are based on the assumption that no solids leaked into the solution.

3.2.5 Rate of moisture loss and rate of solids gain

The rates of moisture loss and solids gain in a given time interval were calculated using the following equation:

$$MLR_i = \frac{ML_i - ML_{i-1}}{t_i - t_{i-1}} \tag{3.4}$$

$$SGR_i = \frac{SG_i - SG_{i-1}}{t_i - t_{i-1}} \tag{3.5}$$

where MLR_i and SGR_i were the moisture loss rate and the solids gain rate between time t_i and t_{i-1}, h^{-1}, respectively. ML_i and SG_i were the fraction moisture loss and the fraction solids gain at time t_i, respectively; ML_{i-1} and SG_{i-1} were the fraction moisture loss and the fraction solids gain at time t_{i-1}, respectively.

3.2.6 Time to get the sample 20% weight reduction, 25% moisture loss and 5% sample solids gain (T_w, T_m and T_s)

The osmotic dehydration time to get the sample weight reduction, moisture loss and solids gain to a given value can be used to compare the osmotic drying effectiveness of different conditions. To be able to compare the different runs in the experimental set up, a level of 20% sample weight reduction and 25% sample moisture loss, and a level of 5% sample solids gain were chosen such that they covered all experimental conditions and times were computed to result in such weight reduction, moisture loss and solids gain using the equations 3.1-3.3.

3.2.7 Process modeling

Mass transfer rate of solutes or water in cellular solids is approximately predicted by the appropriate solutions of simplified unsteady state Fickian diffusion equation under defined initial and boundary conditions. The following assumptions are made:

- The sucrose concentration is constant during the dehydration process.
- The mass transfer coefficient between the sucrose solution and the fruit is infinite, which means that the surface of the apple cylinders assumes the conditions of moisture and solid content of the sucrose solution instantaneously.
- The diffusion process only involves transfer of moisture out of the fruit and solids into the fruit.
- The process is isothermal.
- Each apple cylinder is homogeneous and isotropic with a uniform initial moisture and solids distribution.
- Moisture migration is unidirectional from the center towards the surface of the cylinder.
- The effect of shrinkage is negligible since the solids gain during osmotic dehydration is expected to compensate for product shrinkage.
- The cylinders in each run are of a uniform size.
- The equilibrium moisture loss and solids gain were predicted by Azuara model, concentration was the limit factor affecting equilibrium moisture loss and solids gain.
- The mass diffusivity depends on the conditions of osmotic dehydration only.

For dimensionless mass ratios (M) under transient conditions, the following equation is given for an infinite slab or plate:

$$M = \sum_{n=1}^{\infty} \frac{2\sin\beta_n}{\beta_n + \sin\beta_n \cos\beta_n} * \cos(\beta_n x / l) * e^{-\beta_n^2 F_o} \qquad (3.6)$$

where β_n is the nth positive root of $\beta \tan\beta = Bi$. l = half thickness of a plate (m), x = distance from the plane of the slab with the highest concentration water and the lowest concentration sugar (m). $Fo = Dt/d^2$, D = diffusion coefficient (m^2/s), t = contact time (s) and *l* = thickness of slab (m).

For an infinite cylinder M is defined as follows (Ramaswamy, et al., 1982):

$$M = 2 * Bi \sum_{n=1}^{\infty} \frac{J_o(\gamma_n r / d)}{(Bi^2 + \gamma_n^2) J_o(\gamma_n)} * e^{-\gamma_n^2 F_o} \qquad (3.7)$$

where γ_n is the nth positive root of $\gamma J_1(\gamma) = Bi\ J_0(\gamma)$. J_0 and J_1 = Bessel function of order zero and one respectively, r = radius of the cylinder (m), d = diameter of the cylinder (m).

Bi is formulated for mass transfer as follows: Bi = kr/Dρ_s, with k = convective mass transfer coefficient (m^2/s kg), and ρ_s=density of bone dry apple (kg/m^3).

For sufficiently long contact times the terms in the infinite summation series converge rapidly, which makes it possible to simplify the formula by using only the first term. Furthermore, the formulas where simplified for center mass contents (x = r = 0). For an infinite slab or plate the equation becomes as follows:

$$M_{op} = R_p e^{(-S_p F_o)} \tag{3.8}$$

and for an infinite cylinder:

$$M_{oc} = R_c e^{(-S_c F_o)} \tag{3.9}$$

R$_p$, R$_c$, S$_p$ and S$_c$ are the characteristic functions of Biot number. For an infinite Biot number the values are given in table 3.1.

Table 3.1. Values of R and S for infinite Biot numbers. (Ramaswamy et al., 1982)

Infinite slab		Infinite cylinder	
R_p	S_p	R_c	S_c
1.273	2.467	1.602	5.783

The mass average concentration (C$_m$) is defined as follows:

$$C_m = \int_o^V \frac{C}{V} dV \tag{3.10}$$

where C is a function of V, V = volume (m^3).

The mass average concentration ratios for an infinite slab (M$_{mp}$) and an infinite cylinder (M$_{mc}$) are as follows:

$$M_{mp} = \frac{1}{l}\int_o^x M_{xp} dx = \frac{1}{l}\int_o^x M_{op} \cos(S_p^{1/2} x / l) dx \tag{3.11}$$

$$M_{mc} = \frac{2}{d^2}\int_o^a M_{xc} r dr = \frac{2}{d^2}\int_o^2 M_{oc} J_o(S_c^{1/2} r / d) r dr \tag{3.12}$$

By integration between the limits the following final equation is obtained:

$$M_{mp} = M_{op} \frac{\sin S_p^{1/2}}{S_p^{1/2}} \tag{3.13}$$

$$M_{mc} = M_{oc} \frac{2J_1 S_c^{1/2}}{S_c^{1/2}} \tag{3.14}$$

When tables are not available for the Bessel function, M_{mc} can be approximated, using an empirical equation, suggested by Ramaswamy et al. (1982):

$$M_{mc} = M_{oc}(1 - 0.1250 S_c + 5.208 * 10^{-3} S_c^2 - 1.085 * 10^{-4} S_c^3 + 1.351 * 10^{-6} S_c^4 \tag{3.15}$$

The unsteady mass concentration in a finite cylinder (M_{mfc}) can be obtained by combining an infinite plate and an infinite cylinder as follows:

$$M_{mfc} = M_{mp} * M_{mc} \tag{3.16}$$

The final formula for a finite cylinder is as follows (when length is equal to diameter):

$$M_{mfc} = 0.56 e^{-\frac{8.25}{d^2} Dt} \tag{3.17}$$

where the moisture loss ratio (M_{mfc}) is defined as follows for water transfer:

$$M_{mfcw} = \frac{M_e x_e - M_t x_t}{M_e x_e - M_o x_o} = \frac{ML_\infty - ML_t}{ML_\infty - ML_o} \tag{3.18}$$

where x_t and x_e represent the water content at time 0, t and equilibrium respectively, M_0, M_t and M_e represent the sample masses at time 0, t and equilibrium respectively. ML_∞, ML_t and ML_o represent the sample moisture loss at equilibrium, time t and time 0, respectively. The solids gain ratio (M_{mfcs}) is:

$$M_{mfcs} = \frac{M_e s_e - M_t s_t}{M_e s_e - M_o s_o} = \frac{SG_\infty - SG_t}{SG_\infty - SG_o} \tag{3.19}$$

where s_0, s_t and s_e represent the solids content at time 0, t and equilibrium respectively. SG_∞, SG_t and SG_o represent the sample solids gain at equilibrium, time t and time 0, respectively. By plotting M_{mfcw} and M_{mfcs} against contact time the diffusion coefficient D (m^2/s) can be obtained from the slope of the curve.

3.2.8 Ratio of moisture loss over solids gain

The ratio of ML/SG was used to describe osmotic dehydration efficiency and calculated with ML over SG.

$$ratio = \frac{ML}{SG} \tag{3.20}$$

3.2.9 Experimental design and statistical analysis

The experimental design adopted was a modified configuration of Box's central composite design for two variables at five levels each. The two independent variables were process temperature and solute concentration, while the contact time was not followed the design. The complete design included additional conditions over and above the central composite for a total of 13 experiments with 3 replications of central point. The actual values are given in Table 3.2.

Table 3.2.Experimental conditions used for the osmotic dehydration process

Design points No	Time hr	Temperature (°C)	Concentration (°Brix)
1	0.25, 0.5-5.5	40	40
2	0.25, 0.5-5.5	60	40
3	0.25, 0.5-5.5	40	60
4	0.25, 0.5-5.5	60	60
5 x 3	0.25, 0.5-5.5	50	50
6	0.25, 0.5-5.5	50	34
7	0.25, 0.5-5.5	66	50
8	0.25, 0.5-5.5	50	63
9	0.25, 0.5-5.5	34	50
10	0.25, 0.5-5.5	50	40
11	0.25, 0.5-5.5	60	50

The results obtained from the kinetics data handling were analyzed using the Statistical Systems (SAS, 1999) software. The general second-order polynomial equation given below was used to relate %ML, %SG, moisture diffusivity (D_m) and solids diffusivity (D_s) to the temperature, sucrose concentration and contact time between sample and solution.

$$y = b_o + \sum_{i=1}^{k} b_i x_i + \sum_{i=1}^{k} b_{ii} x_i^2 + \sum_{i=1}^{k-1} \sum_{j=i+1}^{k} b_{ij} x_i x_j \tag{3.21}$$

where: y is the response %ML, %SG, D_m and D_s; b_o, b_i, b_{ii}, b_{ij} are constant coefficients; x_i and x_j represent the temperature, sucrose concentration and, for the analyses where %ML %SG, D_m, and D_s are the response, contact time during osmotic dehydration.

3.3 Results and discussion

3.3.1 Weight reduction (WR)

3.3.1.1 Modeling WR

The percentage of weight reduction (%WR) was related to temperature, solution concentration and contact time as following equations using the statistical analysis software (SAS, 1999).

$$WR\% = -7.0276 - 0.5939*t + 0.1462*T - 0.1046*C + 0.0825*t*T + 0.1620*t*C - 1.1726*t^2 \quad (R^2 = 0.95) \qquad (3.22)$$

Figure 3.1 shows the goodness of the developed models in the form of experimental data vs predicted data with the diagonal line representing the ideal performance. The degree scatter of points around the diagonal line thus represented some deviation from an ideal prediction.

Weight reduction from test samples under selected conditions are shown in Figure 3.2, indicating relatively smooth progression of drying despite the fact that most data points came from several independent test runs. Weight reduction was noticeably different for the different conditions of temperature and concentration of sugar solutions. Weight reduction increased with time, but after 2 hours weight reduction slowed down; however, even after 4 hours a complete equilibrium was not reached for weight reduction. The dehydration curves obtained under a temperature-sucrose concentration conditions of 40°C-60°Brix and 60°C-40°Brix overlapped. That meant for a given condition, a similar percentage weight reduction (%WR) could be attained by either increasing temperature without increasing sucrose concentration or increasing sucrose concentration without increasing temperature. Nsonzi and Ramaswamy (1998) reported similar results for osmotic dehydration of blueberry at 50°C-50°Brix, 40°C-60°Brix and 45°C-55°Brix. Nieuhuijzen *et al.* (2001), Conway *et al.* (1983) reported same osmotic moisture loss behavior for apple slices dehydrated at 40°C-60°Brix, 50°C-50°Brix, and

30°C-70°Brix. Figure 3.2 also shows that higher temperature-high concentration condition (60°C-60°Brix) gave the highest weight reduction and low temperature-low concentration (40°C-40°Brix) gave the lowest weight reduction among them. An increase in concentration of the solution by 20°Brix had more effect on weight reduction than an increase in processing temperature by 20°C, which is agreement with Nieuwnhuijzen *et al.*(2001) results. The weight reduction also increased with increasing temperature, and even sharper at higher temperature periods. Similar results were reported on osmotic dehydration of apple cubes, where weight loss at 85°C for 1-3 min was the same as that when treated for 2h at ambient temperature (Lerici, et al., 1985).

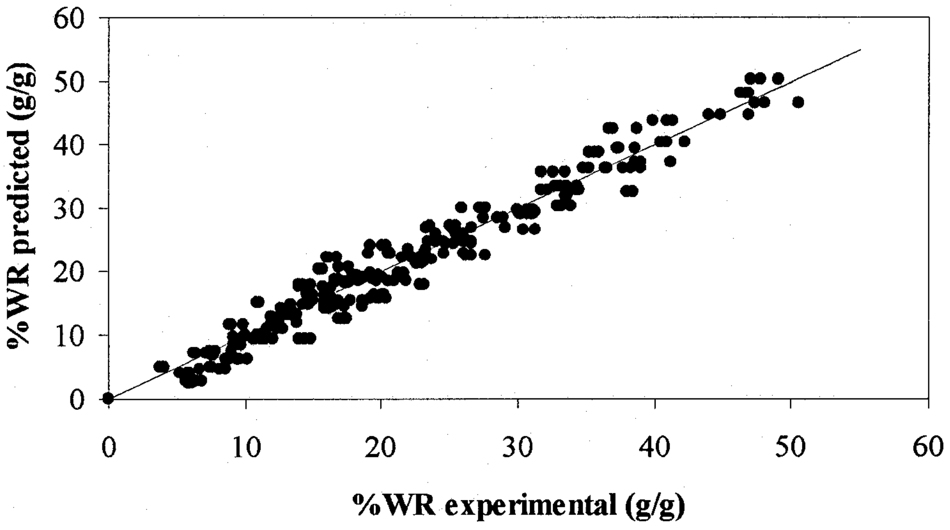


Figure 3.1 Performance testing of models for %WR

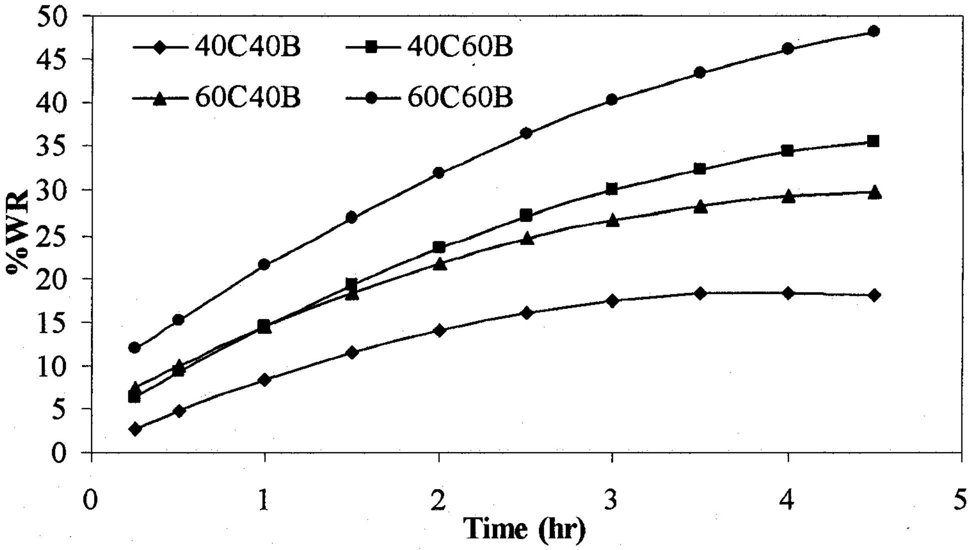


Figure 3.2 Weight reduction of sample as a function of contact time during osmotic dehydration under different conditions

3.3.2 Moisture loss (ML) and solids gain (SG)

3.3.2.1 Modeling ML and SG

The percentage of moisture loss (%ML) and solids gain (%SG) were related to temperature, solution concentration and contact time as following equations using the statistical analysis software (SAS, 1999).

$$ML\% = -40.7065 + 1.5256*t + 0.5025*T + 0.8847*C + 0.0951*t*T + 0.1558*t*C - 1.4396*t^2 - 0.0078*C^2 \quad (R^2 = 0.95) \qquad (3.23)$$

$$SG\% = -33.6789 + 2.1159*t + 0.3563*T + 0.9920*C + 0.0126*t*T - 0.0063*t*C - 0.2670*t^2 - 0.0031*T^2 - 0.0095*C^2 \quad (R^2 = 0.88) \qquad (3.24)$$

Figure 3.3 showed the fitting of the developed models in the form of experimental data vs predicted data with the diagonal line representing the ideal performance. Again there was some degree scatter of points around the diagonal line representng deviation from an ideal prediction. The figures confirmed that the model describing moisture loss was better than the model describing solids gain. A possible reason for the poorer model for the solids gain was the fact that the considerable amount of sucrose may stay on the surface of the apple piece which might be partially removed by the rinsing operation. Another reason might be due to the solids gain increased fast in the first 30 minutes during the dehydration process after which the solids gain increase rate may be reduced. Which has been quite the case in some previous studies (Fito, et al., 1996; Le Mageur, et al., 1996; and Giangiacomo, et al., 1987).

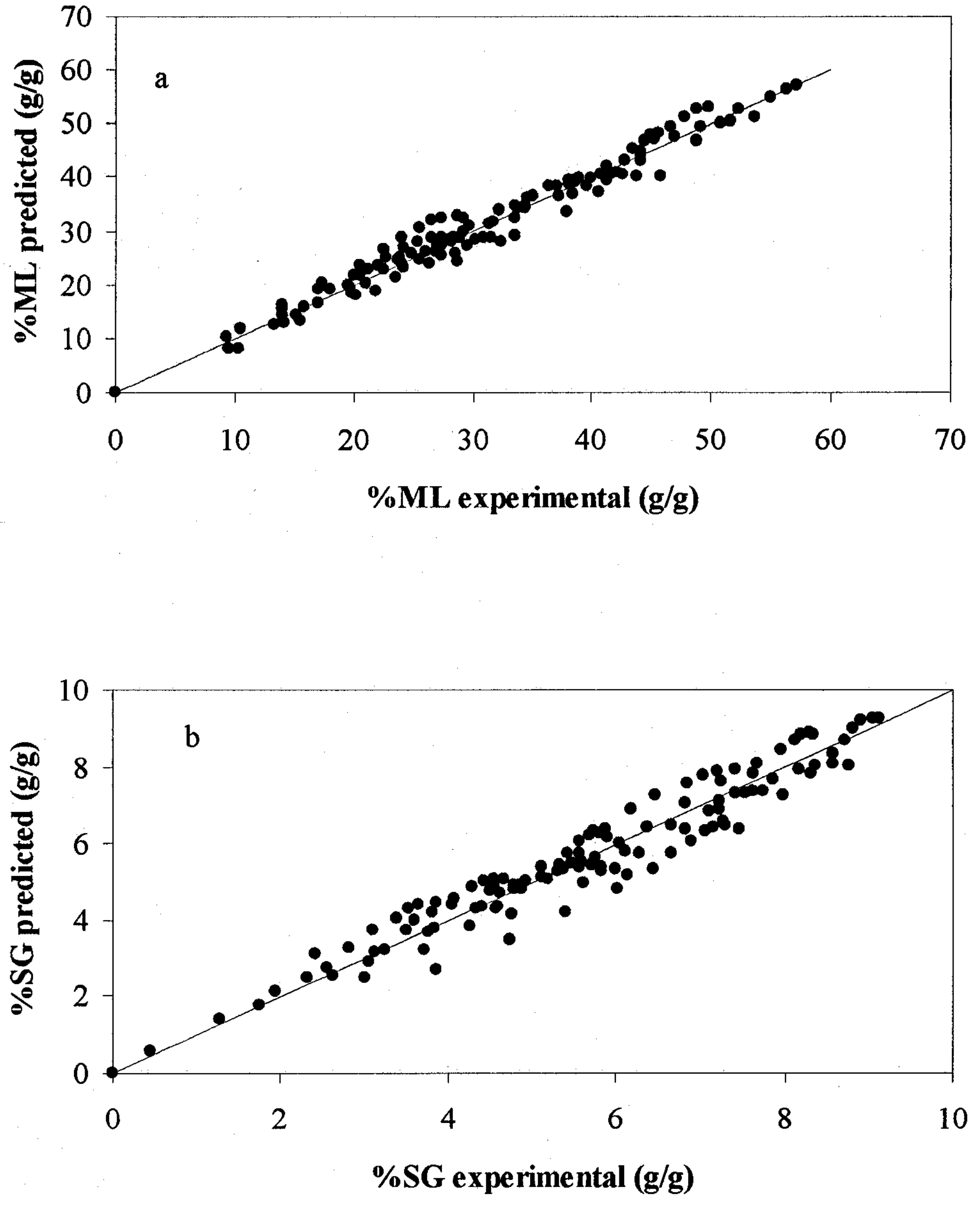


Figure 3.3 Performance testing of models for %ML (a) and %SG (b)

3.3.2.2 Factors affect ML and SG

The results of the analysis of variance (ANOVA) showed that solution concentration and contact time had a high significant effect on moisture loss ($p<0.01$) (Table 3.3). These results are in good agreement with those obtained in other similar studies (Nieuwnhuijzen, *et al.*, 2001; Nsonzi and Ramaswamy, 1998; Raoult-Wack, et al, 1994; Saurel, et al., 1994). The contact time had the largest influence on moisture loss, which is justified by the exponential shape of the dehydration curves (Figure 3.4). The quadratic effect of time and the interaction effects of time with temperature or concentration were highly significant ($P<0.001$) to moisture loss. The quadratic effect of concentration was high significant ($P<0.01$) to moisture loss. Whereas the quadratic effect of temperature and the interaction of temperature and concentration were not significant to moisture loss ($P>0.05$).

The individual effects of temperature and concentration on moisture loss (%ML) for apple cylinders are shown in Figure 3.4. The general trend was moisture loss increased with concentration and contact time increasing.

Table 3.3 ANOVA of the factors influencing moisture loss and solids gain during osmotic dehydration of apple cylinder

Source	Moisture loss (ML)		Solids gain (SG)	
	F value	Probability level	F value	Probability level
Main effects				
Time (t)	14.30	0.0002	70.14	<0.0001
Temp. (°C)	0.02	0.9010	1.96	0.1668
Conc. (°Brix)	8.37	0.0041	13.98	0.0002
Quadratic effects				
Time (t)	548.16	<0.0001	330.52	<0.0001
Temp. (°C)	0.10	0.7474	1.86	0.1738
Conc. (°Brix)	10.80	0.0011	20.48	<0.0001
Interactions				
t*T	77.49	<0.0001	29.11	<0.0001
t*C	117.05	<0.0001	0.13	0.7216
T*C	0.43	0.5122	0.83	0.3628

*P<0.05 significant, P<0.01 high significant, P<0.001 highly significant

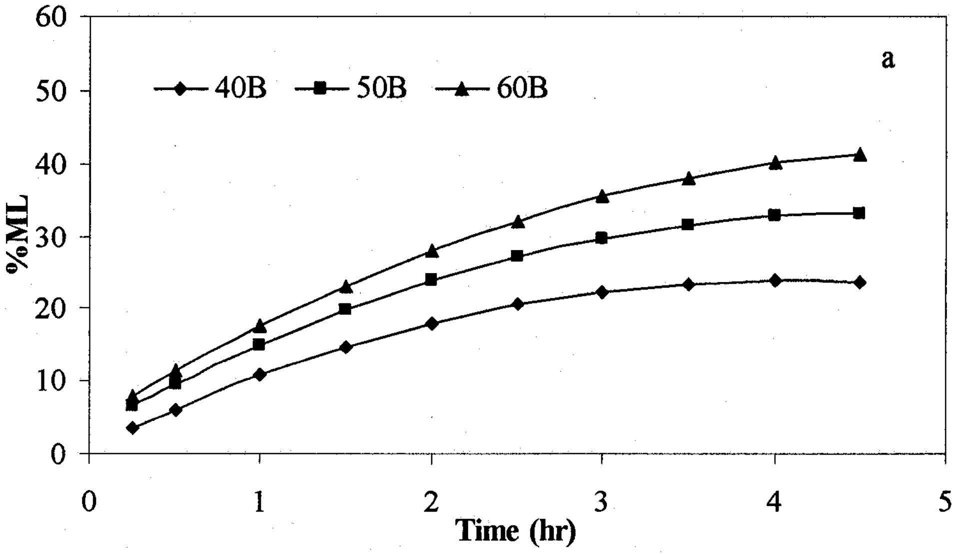
With respect to solids gain, contact time and solution concentration as well as the quadratic effects of time and concentration were highly significant ($p<0.001$) factors. The linear and quadratic effects of temperature were not significant ($P>0.05$) to solids gain. Whereas only the interaction effect of time and temperature was highly significant

(P<0.001) factor, the interaction effect of time and concentration or interaction effect of temperature and concentration were not significant (P>0.05) to solids gain. Again, the contact time had the largest influence on solids gain. The solids gain (%SG) as a function of dehydration time for the different conditions is presented in Figure 3.5. A significant increase of SG was observed within the initial period of 2 hr, even though SG continuous increased similarly after 4 hr osmosis, Ertekin *et al.* (1996) reported same results. However, some authors (Raoult-Wack, 1991; Lerici *et al.* 1985; Biswal and Bozorgmehr, 1992) found that after 2 hours of osmotic treatments the solids gain stabilized in a model agar gel and apple.

From Figure 3.5, solids gain can be observed to be different for different conditions of temperature and concentration of sugar solutions. The %SG variations were also found to be exponential to temperature and concentration. The general trend was solids gain increased with temperature, concentration and contact time increasing. However, solids gain under much higher concentration, 60°Brix conditions, was lower than 50°Brix condition. That might due to too high concentration promote formation of a dense superficial layer, which could block the escape of solutes contained within the fruit. The solution viscosity for 40°C-50°Brix was 7.03mPa and for 40°C-60°Brix was 16.87mPa, an increase of 140%; for 60°C-50°Brix was 3.87mPa and for 60°C-60°Brix was 8.22mPa, an increase of 112%. This mechanism was discussed by Raoult-Wack et al. (1991) for solute uptake in an agar-agar layer model gel. These authors suggested that all effects that favored dewatering would enhance the concentrated superficial layer and could halt or reduce solute uptake. When temperatures were too high, destructive structural changes occurring in the cell membranes and their selective properties were lost. The overall effects would detriment the cell biology properties so as to affect the ML and SG. Whereas when cells remain intact, osmosis was the local driving force for water transport towards the free intercellular spaces and the overall cause of water extraction from the product.

Earlier studies have showed that, during osmotic preconcentration sucrose penetrates only to a depth of *ca* 2-3 mm (Lenart & Flink, 1984a). Progressive sugar uptake results in the formation of a high sugar subsurface layer. Such a layer interferes with the concentration gradients across the product-medium interface and acts as a barrier against further removal of water and uptake of sugar (Hawkes & Flink, 1978). Besides, rapid loss of moisture and uptake of sugar near the surface in the beginning result in structural changes (*i.e.* shrinkage and collapse of surface cells), leading to compaction of the surface layers and increased mass transfer resistance for water and solutes (Lenart & Flink, 1984b). Decreasing availability of free or loosely bound water could be another factor leading to progressively slower moisture removal with the process proceeding. Even though, our results indicated that by choosing a higher concentration medium (60°Brix) we have some benefit in terms of faster moisture loss (20% increase) compared with 50°Brix at first 2hr over the same time period. Genina-Soto et al. (2001), studied and reported that increasing the sucrose concentration from 30% to 70%, caused a mass reduction of up to 20%. Similar results had been reported by other authors (Pointing, et al., 1966; Farkas and Lazar, 1969; Lenart and Flink, 1984b; Ertekin and Cakaloz, 1996; Nieuwenhuijzen, et al., 2001), who found that an increment on the sucrose concentration, cause a rise in the driving force for the water loss.

It is also important to notice that, in every temperature /concentration combination tested, moisture loss and solid gain increased with each other throughout the treatment for dehydration process. Moisture loss proceeds in parallel with solid uptake. The rate of water removal is always higher than the rate of osmosis agent penetration, which is in agreement with the results of other workers (Lenart, 1990). The two transfer processes seem to be interdependent and different. It is well recognized that diffusion is a temperature-dependent phenomenon. Higher process temperatures seem to promote faster moisture loss through swelling and plasticising of cell membranes, faster moisture diffusion within the product and better mass (water) transfer characteristics on the surface due to lower viscosity of the osmotic medium. An increase in temperature and processing time also increased solid gain.



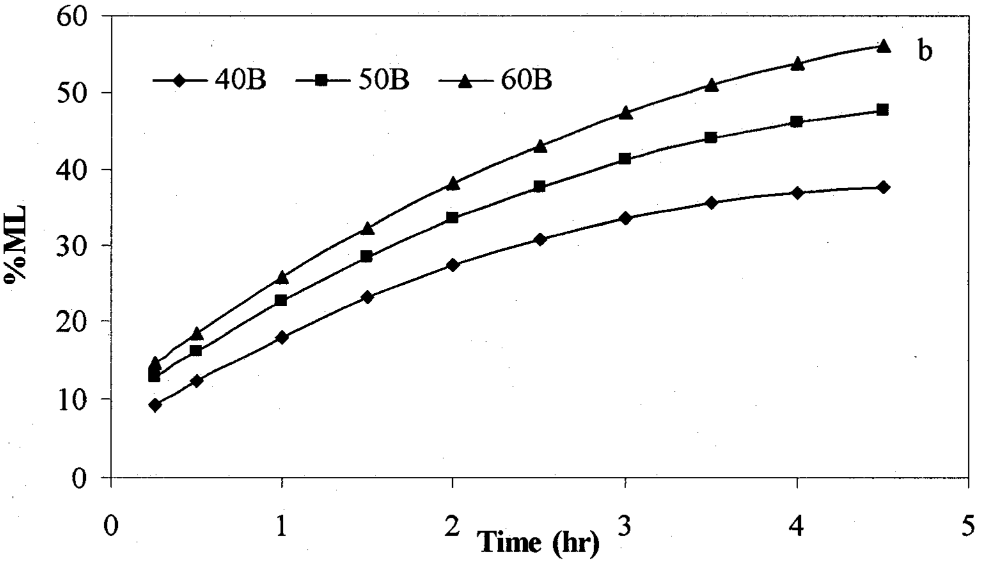
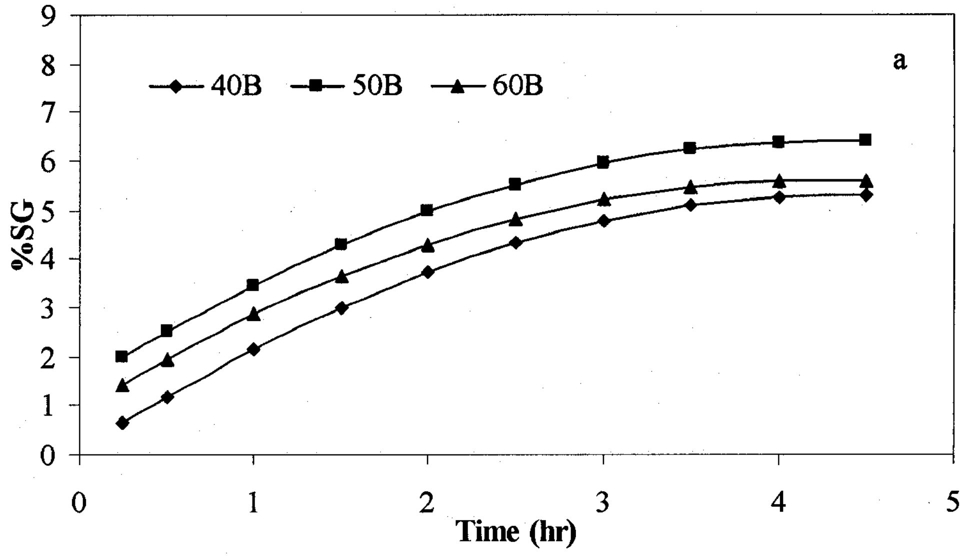


Figure 3.4 Moisture loss (%ML) as a function of time of osmotic dehydration under different conditions. (a) 40°C, solution concentration effect; (b) 60°C, solution concentration effect.



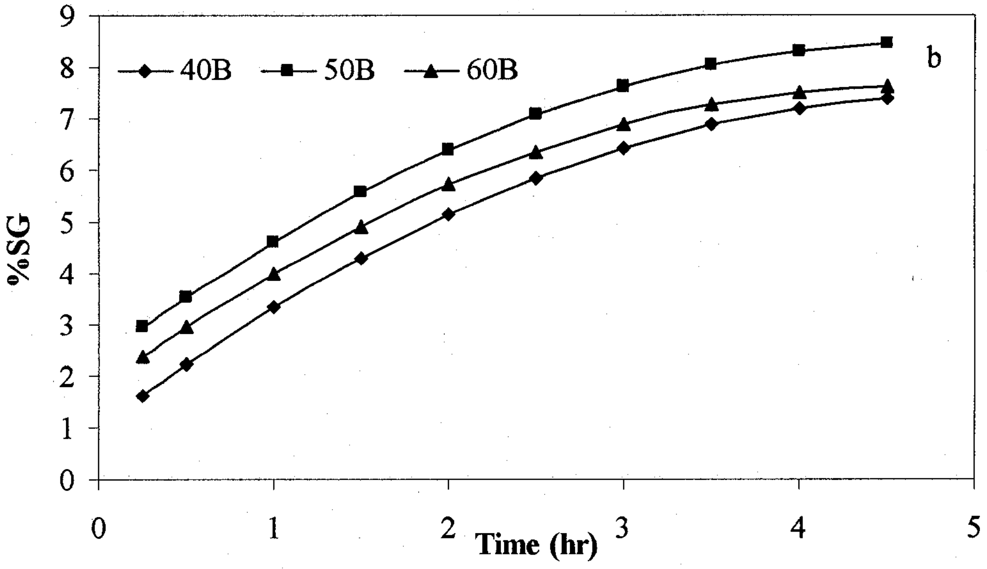


Figure 3.5 Solids gain (%SG) as a function of time of osmotic dehydration under different conditions. (a) 40°C, solution concentration effect; (b) 60°C, solution concentration effect.

3.3.3 Moisture loss rate (MLR) and solids gain rate (SGR)

3.3.3.1 Modeling MLR and SGR

The percentage of moisture loss (%MLR) and solids gain rate (%SGR) were related to temperature, solution concentration and contact time as following equations using the statistical analysis software (SAS, 1999).

$$MLR\% = 0.0171*T^{0.7031}*C^{0.9571}*t^{-0.8763} \quad (R^2 = 0.85) \tag{3.25}$$

$$SGR\% = 0.0862*T^{0.5521}*C^{0.2199}t^{-1.0308} \quad (R^2 = 0.82) \tag{3.26}$$

Figure 3.6 shows the goodness of the developed models in the form of experimental data vs predicted data with the diagonal line representing the ideal performance. The figures confirmed that the model describing moisture loss rate was again better than the model describing solids gain rate.

3.3.3.2 Factors affect MLR and SGR

The evolution of moisture loss rates (MLR) and solids gain rates (SGR) with osmotic dehydration progressing is shown in Figures 3.7 and 3.8. The most significant changes of moisture loss rate (MLR) and solids gain rate (SGR) took place during the first two-hour of dehydration. Thus data were only shown for the first two-hour periods. During the first hour of dewatering, the rate decreased almost 3-5 times independently of the type of conditions (not including first point). The rate of moisture loss was also the highest at the beginning of the process. Similar results reported by Kowalska et al. (2001) and Lazarides et al. (1995a). Farkas et al. (1969) found that the maximum rate of weight loss decreased rapidly from about 10% to 5% per h after 20% to 30% of the moisture was removed. In our experiment during this time period MLR was reduced more than 40% (from 17.9 to 9.7 h^{-1}, 22.1 to 12.0 h^{-1} and 27.6 to 15.0 h^{-1}, respectively, for 50°C and different solution concentration) (Figure 3.7a); whereas for the test time from 1h to 2h, MLR was reduced by only 20%. At times longer than 1 hr the rate was low and decreased less with time. This meant that the rate of water removal for the first time period was more than double that for the second period.

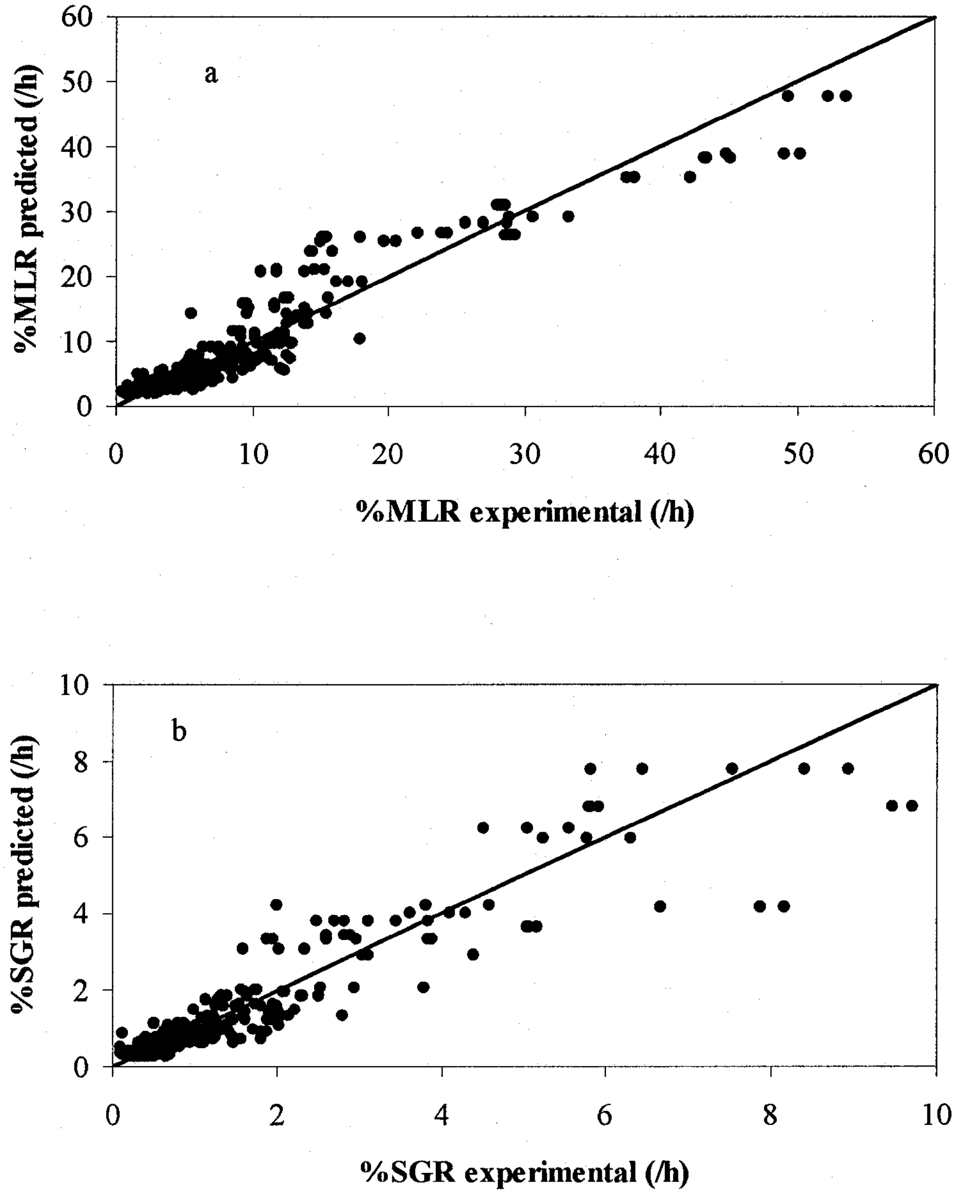
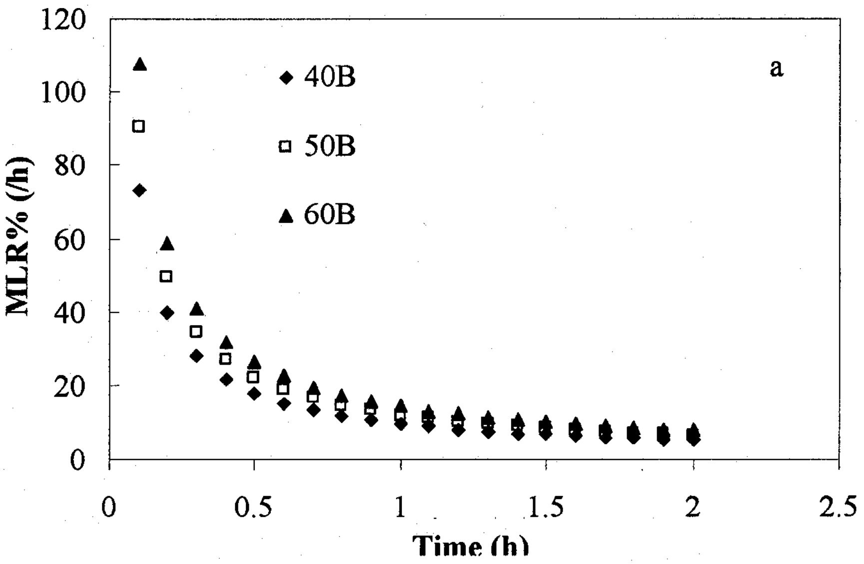


Figure 3.6 Performance testing of models for %MLR (a) and %SGR (b)



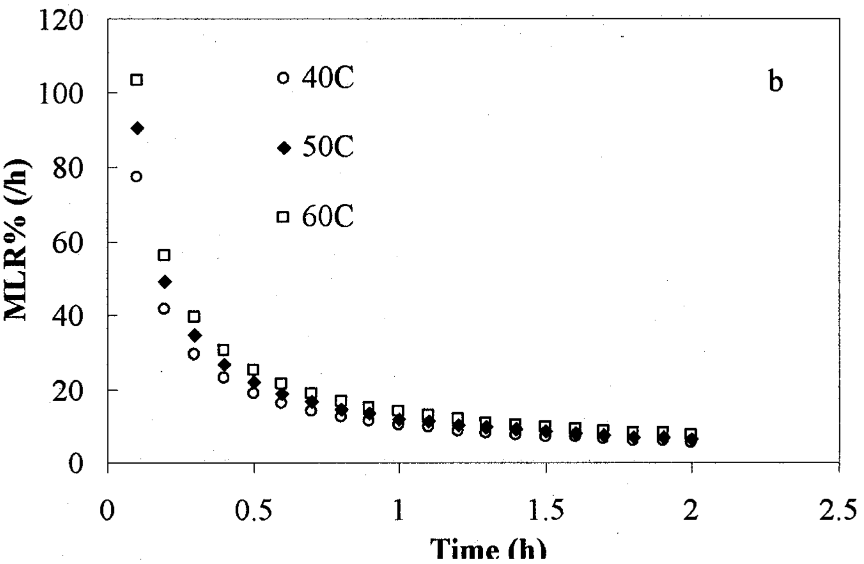


Figure 3.7. Effects of process time on moisture loss rates during osmotic dehydration of apple cylinders in sugar solutions. (a) 50°C, solution concentration effect; (b) 50°Brix, process temperature effect.

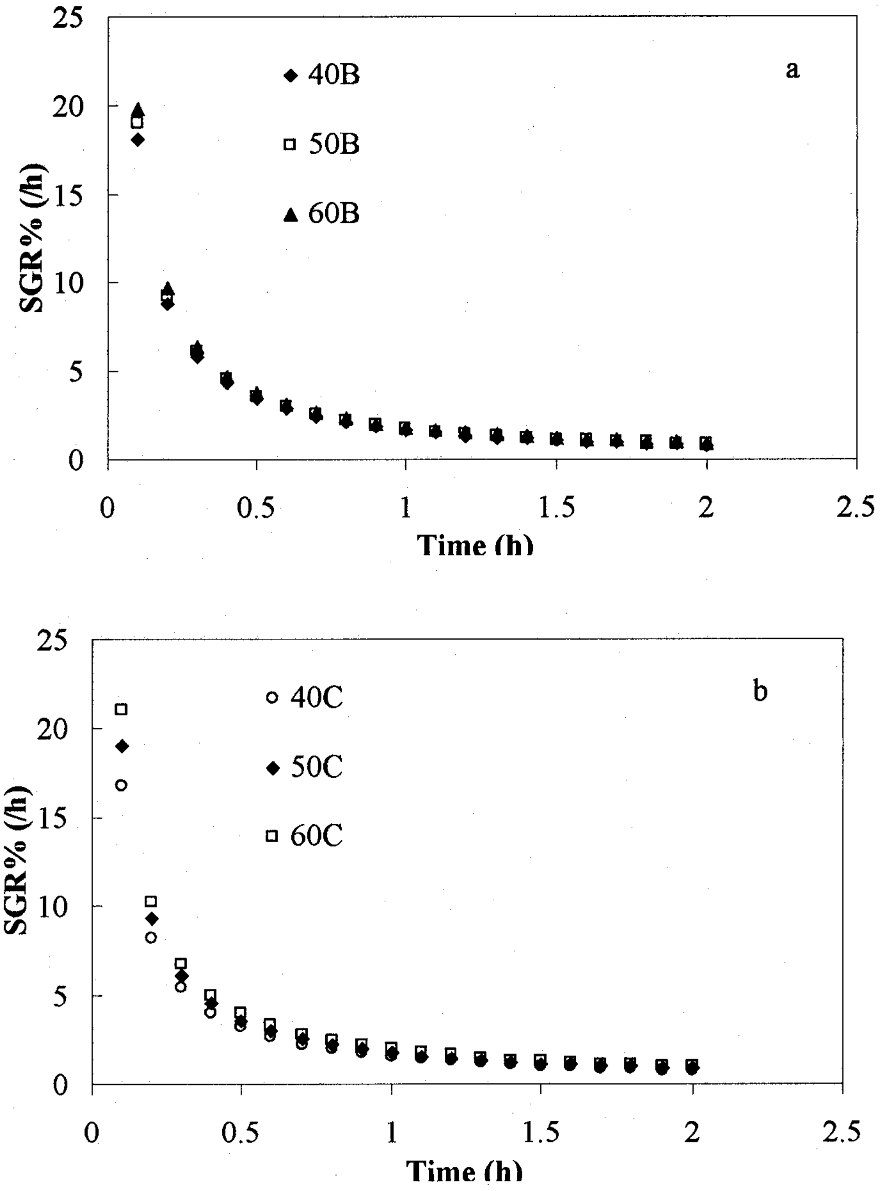


Figure 3.8. Effects of process time on solids gain rates during osmotic dehydration of apple cylinders in sugar solutions. (a) 50°C, solution concentration effect; (b) 50°Brix, process temperature effect.

The rate of osmotic dehydration was the highest at the beginning of the process. It results from the largest difference of osmotic pressure between osmotic solution and the cell sap of the material and small mass transfer resistance at this stage of the process (Salvatori et al., 1998). On the other hand, rapid drop of the moisture loss rate within the first hour (despite the continuing presence of a high sugar concentration) seemed to result from a serious disturbance of the initial osmotic concentration difference due to superficial sugar uptake.

Higher concentration gave higher MLR (Fig.3.7a). A higher sugar concentration increased the moisture loss rate (Farkas and Lazar, 1969). For SGR (Fig. 3.8a), higher concentration gave higher SGR; with the process proceeding, concentration effect was not significant, even though the solids gain was still increased. Ertekin et al. (1996) reported that in their study that ML and SG increased with increasing concentration of solution, a similar results to our observation.

Increased temperatures gave increased values of MLR (Fig 3.7b) and SGR (Fig 3.8b). MLR increased 32% for temperature increasing from 40°C to 50°C and increased 14% for temperature increasing from 50°C to 60°C at 0.5h and 50°Brix condition. SGR increased 23% for temperature increasing from 40°C to 50°C and increased 10% for temperature increasing from 50°C to 60°C at 0.5h and 50°Brix condition. Beristain et al. (1990) reported, in their experiments, higher temperature promoted faster moisture migration from the fruit. The rate of moisture loss increased with temperature increasing.

Table 3.4 ANOVA of the factors influencing moisture loss rate and solids gain rate during osmotic dehydration of apple cylinder

Source	Moisture loss rate (MLR)		Solids gain rate (SGR)	
	F value	Probability level	F value	Probability level
Main effects				
Time (t)	1603.76	<0.0001	1297.78	<0.0001
Temp. (°C)	43.47	<0.0001	15.71	<0.0001
Conc. (°Brix)	75.56	<0.0001	2.33	0.1278

*P<0.05 significant, P<0.01 high significant, P<0.001 highly significant

3.3.4 Time to get the sample 20% weight reduction, 25% moisture loss and 5% sample solids gain (T_w, T_m and T_s)

The dehydration times for each condition were calculated using equations (3.1-3.3). The data for dehydration time with respect to weight reduction (T_w), moisture loss (T_m) and solids gain (T_g) are summarized in Figure 3.9 (a, b and c) for the different conditions. As expected, the dehydration time (T_w and T_m) decreased with increasing temperature and sucrose concentration. However, the solids gain (T_s) was not strictly followed this trend. The shortest T_w and T_m were 1.54h and 0.94h for the condition of 60°C-60°Brix, which represented one of the high temperature-high concentration conditions used in this study. The longest T_w and T_m were 4.50h and 4.00h for the condition of 50°C-40°Brix, which represented one of the lower temperature-low concentration conditions used in this study. While the shortest T_s was 1.04h for the condition of 66°C-50°Brix and the longest T_s was 4.00h for the condition of 50°C-34°Brix (not shown in the figure). From these observations, we could compare the efficiency of the different conditions with respect to dehydration time for respective weight reduction (T_w), moisture loss (T_m) and solids gain (T_g).

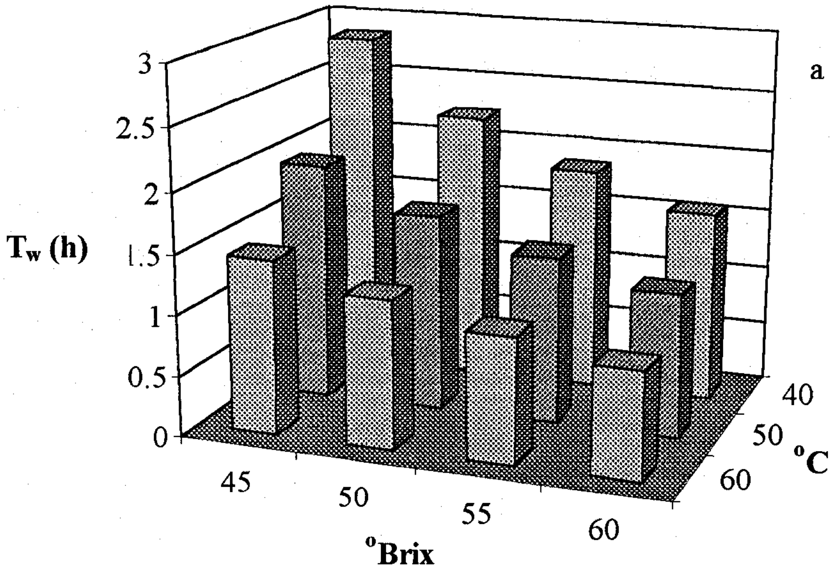
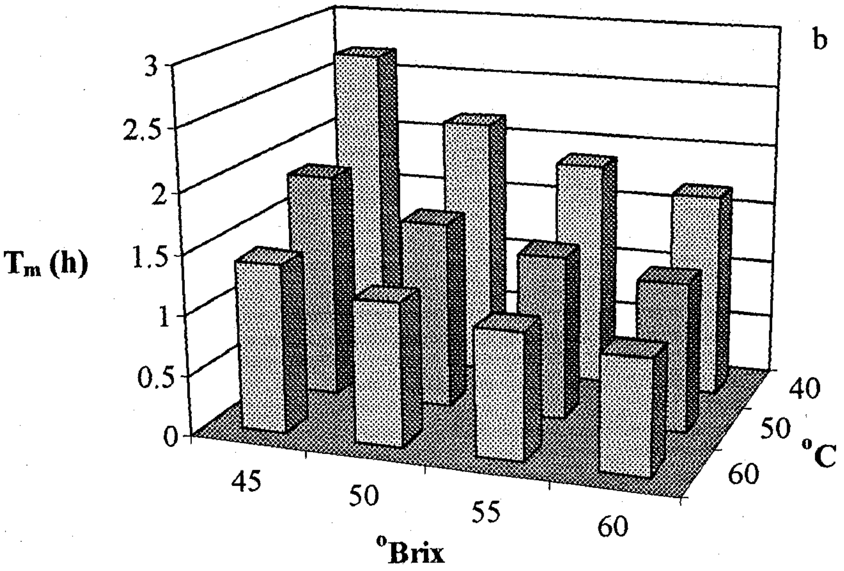


Figure 3.9a Time to get the sample 20% weight reduction T_w under different conditions



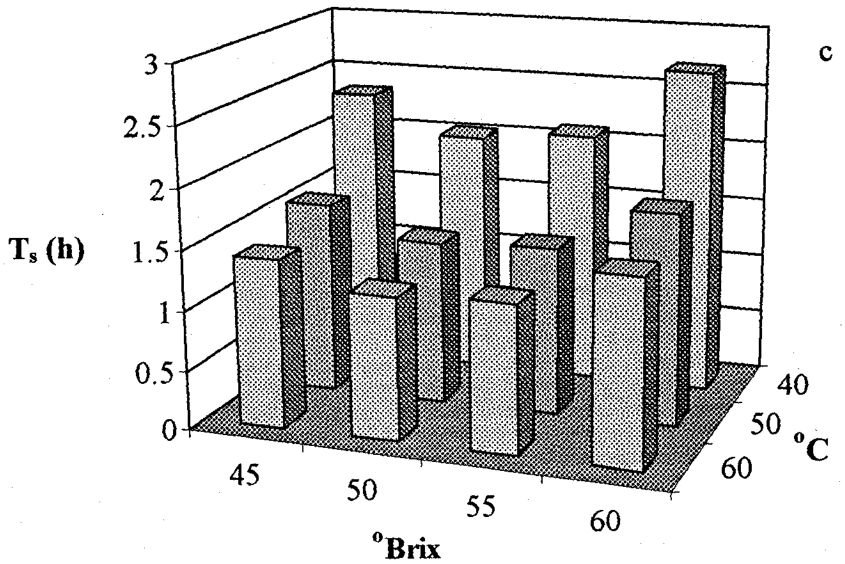


Figure 3.9 Time to get the sample 25% moisture loss T_m (b) and 5% sample solids gain T_s (c) under different conditions

3.3.5 Diffusion coefficients

Since all the MLR and SGR rates were in the falling rate period, moisture transfer and solute transfer could be described by applying unsteady state Fick's law of diffusion. The appropriate solution of the unsteady state diffusion equation for finite cylinder under defined initial and boundary conditions (equation 3.18 and 3.19) were applied. In order to get the diffusion coefficients of mass transfer during the osmotic dehydration process, characteristic drying curves were plotted as residual moisture ratio or residual solids ratio vs osmotic dehydration time. Equilibrium moisture loss and solids gain were the highest moisture loss and solids gain under same concentration condition. Nevertheless, in this study as well as in most studies using Fick's diffusion law on modeling the osmotic dehydration process (Conway, et al., 1983; Beristain, et al., 1990; Hough, et al., 1993; Rastagi, et al., 1997 a; Nsonzi, et al, 1998; Kayamak-Ertekin, et al., 2000), good correlations were observed between experimental and predicted data. Using these equations the moisture and solids diffusivities were calculated. The results were shown in table 3.5

Table 3.5. Diffusivity of moisture (D_m) and solids (D_s) during the osmotic dehydration of apple cylinders

Combination (°C/°Brix)	Equilibrium value (ML_∞/SG_∞)	$D_m*10^{10}m^2/s$	R^2	$D_s*10^{10}m^2/s$	R^2
50/34	40.36/10.40	13.93	0.95	15.04	0.94
40/40	46.73/10.22	9.01	0.90	7.82	0.89
50/40	46.73/10.22	13.18	0.95	17.00	0.95
60/40	46.73/10.22	24.26	0.93	20.22	0.95
34/50	60.56/9.80	8.20	0.98	16.41	0.94
50/50	60.56/9.80	18.63	0.93	26.85	0.92
60/50	60.56/9.80	19.44	0.97	37.24	0.93
66/50	60.56/9.80	21.14	0.96	34.31	0.72
40/60	68.49/9.46	12.53	0.98	10.65	0.91
60/60	68.49/9.46	24.04	0.95	30.88	0.88
50/63	69.44/9.44	20.88	0.86	30.53	0.89

3.3.5.1 Modeling moisture diffusivity (D_m) and solids diffusivity (D_s)

Moisture diffusivity (D_m) and solids diffusivity (D_s) were related to temperature, solution concentration and contact time as following equations using the statistical analysis software (SAS, 1999).

$$D_m = -51.9393 + 1.7489*T + 0.2954*C - 0.0078*T^2 \quad (R^2 = 0.89) \qquad (3.27)$$

$D_s = -101.6648 + 1.0614*T + 2.9547*C - 0.0348*C^2 \quad (R^2 = 0.83)$ (3.28)

Figure 3.10 shows the adaptbility of the developed models in the form of experimental data vs predicted data with the diagonal line representing the ideal performance.

3.3.5.2 Factors affect D_m and D_s

Moisture diffusion was influenced more by temperature variation in low concentration region than in higher concentration region (Figure 3.11), for example, the moisture diffusivity (D_m) at 60°C-40°Brix was higher than the moisture diffusivity at 40°C-60°Brix, as shown in Table 3.5. The analysis of variance (ANOVA) used to establish the influence of temperature and sucrose concentration on moisture diffusivity (Table 3.6) confirmed that temperature and concentration effects were highly significant influenced ($P<0.001$) moisture diffusivity, the quadratic effect of temperature was significant ($P<0.05$) to D_m, whereas the quadratic effect of concentration and the interaction of temperature and concentration were not significant ($P>0.05$) to D_m. Figure 3.11 shows concentration and temperature effects on moisture diffusivity. With increasing concentration, moisture diffusivity showed an increasing trend; similarly with concentration increasing, moisture diffusivity had the trend of increasing. Lazarides et al. (1997) reported that as temperature increased from 20 to 50°C, moisture diffusivity increased 2.5 times, while increasing concentration (between 45 and 65%) caused an increase of D_w only by a factor of 1.3-1.4. However, Hawkes and Flink (1978) studied the mass transport in the osmotic concentration of apples, and found mass transfer coefficient increased with sucrose concentration when the concentration of the sugar solution was 50% or greater.

With much more sucrose concentration, moisture diffusivity increasing trend was reduced. Probably due to a thicker layer of sucrose solution may have formed around the surface of the sample and impeded the moisture loss. The high viscous sucrose solution may even have initiated crystallization of sugar along the relatively stagnant liquid film on the surface of the sample thus inhibiting moisture loss. Early formation of a surface layer of solute hinders both moisture loss from the interior of the sample and further uptake of sucrose from the solution (Lenart and Flink, 1984a). Increase in viscosity increases resistance to mass transfer as the diffusion coefficient is inversely proportional to system viscosity (Einstein or Wilke-Chang equation). Furthermore, the difference in sucrose concentration at the interface of the product provides an impetus for solids gain into the product to increase. The resulting weaker internal concentration gradient and increased concentration of sucrose in the product limit moisture transfer inside the product (Raoult-Wack, et al., 1989). With much more high temperature, moisture diffusivity increasing trend was reduced as well. Probably due to the sample cell structure changes occurred which impeded the moisture loss.

Solids diffusivity calculation method in this study was different. The equilibrium solids gain was used according to the Azuara model predicted value combined with experimental data. Increased temperature and concentration caused an increase in solids diffusivity (Table 3.5). Solids diffusion was influenced both by temperature and concentration as shown in Table 3.6. The analysis of variance (ANOVA) to establish the influence of temperature and sucrose concentration on solid diffusivity (Table 3.6) confirmed that temperature and concentration effects highly significant influenced ($P<0.001$) solids diffusivity; concentration quadratic effect high significant ($P<0.01$) influenced solids diffusivity (D_s), whereas temperature quadratic effect and interaction of temperature and concentration were not significant ($P>0.05$) to D_s. Figure 3.12 shows temperature and concentration effect on solids diffusivity. Temperature and concentration variation had a positive effect to solid diffusivity, similar to Lazarides et al. (1997) result. However, with much more sucrose concentration (>55°Brix), both solids diffusivity increasing trend and solids diffusivity were reduced in our experiments.

Table 3.6 ANOVA of the factors influencing D_m and D_s during osmotic dehydration of apple cylinder

Source	D_m		D_s	
	F value	Probability level	F value	Probability level
Main effects				
Temp. (°C)	187.00	<0.0001	90.63	<0.0001
Conc. (°Brix)	21.46	<0.0001	27.77	<0.0001
Quadratic effects				
Temp. (°C)	5.99	0.0212	0.30	0.5856
Conc. (°Brix)	0.43	0.5190	8.09	0.0084
Interactions				
T*C	2.69	0.1126	2.13	0.1560

*$P<0.05$ significant, $P<0.01$ high significant, $P<0.001$ highly significant

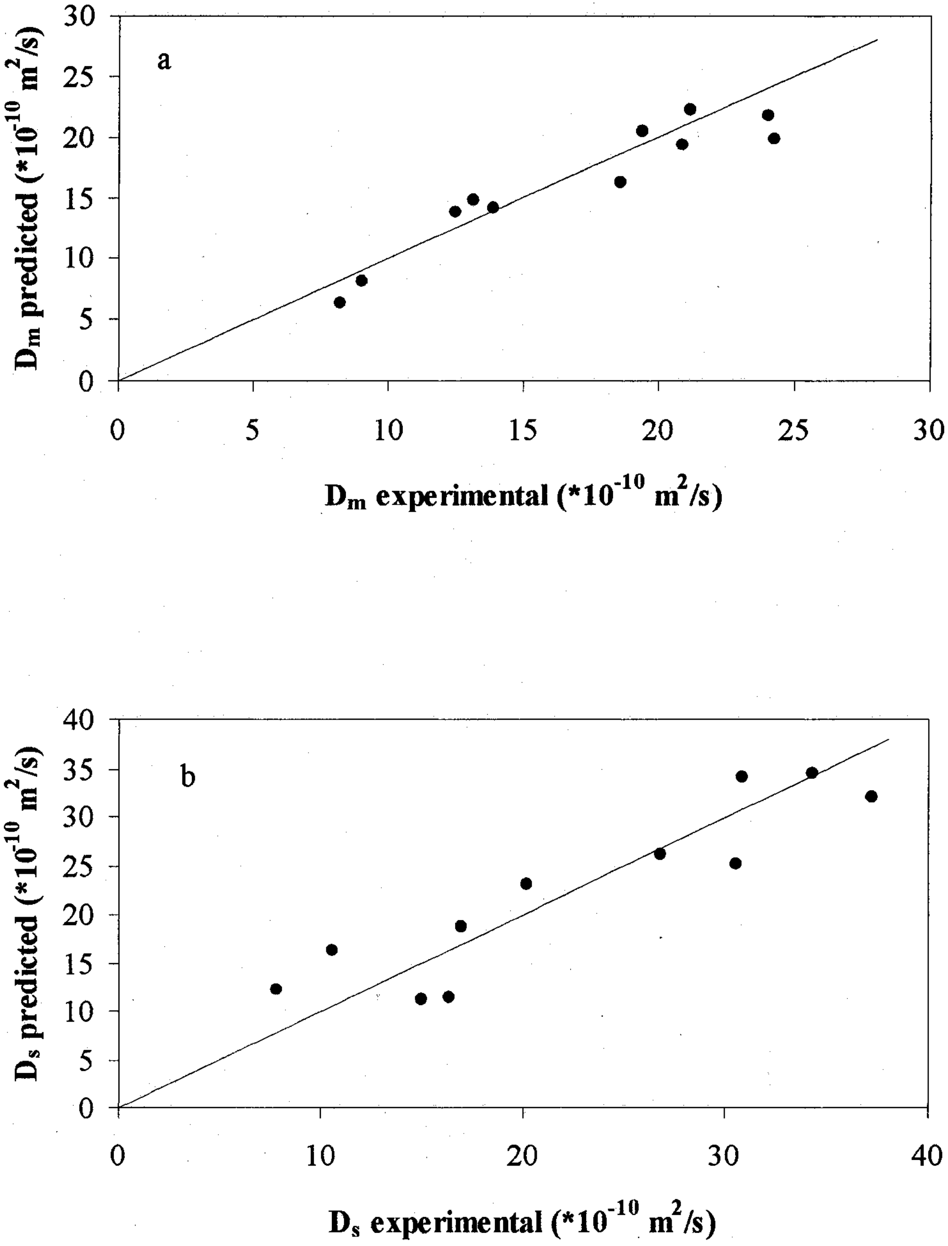


Figure 3.10 Performance of testing of models for moisture diffusivity (D_m) (a) and solids diffusivity (D_s) (b)

5 h OD

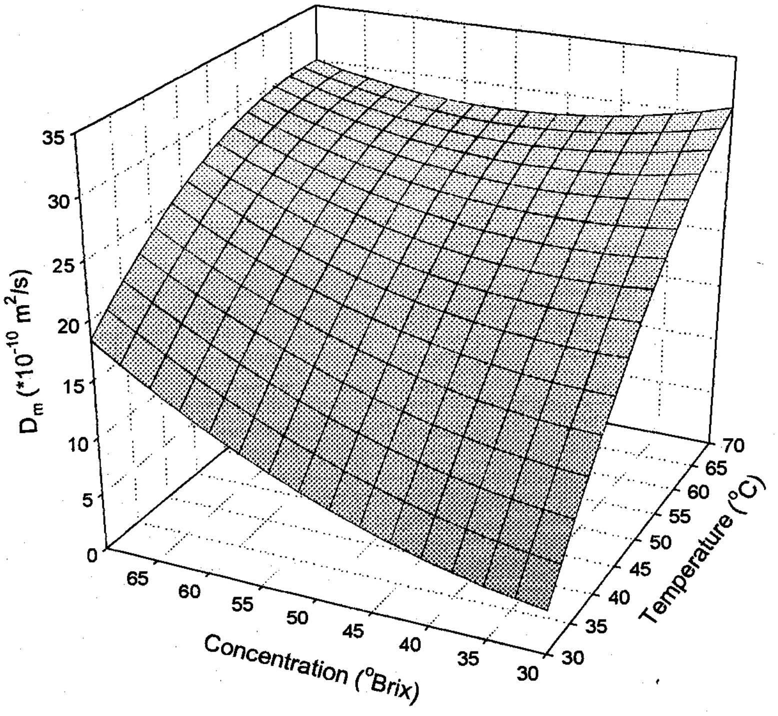


Figure 3.11 Moisture diffusivity (D_m) variation as a function of concentration and temperature for 5h of osmotic dehydration

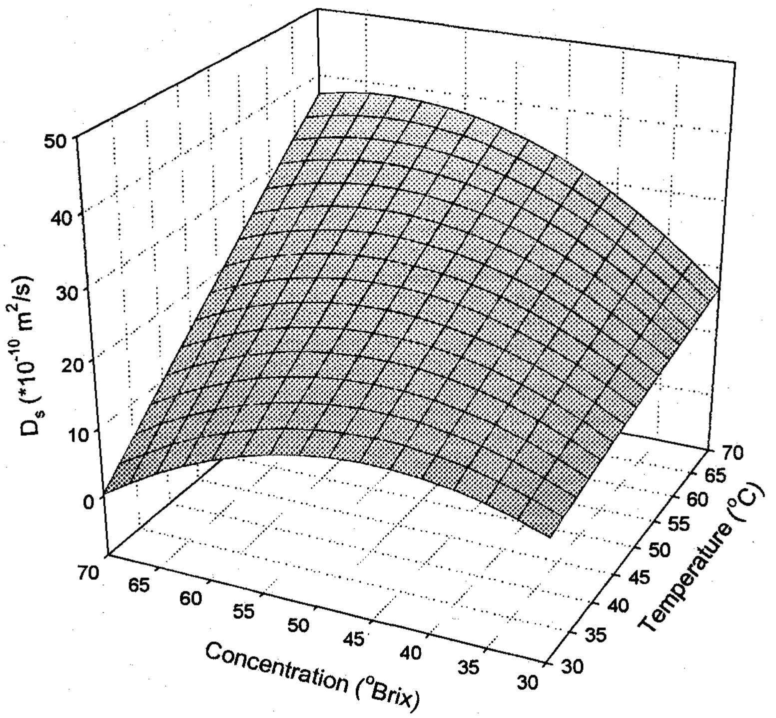

5 h OD

Figure 3.12 Solids diffusivity (D_s) variation as a function of concentration and temperature for 5h osmotic dehydration

3.3.6 Ratio of ML/SG

Another parameter characterizing osmotic dehydration is the ratio of ML/SG change with time (Figure 3.13). For most of the conditions, osmotic dehydration process favored dehydration. Increasing solution concentration, the ratio of ML/SG increased value; except for 40°C-40°Brix at the first two hour due to the relative small quantity of solids gain (Fig 3.13 a). Lazarides et al. (1995a) reported that increased concentrations resulted in higher WL and SG rates; yet, they favored faster solid uptakes (lower WL/SG ratios), contrary to our observation. Likely due to the different samples or the different solutes used during the osmotic dehydration process. Comparing the relative increased rates might be also important need to be considered. Waliszewski et al. (1997) had demonstrated that process variables, temperature and osmotic concentration, had a significant effect on water loss and solute gain. Higher temperature favored faster water loss yielding also higher water loss/sugar gain ratio, which were agreeing with our observations.

Yet the ratio of ML/SG was not constant with temperature, as suggested by Lenart and Lewicki (1989). Figure 3.13 (b) represents the effect of temperature on ML/SG ratio trend among treatments, it was quite clear that optimize the process factors would improve osmotic dehydration efficiency. Raoult et al. (1989) explained the appearance of different ML/SG ratios in modeling food gels on the basis of opposing responses and reciprocal influence between moisture and solute flows. Farkas and Lazar (1969) studied the effect of temperature and concentration on moisture removal rates and suggested 70°Brix and 50°C as the most appropriate process conditions; whereas, in our case, 60°Brix and 50°C was the most process conditions.

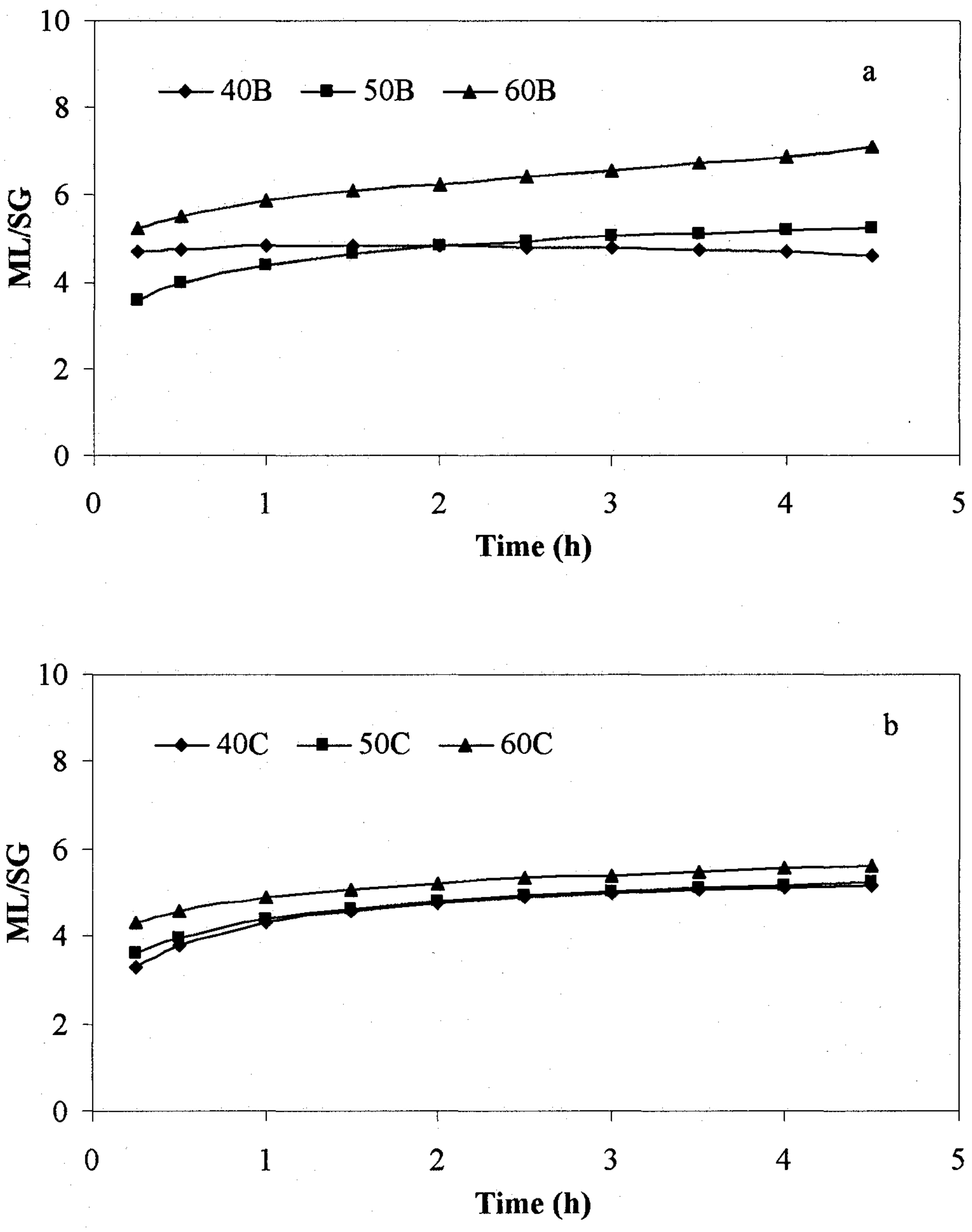


Figure 3.13. Effects of process time on the ratio of moisture loss over solids gain (ML/SG) during osmotic dehydration of apple cylinders in sugar solutions. (a) solution concentration effect; (b) process temperature effect.

3.3.7 Identification of osmotic dehydration conditions

The aim of this osmotic dehydration was to study main factors: process time, solution concentration and process temperature effects on mass transfer influence during osmotic dehydration process. The results of this work indicated that the aim of this study was reached. Experimental results showed that selecting time period: 0.25-3hr; solution concentration range: 40°Brix-60°Brix and temperature range 40-60°C are suitable for further osmotic dehydration kinetics study.

3.4 Conclusions

- The moisture loss (ML) and solids gain (SG) generally increased with increasing treatment time, temperature and concentration of osmotic solution.
- Moisture loss rate (MLR) and sugar gain rate (SGR) were reduced with process proceeding. MLR always higher than SGR under current experimental conditions. The ratio of ML/SG was an indicator of process efficiency in terms of extensive moisture removal with minimal solids uptake and depended on the solution concentration and duration of the process.
- Higher process temperature favored faster moisture loss yielding higher ML/SG value; higher sucrose concentrations favor faster moisture loss and slow sugar uptake. Depending on specific process goals one could choose from a range of process conditions to direct treatment towards dewatering, impregnation or a mixed effect.
- Moisture loss rate (MLR) and solids gain rate (SGR) variation trend, combined with the dehydration time (T_w, T_m and T_s) and mass diffusivity (D_m and D_s) change could be used as osmotic dehydration condition selection parameters.
- At temperature (T<66°C) and short processing times (t<30min), osmosis had a direct effect on dehydration.

Preface to Chapter 4

In the previous chapter, effects of solution concentration, temperature and processing time in batch mode osmotic drying (OD) were reported. The objective of this work was to develop a separate osmotic dehydration contactor under continuous flow circulation condition and to evaluate its performance, using response-surface methodology to compare the efficiency of continuous flow osmotic dehydration (CFOD) with conventional osmotic dehydration (COD); to evaluate the effectiveness of the system (CFOD) with some parameters: operation mode, solution sample contacting mode and operation control etc.

Effect of agitation on mass transfer kinetics during osmotic dehydration has been studied in a limited number of studies despite the major significance from a practical and theoretical point of view of optimizing the OD processes (Mavroudis, et al., 1998). The solution flow rate variation in laminar region has not been studied earlier and has been shown some effects presented in this chapter. Previous analysis of the agitation effect was limited to comparison of agitation with non-agitation treatments. Few of these studies attempted quantification of agitation in engineering terms (Mavroudis, et al., 1998), especially at laminar flow region. A continuous flow osmotic dehydration (CFOD) contactor was developed to be an efficient process in terms of osmotic dehydration efficiency compared with conventional osmotic dehydration (COD). This work would partially fulfill the first and second objectives of this thesis. The results obtained in this study are important for research work on developing microwave assisted osmotic dehydration technique detailed in chapter 5

Part of this research has been presented in some conferences and/or being prepared for publication in scientific journals detailed earlier. The experimental work and data analysis were carried out by the candidate under the supervision of professor Dr. H.S. Ramaswamy.

CHAPTER 4

OSMOTIC DEHYDRATION OF APPLE CYLINDERS UNDER CONTINUOUS MEDIUM FLOW CONDITIONS

Abstract

Mass transfer of apple cylinders during osmotic dehydration was quantitatively investigated under continuous medium flow conditions. The influences of the main process variables (solution concentration, operation temperature, contact time and solution flow rate) were determined. A second order polynomial regression model was used to relate weight reduction (WR), moisture loss (ML), solids gain (SG), and mass diffusivity (D_m and D_s) to process variables. The conventional diffusion model using a solution of Fick's unsteady state law involving a finite cylinder was applied for moisture diffusivity and solute diffusivity determination. Diffusion coefficients were in the range of 10^{-9}-10^{-10} m^2/s, and moisture diffusivity increased with temperature and flow rate; increased with solution concentration (>50°Brix); decreased with increasing solution concentration (<50°Brix); but solids diffusivity increased with temperature and concentration and decreased with increasing flow rate. A continuous flow osmotic dehydration (CFOD) contactor was developed to be more efficient process in terms of osmotic dehydration efficiency: time reach certain weight reduction (T_w) and moisture loss (T_m) were shorter than that of conventional osmotic (COD) dehydration process. Effectiveness evaluation functions used in this study could be widely applied to osmotic dehydration system evaluation.

4.1 Introduction

Osmotic dehydration is a useful technique for partial dewatering and direct formulation of food pieces by immersing them in concentrated solutions. During the osmotic treatment, there is water outflow from product to solution and solute inflow from solution to product, in addition to leaching of some solutes from the product (sugars, organic acids, minerals, vitamins, etc), which can influence the composition and quality of the finished product (Raoult-Wack, 1994). This process can be used as a pretreatment before any complementary processing, and may lead to energy savings and quality (nutritional, organoleptical and functional) properties improvement.

However, the industrial application of the osmotic dehydration faces engineering problems related to the movement of great volumes of concentrated sugar solutions and to the equipment for continuous operations. The highly concentrated sugar solution creates two major problems: high viscosity inhibits mass transfer on the solution side and high density of the solution makes the product float. Overall, industrial applications of the process have mainly been limited to semi-candied fruit production lines, the control of which has mostly been empirical (Raoult-Wack, 1994). Reasons for this discrepancy have been given in recent reviews (Le Maguer, 1988; Raoult-Wack, et al., 1992; Torreggiani, 1993; Raoult-Wack, 1994; Qi, et al., 1998; Marouzé, et al., 2001).

Solution concentration, temperature and processing time have been considered as important factors in many osmotic dehydration studies. The effect of agitation on mass transfer kinetics has been studied in a limited number of studies despite the major significance from a practical and theoretical point of view of optimizing the OD processes (Mavroudis, et al., 1998). The solution flow rate variation in laminar region has not been studied before and some effects are presented in this chapter. Previous analysis of the agitation effect was limited to compare agitation with non-agitation treatments. It was showed that agitated samples exhibited greater weight loss than non-agitated ones thus agitation was found to be another process parameter. Few of these studies attempted quantification of agitation in engineering terms (Mavroudis, et al., 1998), especially in the laminar flow region. Osmotic dehydration is a kind of solid-liquid extraction processes, the special feature of the process is that the solids are usually a fragile, less dense and divided particles with a more density and viscous liquid phase, coupled with the need for homogeneous treatment of all of food (Marouzé, et al., 2001). Osmotic dehydration processes may fall into the following categories:

- Those in which the solution is external to the food, involving either immersion, with or without continuous or intermittent agitation, or the flow of solution around the food.
- Those in which solid solutes are applied to the surface of the food.

- Those processes using different pretreatment improving food sample cell membrane permeability to facilitate mass transfer.
- And, lastly, processes using different processes before or during osmotic dehydration to improve osmotic mass transfer.

The main objective of this work was to develop a separate osmotic dehydration contactor under continuous flow circulation condition and to evaluate its performance; to determine the effect of the main process variables and their interactions on mass transfer phenomenon, including weight reduction (WR), moisture loss (ML), solids gain (SG) and mass transfer coefficient (D_m and D_s), using response-surface methodology; to compare the efficiency of continuous flow osmotic dehydration (CFOD) with conventional osmotic dehydration (COD); and to evaluate the effectiveness of the system (CFOD) with some parameters: operation mode, solution sample contacting mode and operation control etc.

4.2 Materials and methods

4.2.1 Materials

Apples (Idared variety) of uniform size and ripeness were obtained from the local farm of the campus, and commercial sucrose (sugar) was obtained from a local supermarket. The fruits were stored and refrigerated at 2°C-5°C and at 95% relative humidity until being used for the experiments. After cutting the calyx end and pedicel end, apple cylindroids were cut vertical to their axis and five cylinders of 2.0 cm in diameter and 2.0 cm in height were prepared from each fruit.

4.2.2 Osmotic dehydration procedure

Sucrose solution of a known concentration (34, 40, 50, 60 and 63°Brix) was heated in a steam jacketed kettle (Model TDB/4, Groen Division, Dover Corp, IL). Once the solution attained the required temperature, (34, 40, 50, 60 and 66°C) it was pumped at a known flow rate (330, 400, 500, 600 and 670 ml/min) into the dehydration contactor with a peristaltic pump. The solution entered the chamber from the lower opening and exited from the upper opening so as to increase the mixing effect and assure the constant concentration of the solution. The solution in the storage tank was mechanically stirred with a low speed motor (40rpm) to ensure uniform concentration. After leaving the chamber, the solution was forced back into the storage tank. Since the solution inside the chamber was in a moving state, the concentration of the solution was constant.

4.2.3 Reynolds number

The Reynolds number was calculated by the following equation:

$$\mathrm{Re} = \frac{D_c * v * \rho}{\mu} \qquad (4.1)$$

where D_c: contactor diameter

v: average velocity

ρ: density of the fluid

μ: viscosity of the fluid

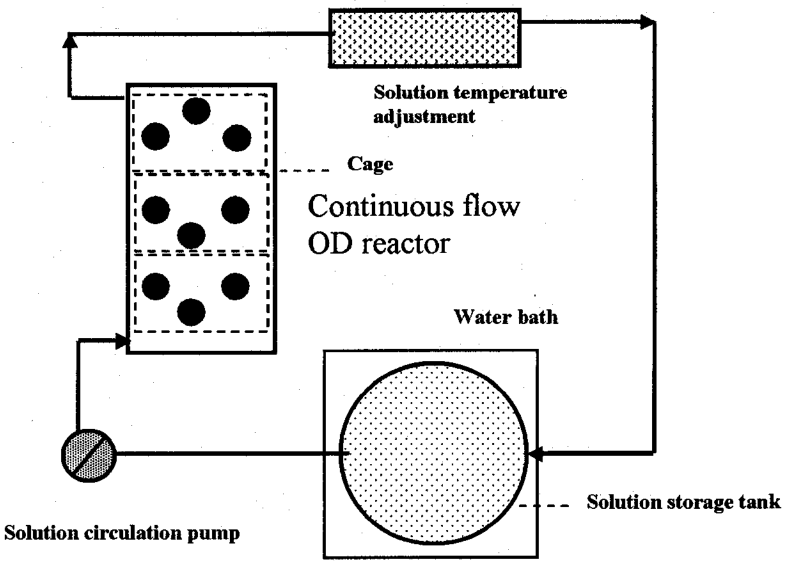


Figure 4.1. Schematic diagram of the continuous flow osmotic dehydration system

4.2.4 Weight reduction, moisture loss and solids gain

The weight reduction, moisture loss and solids gain were calculated based on the general balance of concentration driven mass transfer between the liquid and solid phases:

$$\%WR = 100\frac{M_o - M_t}{M_o} \qquad (4.2)$$

$$\%ML = 100\frac{(M_0x_0 - M_tx_t)}{M_0} \quad (4.3)$$

$$\%SG = 100\frac{(M_ts_t - M_0s_0)}{M_0} \quad (4.4)$$

where: M_0 and M_t are the sample mass (kg) at time 0 and time t; x_0 and x_t are the moisture fractions (kg/kg wet basis) at time 0 and time t; s_0 and s_t are the solid fractions (kg/kg wet basis) at time 0 and time t. These equations are based on the assumption that no solids leaked into the solution.

4.2.5 Time to get the sample 20% weight reduction, 25% moisture loss and sample 5% solids gain (T_w, T_m and T_s)

The osmotic dehydration time to get the sample weight reduction, moisture loss and solids gain to a given value can be used to compare the osmotic drying effectiveness of different conditions. To be able to compare the different runs in the experimental set up, a level of 20% sample weight reduction, a level of 25% sample moisture loss, and a level of 5% sample solids gain were chosen, and the times were computed to result in such weight reduction, moisture loss and solids gain using the equations 4.2-4.4.

4.2.6 Diffusion coefficient calculation

The final formula for a finite cylinder is as follows (detailed in Chapter 3):

$$M_{mfc} = 0.56e^{-\frac{8.25}{d^2}Dt} \quad (4.5)$$

where the moisture loss ratio (M_{mfc}) is defined as follows for water transfer:

$$M_{mfcw} = \frac{M_ex_e - M_tx_t}{M_ex_e - M_ox_o} = \frac{ML_\infty - ML_t}{ML_\infty - ML_o} \quad (4.6)$$

The solids gain ratio (M_{mfcs}) is:

$$M_{mfcs} = \frac{M_es_e - M_ts_t}{M_es_e - M_os_o} = \frac{SG_\infty - SG_t}{SG_\infty - SG_o} \quad (4.7)$$

By plotting M_{mfcw} and M_{mfcs} against contact time, the diffusion coefficient D (m^2/s) can be obtained from the slope of the curve.

4.2.7 Analyses

The sugar concentration (total soluble solids: TSS) was measured with a portable refractometer (ATAGO, Japan) at 20°C. Moisture content of fresh and osmotically treated apple cylinders was determined by an oven method. The moisture content and total solids were measured gravimetrically on apple cylinders after different contact times. For measuring solids content, the samples were air dried in a convection oven at 105°C for 24h.

4.2.8 Experimental design and statistical analysis

The experimental design adopted was a configuration of Box's central composite rotatable design (CCRD) for four variables at five levels each. The four independent variables were process temperature, solution concentration, solution circulation flow rate and processing time. The complete design included 31 experiments, with seven replications of the central point, and was rotatable as described by Saurel (1992). The actual factor values, chosen from preliminary studies, and the corresponding coded values (-1.68, -1, 0, 1, 1.68) are given in Table 4.1. Response-surface methodology (RSM) was selected to estimate the main effect of the process variables on mass transfer variables during the osmotic dehydration of the apple cylinders.

Variance analysis and the calculation of regression coefficients were done using SAS program; tridimensional graphs were drawn using Sigmaplot program. Response surfaces were drawn using a definite model that minimizes the influence of non-significant coefficients. The definitive model was obtained for each dependent variable (or response) with stepwise regression where factors were rejected when their significance level was less than 95%.

$$y = b_o + \sum_{i=1}^{k} b_i x_i + \sum_{i=1}^{k} b_{ii} x_i^2 + \sum_{i=1}^{k-1} \sum_{j=i+1}^{k} b_{ij} x_i x_j \quad (4.8)$$

where: y is the response %WR, %ML, %SG and D_m or D_s; b_o, b_i, b_{ii}, b_{ij} are constant coefficients; x_i and x_j represent the temperature, sucrose concentration, flow rate or contact time during osmotic dehydration.

Table 4.1.Experimental conditions used for the osmotic dehydration process

	Independent variables or factors				Dependent variables		
Design points	Temp. (°C)	Conc. (°Brix)	Flow rate ml/min Re*<2000	Time (hr)	WR %^{a}	ML %^{b}	SG %^{c}
1	40 (-1)	40 (-1)	400 (-1)	0.5 (-1)	5.34	8.61	0.89
2	60 (1)	40 (-1)	400 (-1)	0.5 (-1)	7.09	12.06	1.52
3	40 (-1)	60 (1)	400 (-1)	0.5 (-1)	9.63	12.36	2.77
4	60 (1)	60 (1)	400 (-1)	0.5 (-1)	13.45	18.53	3.19
5	40 (-1)	40 (-1)	600 (1)	0.5 (-1)	8.10	10.55	1.86
6	60 (1)	40 (-1)	600 (1)	0.5 (-1)	9.85	13.20	3.04
7	40 (-1)	60 (1)	600 (1)	0.5 (-1)	11.59	14.30	3.53
8	60 (1)	60 (1)	600 (1)	0.5 (-1)	15.41	19.67	4.31
9	40 (-1)	40 (-1)	400 (-1)	1.5 (1)	12.31	18.21	2.92
10	60 (1)	40 (-1)	400 (-1)	1.5 (1)	17.56	25.09	4.21
11	40 (-1)	60 (1)	400 (-1)	1.5 (1)	19.69	25.57	5.06
12	60 (1)	60 (1)	400 (-1)	1.5 (1)	27.02	35.07	5.96
13	40 (-1)	40 (-1)	600 (1)	1.5 (1)	15.79	20.15	4.08
14	60 (1)	40 (-1)	600 (1)	1.5 (1)	21.04	26.23	5.73
15	40 (-1)	60 (1)	600 (1)	1.5 (1)	22.37	27.51	5.82
16	60 (1)	60 (1)	600 (1)	1.5 (1)	29.70	36.31	7.08
17	34 (-1.68)	50 (0)	500 (0)	1 (0)	12.44	16.39	3.13
18	66 (1.68)	50 (0)	500 (0)	1 (0)	19.70	26.18	4.79
19	50 (0)	34 (-1.68)	500 (0)	1 (0)	10.71	15.52	2.74
20	50 (0)	63 (1.68)	500 (0)	1 (0)	19.76	25.37	5.22
21	50 (0)	50 (0)	330 (-1.68)	1 (0)	13.16	19.23	3.14
22	50 (0)	50 (0)	670 (1.68)	1 (0)	17.78	21.85	5.08
23	50 (0)	50 (0)	500 (0)	0.14 (-1.68)	4.06	6.85	1.40
24	50 (0)	50 (0)	500 (0)	1.86 (1.68)	22.34	29.42	5.69
25	50 (0)	50 (0)	500 (0)	1 (0)	14.89	20.54	4.11
26	50 (0)	50 (0)	500 (0)	1 (0)	12.68	17.79	3.58
27	50 (0)	50 (0)	500 (0)	1 (0)	13.81	19.20	3.85
28	50 (0)	50 (0)	500 (0)	1 (0)	15.93	21.82	4.35
29	50 (0)	50 (0)	500 (0)	1 (0)	16.93	20.04	4.58
30	50 (0)	50 (0)	500 (0)	1 (0)	17.88	24.19	4.80
31	50 (0)	50 (0)	500 (0)	1 (0)	13.25	18.50	3.72

[a] In grams of mass reduction per 100g of fresh sample, [b] in grams of water loss per 100g of fresh sample and [c] in grams of solute gain per 100g of fresh sample.

*: under different flow rate (300ml/min-1000ml/min), all the Re numbers of the solution were below 2000, within laminar flow region.

4.3 Results and discussion

4.3.1 Effect of the main process variables and their interactions on mass transfer

4.3.1.1 Weight reduction (WR), moisture loss (ML) and solids gain (SG)

The second order polynomial model, as given in Equation (4.8) was fitted to the experimental data (Table 4.1). The regression coefficients and ANOVA results are presented in Table 4.2 and indicated that a good fit was obtained for weight reduction ($R^2 = 0.93$), moisture loss ($R^2 = 0.97$) and solid gain ($R^2 = 0.87$). Figures 4.2-4.4 show response surfaces for two factors, with other factors kept constant at their central values. Central values for temperature, concentration, flow rate and time were 50°C, 50°Brix, 500 ml/min and 1h, respectively.

The results given in Table 4.2 verify that weight reduction was mainly influenced by processing time, and to a lesser extent by temperature and concentration of the dehydration solution, which showed similar effects. Weight reduction increased as time, temperature or concentration increased. The linear effect of the flow rate was not significant ($P>5\%$) to weight reduction, but its interaction effect with processing time was significant at 0.1% level. The difference of flow rate effects on weight reduction was probably due to the osmotic dehydration system specialty. Temperature showed linear, quadratic effects and interaction effects on weight reductions ($P<0.1\%$, $P<1\%$ and $P<0.1\%$); while concentration showed linear, quadratic and interaction effects ($P<5\%$, $P<5\%$ and $P<0.1\%$) on weight reduction; whereas time showed linear ($P<1\%$), quadratic ($P<0.1\%$) and interaction effects ($P<0.1\%$) indicating its larger influence on weight reduction. Figure 4.2a shows variations in weight reduction as a function of flow rate and processing time. The weight reduction increased sharply with processing time and more so at higher flow rate region. For short processing time ($t<30$min), flow rate showed less effect on weight reduction. Figure 4.2b depicts variations in weight reduction with changing temperature and concentration. Weight reduction increased with both temperature and concentration increasing. However, concentration showed more of an effect on weight reduction at certain temperature periods; higher concentration accelerated weight reduction especially at higher temperature regions. Similar results were reported by Videv et al. (1990) in the osmotic dehydration of apples and by Vijayanand et al. (1995) in the osmotic dehydration of cauliflower.

Table 4.2 Regression coefficients and analysis of variance of the second order polynomial model for the three dependent variables. X_1 = temperature; X_2 = concentration; X_3 = flow rate; X_4 = processing time.

	Apple cylinders		
	Weight reduction (%WR)	Moisture loss (%ML)	Solids gain (%SG)
Coefficient	Y_1	Y_2	Y_3
b_o	20.1837**	9.5542	-11.7269***
linear			
b_1	-0.6682***	-0.3952**	0.0934*
b_2	-0.3809*	-0.3746*	0.1813***
b_3	-0.0164	0.0177	0.0062
b_4	3.0803**	2.0516*	2.6321***
quadratic			
b_{11}	0.0046**	0.0029**	-0.0006
b_{22}	0.0039*	0.0020	-0.0005
b_{33}	0.00002	-0.000005	-0.000004
b_{44}	-2.2854***	3.2539***	-0.7600***
interactions			
b_{12}	0.0052***	0.0068***	-0.0010**
b_{13}	0.00002	-0.0002	0.0001**
b_{14}	0.1750***	0.1714***	0.0235***
b_{23}	-0.0002	-0.00009	-0.0001***
b_{24}	0.1546***	0.1802***	0.0041
b_{34}	0.0036***	0.0006	-0.0001
R^2	0.93	0.97	0.87

***, **, *: Coefficient significant at $P<0.1\%$, $P<1\%$, $P<5\%$ respectively.

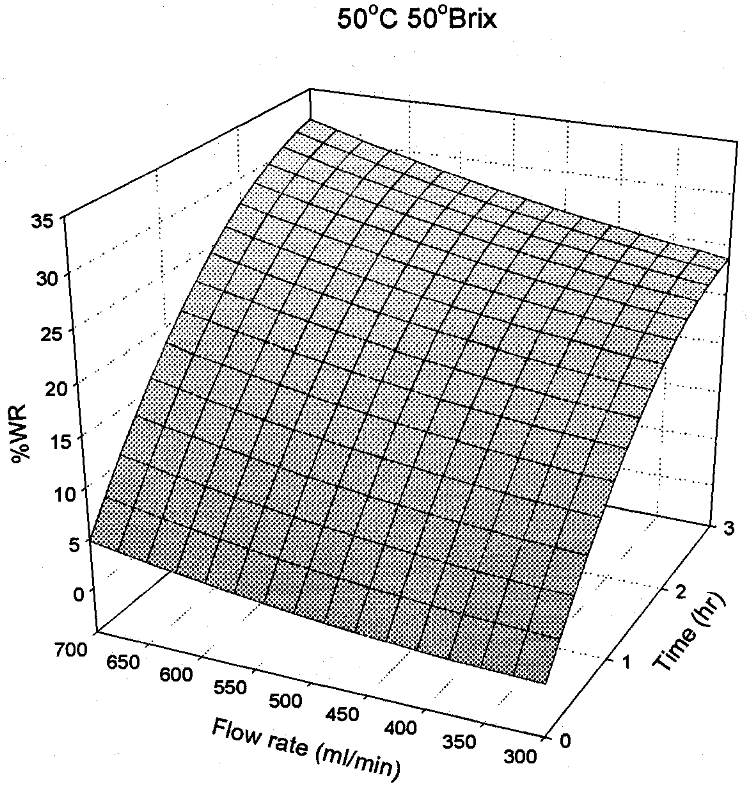


Figure 4.2a Weight reduction variation as a function of flow rate and time

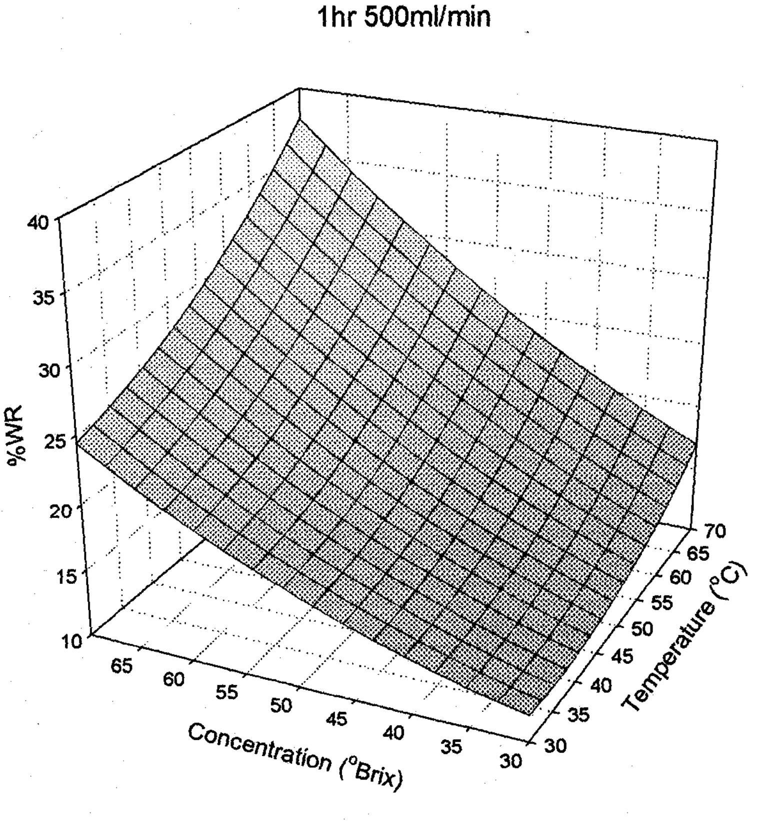


Figure 4.2b Weight reduction variation as a function of concentration and temperature

While an increase in concentration, temperature or processing time increased moisture loss, an increase in flow rate did not significantly (P>5%) influence moisture loss. Temperature showed linear, quadratic and interaction effects on moisture loss (P<1% P<1% and P<0.1%); while concentration showed linear (P<5%) and interaction effects (P<0.1%) on moisture loss; time showed linear (P<5%), quadratic (P<0.1%) and interaction effects (P<0.1%) indicating its larger influence on moisture loss. Variations in moisture loss with main variables are shown in Figure 4.3. Results revealed that moisture loss increased markedly with time under all flow conditions. Flow rate change might affect moisture loss (Fig 4.3a), however it was not a statistically significant factor. In the high temperature regions (T>45°C), concentration variation showed more of an effect compared with low temperature regions (T<45°C) (Fig 4.3b) on moisture loss, higher concentration gave much larger moisture loss in higher temperature regions than at lower temperature regions. Similarly, in the lower concentration regions (<45°Brix), temperature variation showed less of an effect compared to higher concentration regions (>45°Brix). On moisture loss, higher temperature gave much substantial moisture loss at more concentrated concentration regions than at less concentrated concentration regions.

For solids gain, the linear effect of flow rate was not significant (P>5%), but its interaction effects with temperature and concentration were significant at the 1% and 0.1% level, respectively. The difference of flow rate effects on solids gain might due to the solution circulation specialty. Temperature and concentration showed linear (P<5% and P<0.1%) and interaction effects (P<1%) indicating their certain influence on solids gain; time showed linear (P<0.1%), quadratic (P<0.1%) and interaction effects (P<0.1%) indicating its larger influence on solids gain. Variations in solids gain with main variables are shown in Figure 4.4. Results revealed that solids gain increased with time, regardless of flow rate. Flow rate change showed less effect on solids gain (Fig 4.4a), and thus was not a statistically significant factor. At low concentration (<50°Brix) conditions, temperature variation showed higher effects on solids gain than at high concentration (>50°Brix) conditions. At lower temperature regions (<50°C), concentration change showed higher effects on solids gain than at higher temperature (>50°C) regions (Fig 4.4b).

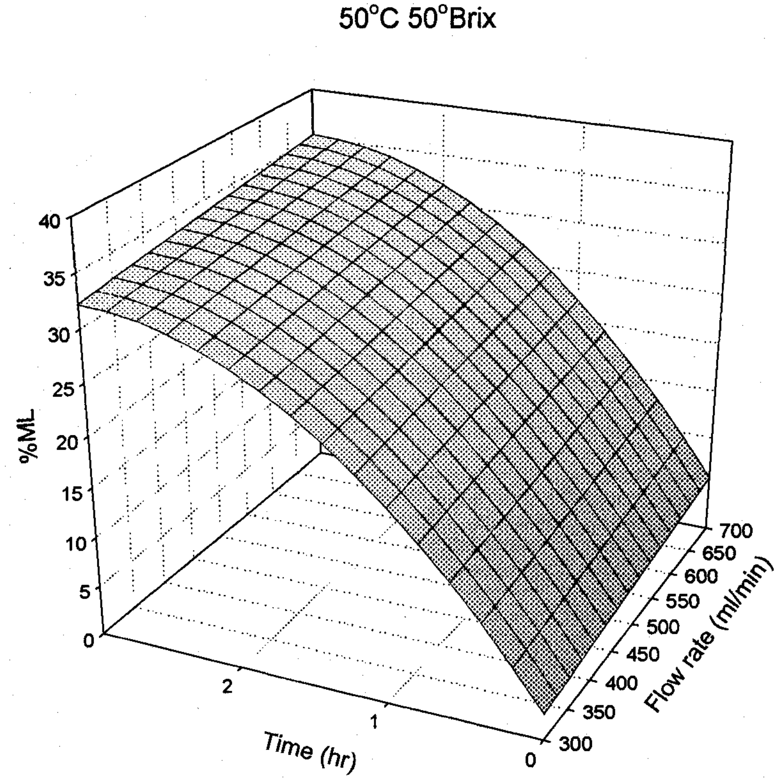


Figure 4.3a Moisture loss as a function of time and flow rate

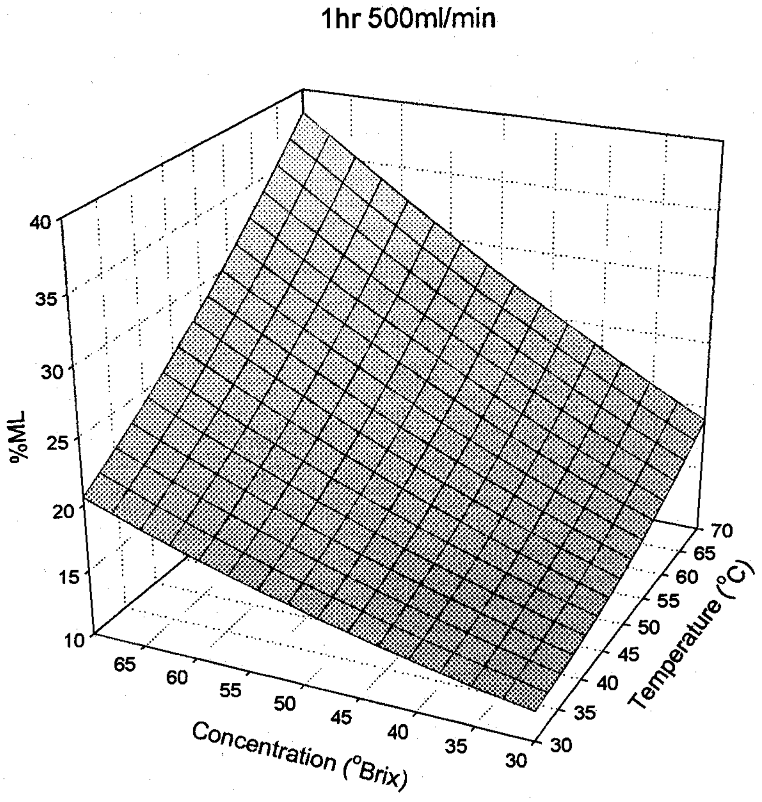


Figure 4.3b Moisture loss as a function of concentration and temperature

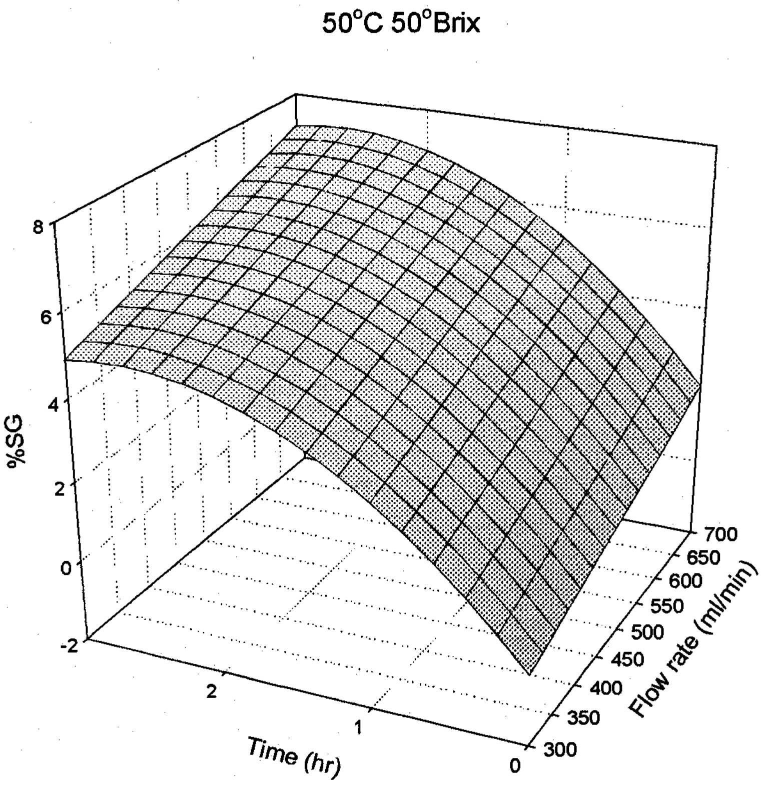


Figure 4.4a Solids gain as a function of time and flow rate

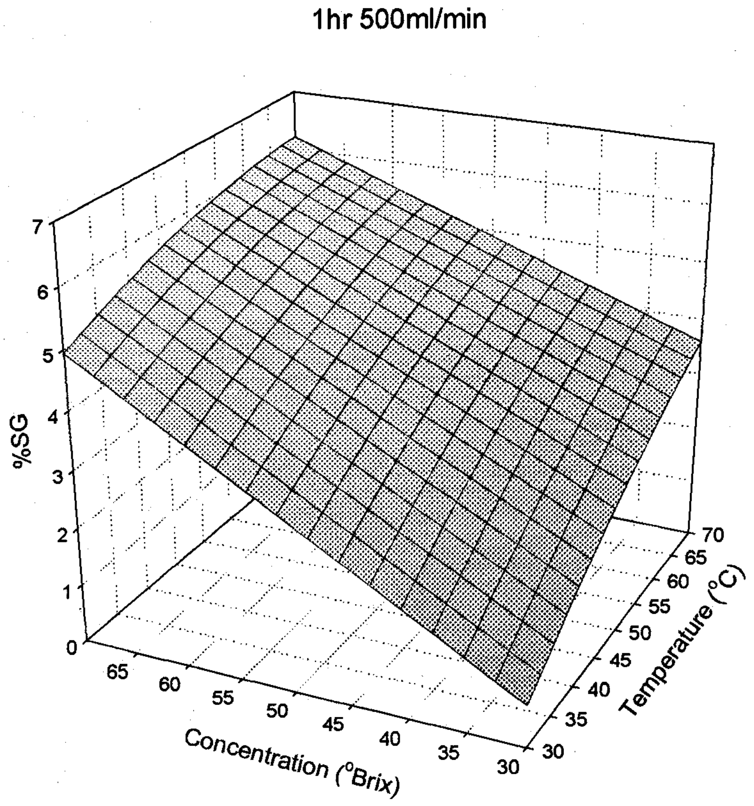


Figure 4.4b Solids gain as a function of concentration and temperature

4.3.1.2 Diffusion coefficients (D_m and D_s)

The polynomial second order model, as given in Equation 4.8 was also fitted to the calculated diffusivity data. The ANOVA results are presented in Table 4.3 and indicated that a good fit was obtained for moisture diffusivity (R^2 = 0.93) while solids diffusivity (R^2 = 0.75) was less satisfactory. Figures 4.5-4.6 show response surfaces for two factors, with other factors kept constant at their central value. Central values for temperature, concentration and flow rate were 50°C, 50°Brix and 500 ml/min, respectively.

In table 4.3, temperature, concentration and flow rate showed significant linear effects ($P<5\%$, $P<0.1\%$ and $P<5\%$) on moisture diffusivity; concentration showed a significant quadratic effect ($P<0.1\%$) on moisture diffusivity; whereas interaction effect of temperature and concentration, and interaction effect of temperature and flow rate significantly influenced moisture diffusivity ($P<5\%$ and $P<1\%$). Figure 4.5 shows variations in moisture diffusivity with main process variables. The moisture diffusivity increased sharply with processing temperature and more so at lower flow rate regions (Figure 4.5a). For low temperature regions ($T<50^{\circ}C$), flow rate showed a positive effect on moisture diffusivity, whereas at high temperature regions ($T>50^{\circ}C$), flow rate showed negative effects on moisture diffusivity. Figure 4.5b depicts variations in moisture diffusivity with temperature and concentration. Moisture diffusivity increased with temperature increasing; decreased with concentration increasing (<50°Brix) and increased with concentration increasing (>50°Brix). Temperature showed more of an effect on moisture diffusivity, especially at higher concentration region (>50°Brix). The difference of moisture diffusivity was probably due to the system specialty.

Lazarides et al. (1997) reported that as temperature increased from 20°C to 50°C, moisture diffusivity increased 2.5 times, while increasing concentration (between 45 and 65%) caused an increase of D_w only by a factor of 1.3-1.4. However, Hawkes and Flink (1978) studied mass transport in the osmotic concentration of apples, and found that the mass transfer coefficient increased with sucrose concentration when the concentration of the sugar solution was 50% or greater, which is agreement with our observations. And in our study we also found that at lower solution concentration ranges (40°Brix-50°Brix), with solution concentration increasing, moisture diffusivity decreased; moisture diffusion is affected by different concentration. At low concentration below 40°Brix, the process is impregnation situation (Rauout-Wack et al., 1994); at higher concentration above 50°Brix, the process is dehydration situation; within 40°Brix-50°Brix range, it might be intermediate situation. Whereas within the range of 50°Brix-65°Brix, with solution concentration increasing moisture diffusivity increased. However, with a much more sucrose concentration, the increasing trend of moisture diffusivity was reduced. Probably due to a thicker layer of sucrose solution being formed around the surface of the sample and impeding moisture loss. Early formation of a surface layer of solute hinders both moisture loss from the interior of the sample and further uptake of sucrose from the solution (Lenart and Flink, 1984a). Furthermore, the difference in sucrose concentration at the interface of the product provides an impetus for solids gain into the product to increase. The resulting weaker internal concentration gradient and increased concentration of sucrose in the product limit moisture transfer inside the product (Raoult-Wack et al., 1989). With a much higher temperature, the increasing moisture trend was reduced as well. This is probably due to the sample cell structure changes that occurred which impeded the moisture loss.

Table 4.3 Regression coefficients and analysis of variance of the second order polynomial model for the three dependent variables. X_1 = temperature; X_2 = concentration; X_3 = flow rate.

	Apple cylinders	
	Moisture diffusivity (D_m)	Solids diffusivity (D_s)
Coefficient	Y_1	Y_2
b_o	23.2016	-26.6479
linear		
b_1	0.7084*	1.5547*
b_2	-2.0243***	-0.6865
b_3	0.0508*	0.0447
quadratic		
b_{11}	-0.0004	-0.0030
b_{22}	0.0197***	0.0222**
b_{33}	--	--
interactions		
b_{12}	0.0061*	-0.0188**
b_{13}	-0.0007**	0.0004
b_{23}	-0.0003	-0.0010*
R^2	0.93	0.75

***, **, *: Coefficient significant at $P<0.001$, $P<0.01$, $P<0.05$ respectively

For solids diffusivity, flow rate change was not significant (P>5%). Temperature and concentration showed linear (P<5%) and quadratic (P<1%) effects on solids diffusivity, respectively; interaction effect of temperature and concentration, and interaction effect of concentration with flow rate showed significant effects (P<1% and P<5%) on solids diffusivity. Variations in solids diffusivity with main variables are shown in Figure 4.6. Results revealed that solids diffusivity increased with temperature, regardless of flow rate variation. Flow rate change showed a negative effect on solids diffusivity (Fig 4.6a); increased flow rate reduced solids diffusivity. At lower concentration regions (<50°Brix), temperature change showed higher effects on solids diffusivity than at higher concentration (>50°Brix) regions (Fig 4.6b). Similarly, at higher temperature regions (>50°C), concentration variance showed less effects on solids diffusivity than at lower temperature regions (<50°C).

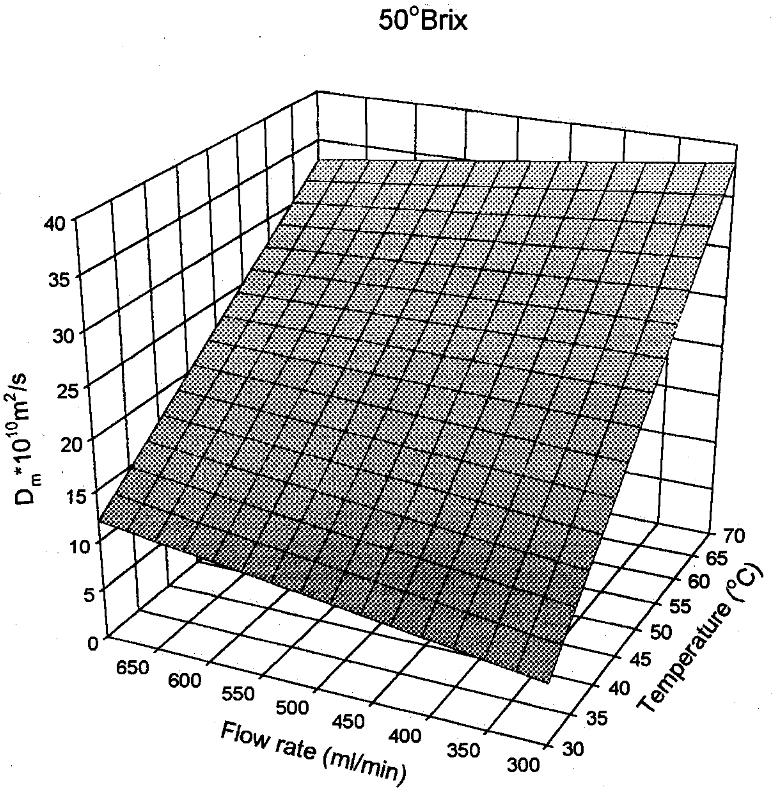


Figure 4 5a Moisture diffusivity as function of flow rate and temperature.

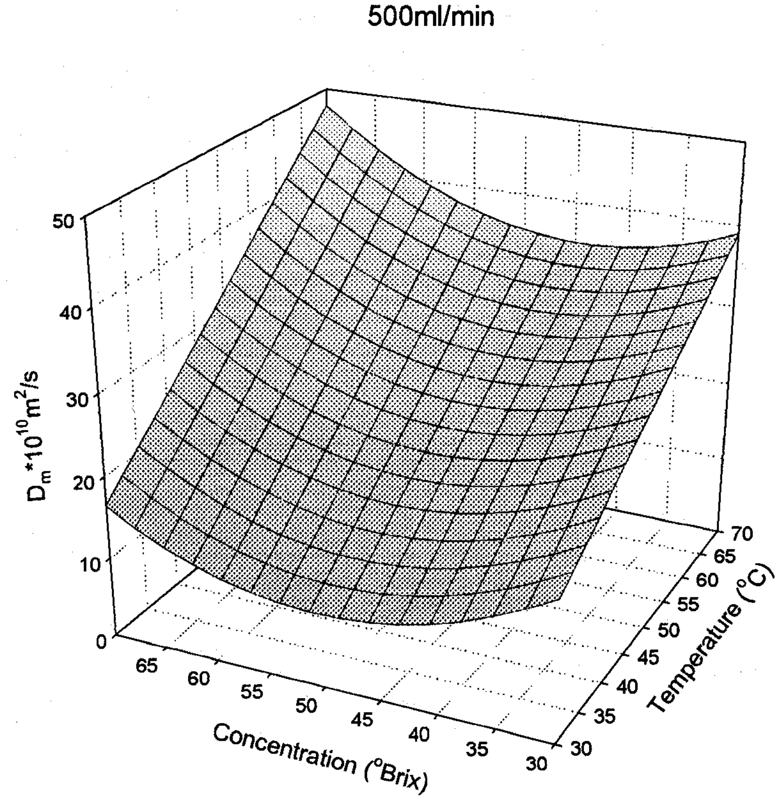


Figure 4.5b Moisture diffusivity as a function of concentration and temperature

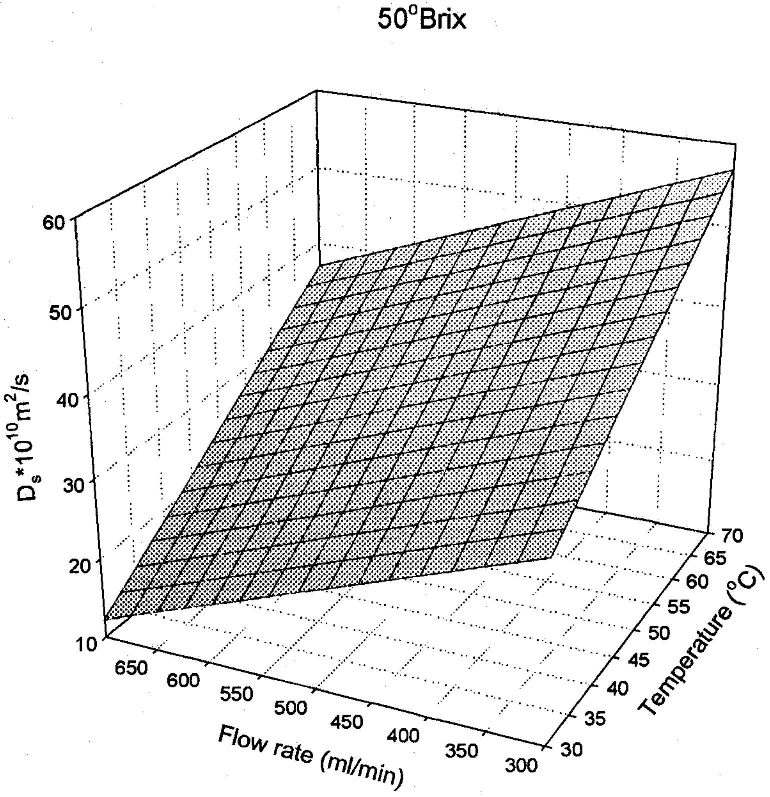


Figure 4.6a Solids diffusivity as function of flow rate and temperature

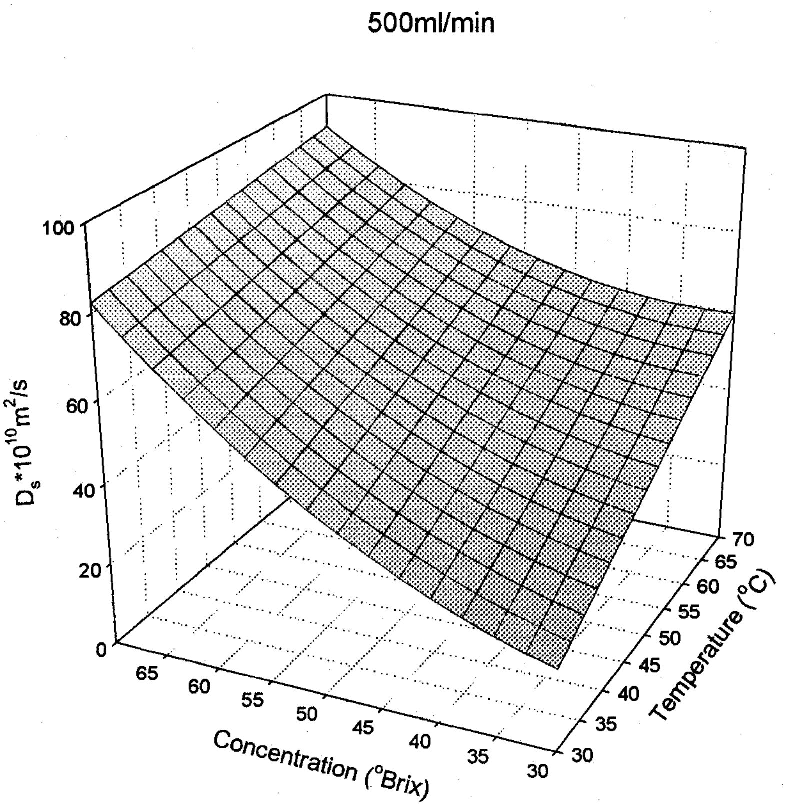


Figure 4.6b Solids diffusivity as function of concentration and temperature

4.3.1.3 Time to get the sample 20% weight reduction, 25% moisture loss and 5% sample solids gain (T_w, T_m and T_s)

The dehydration times for each condition were calculated using equations (4.2-4.4). The data for dehydration time with respect to weight reduction (T_w), moisture loss (T_m) and solids gain (T_g) are summarized in Figure 4.7 (a, b and c) for the different conditions. As expected, the dehydration time (T_w T_m and T_s) decreased with increasing temperature and sucrose concentration. The shortest T_w and T_m were 0.62h and 0.60h for the condition of 65°C-65°Brix, which represented one of the high temperature-high concentration conditions used in this study. The longest T_w and T_m were 2.21h and 1.87h for the condition of 45°C-45°Brix, which represented one of the lower temperature-low concentration conditions used in this study. In addition, the shortest T_s was 0.75h for the condition of 65°C-65°Brix and the longest T_s was 2.03h for the condition of 45°C-45°Brix. From these observations, we could compare the efficiency of the different conditions with respect to dehydration time for respective weight reduction (T_w), moisture loss (T_m) and solids gain (T_g).

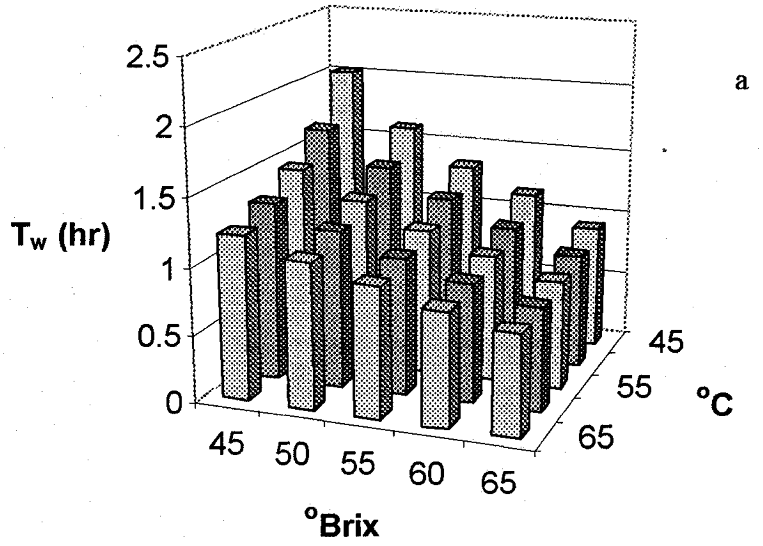
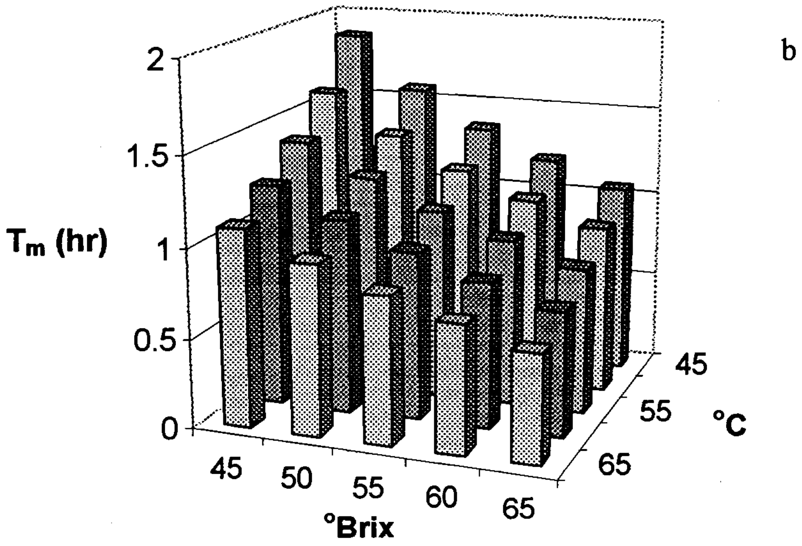


Figure 4.7a Time to get the sample weight reduction 20% T_w under different conditions



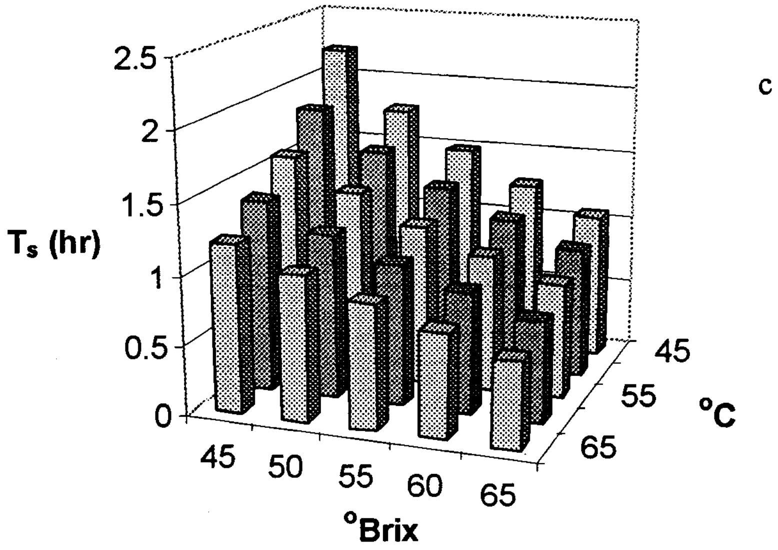


Figure 4.7 Time to get the sample moisture loss 25% T_m (b) and sample solids gain 5% T_s (c) under different conditions

4.3.2 Comparison the efficiency of continuous flow osmotic dehydration (CFOD) with conventional osmotic dehydration (COD) process

The comparable parameters of the two systems are general trend parameter: %ML and %SG during same time period, mass transfer coefficients (D_m and D_s) under same time period and times to reach certain weight reduction (T_w), certain moisture loss (T_m) and certain solids gain (T_s). The results are shown in Table 4.4-4.6 respectively. Moisture loss (ML%) and solid gain (SG%), in terms of percentage were calculated for the three combinations of temperatures (40, 50 and 60°C), concentrations (40, 50 and 60°Brix) and the flow rate (500 ml/min) from equation 4.3 and 4.4. The range of temperatures and concentrations chosen were justified by previous work. Flow rates were considered based on the ratio of contactor solution volume to flow rate: $V_{solution}$ /flow rate = 1. Inside the dehydration contactor, the volume ratio of sample to osmotic solution is 1: 5.

Table 4.4a Continuous flow osmotic dehydration ML% and conventional osmotic dehydration ML% comparison under different conditions

Conditions		Continuous flow OD*	Conventional OD
°C °Brix	Time (h)		
40°C40°B	0	0	0
	0.5	8.99±0.83	9.56±0.95
	1.0	13.00±1.14	12.04±0.41
	1.5	16.31±0.92	15.07±0.12
	2.0	19.13±1.58	16.26±0.38
	2.5	20.34±0.88	19.53±0.47
	3.0	22.26±1.26	18.22±0.95
50°C50°B	0	0	0
	0.5	12.54±0.47	12.85±0.48
	1.0	18.49±0.57	18.84±0.58
	1.5	23.25±1.24	23.86±0.53
	2.0	27.48±0.52	30.29±1.18
	2.5	29.47±1.15	34.01±0.46
	3.0	32.65±0.43	37.79±0.38
60°C60°B	0	0	0
	0.5	20.67±0.26	22.24±0.36
	1.0	27.64±1.33	28.12±0.11
	1.5	33.12±0.51	31.81±2.91
	2.0	39.80±0.14	39.91±0.18
	2.5	42.29±0.91	44.09±0.69
	3.0	47.66±1.41	48.54±0.93

t-test: paired two sample for means showed that the two ML% were same at 95% confidence (P>0.05).

Table 4.4b Continuous flow osmotic dehydration SG% and conventional osmotic dehydration SG% comparison under different conditions

Conditions		Continuous flow OD	Conventional OD
°C °Brix	Time (h)		
40°C40°B	0	0	0
	0.5	1.85±0.11	1.76±0.20
	1.0	2.66±0.37	2.62±0.22
	1.5	3.48±0.17	3.12±0.06
	2.0	3.71±0.71	3.23±0.02
	2.5	3.90±0.17	3.46±0.22
	3.0	4.04±0.09	3.49±0.07
50°C50°B	0	0	0
	0.5	3.84±0.14	3.43±0.13
	1.0	4.14±0.36	4.68±0.11
	1.5	4.73±0.22	4.86±0.11
	2.0	5.61±0.21	5.75±0.43
	2.5	6.02±0.35	6.23±0.15
	3.0	6.50±0.12	6.65±0.16
60°C60°B	0	0	0
	0.5	3.80±0.34	4.50±0.56
	1.0	4.70±0.26	5.37±0.31
	1.5	5.48±0.47	5.79±0.13
	2.0	5.50±0.20	6.32±0.20
	2.5	6.16±0.10	7.23±0.11
	3.0	6.21±0.06	7.36±0.14

T-test: paired two sample for means showed that the two SG% was same at 95% confidence ($P>0.05$). Continuous flow osmotic dehydration at flow rate 500ml/min.

Table 4.4 shows both the %ML and the %SG under the continuous flow osmotic dehydration process and conventional osmotic dehydration process was similar. The efficiency of the systems: continuous flow osmotic dehydration process and conventional osmotic dehydration process in terms of moisture loss and solids gain were statistically same ($P>0.05$).

Table 4.5. Comparison of moisture diffusivity (D_m) and solids diffusivity (D_s) during continuous flow osmotic dehydration process and conventional osmotic dehydration process

Combination	Continuous flow OD		Conventional OD	
(°C/°Brix)	$^{a}D_m*10^{10}m^2/s$	$^{b}D_s*10^{10}m^2/s$	$^{a}D_m*10^{10}m^2/s$	$^{c}D_s*10^{10}m^2/s$
40/40	16.50	12.33	12.34	12.33
40/50	14.95	15.91	15.65	20.05
40/60	17.52	19.37	15.83	17.60
50/40	22.14	18.77	21.32	21.23
50/50	21.26	20.61	24.01	28.61
50/60	24.50	22.33	23.57	25.82
60/40	27.84	25.57	26.96	28.69
60/50	27.63	25.67	29.03	35.73
60/60	31.54	25.66	27.97	32.60

T-test: paired two sample for means showed that the two D_m was same at 95% confidence ($P>0.05$); the two D_s was different at 95% confidence ($P<0.05$).
Continuous flow osmotic dehydration at flow rate 500ml/min.

The values of calculated moisture diffusivity in the continuous flow osmotic dehydration process were found to be in the range of 10^{-9}-$10^{-10}m^2/s$ and comparable with conventional osmotic dehydration coefficients ($P>0.05$) (Table 4.5). The values of calculated solids diffusivity in the continuous flow osmotic dehydration process were found to be in the same range of 10^{-9}-10^{-10} m^2/s, but lower than that of conventional osmotic dehydration solids diffusivity ($P<0.05$).

Table 4.6. Comparison of certain dehydration time* (T_w and T_m) during continuous flow osmotic dehydration process and conventional osmotic dehydration process

Conditions	T_w (hr)		T_m (hr)	
	CFOD[a]	COD[b]	CFOD[a]	COD[b]
40°C45°Brix	2.83	2.85	2.60	2.70
40°C50°Brix	2.10	2.24	1.83	2.17
40°C55°Brix	1.68	1.86	1.55	1.87
40°C60°Brix	1.40	1.58	1.36	1.68
50°C45°Brix	1.85	1.96	1.76	1.86
50°C50°Brix	1.55	1.64	1.60	1.56
50°C55°Brix	1.32	1.39	1.38	1.37
50°C60°Brix	1.13	1.19	1.20	1.24
60°C45°Brix	1.39	1.45	1.24	1.41
60°C50°Brix	1.20	1.23	1.08	1.19
60°C55°Brix	1.04	1.04	0.94	1.05
60°C60°Brix	0.88	0.89	0.81	0.95

t-test: paired two sample for means showed that the two system dehydration time (T_w and T_m) were different at 95% confidence ($P<0.05$).
*:due to the T_s of COD was not strictly followed temperature and concentration variation, it is not compared with CFOD T_s in this table.

The efficiency of the continuous flow osmotic dehydration (CFOD) process and conventional osmotic dehydration (COD) process systems, in terms of time reach certain weight reduction (T_w) and moisture loss (T_m) were higher than that of the conventional osmotic dehydration process.

4.3.3 Effectiveness of the system

To evaluate the contactor system effectiveness, the following functions have been employed (Marouzé, et al., 2001):

- Function F1: allowing solid food to be contacted with a liquid phase consisting of a solution with a high concentration of solutes (salts, sugars, mixed, etc.). There are six assessment criteria:
    - C11: creating relative movement between the solution and the food, characterized by relative speed and homogeneity for all the food,
    - C12: absence of mechanical damage to be the food (not broken, worn or crushed),
    - C13: control of treatment time and, for equipment used for continuous processing, control of the spread of residence times (SRT) in the contactor to ensure homogenous treatment of the food,
    - C14: ability to accept different shapes of food (whole or in cubes, slices or fillets),
    - C15: reduction of the solution/mass ratio (a low mass ratio is of particular interest if the cost of the solution is high; it also restricts equipment size),
    - C16: avoidance of oxidation reaction in food in contact with the air.
- Function F2: allowing the solution to be introduced and removed.
- Function F3: allowing the food to be introduced and removed (for continuous processing: continuous introduction, and removal of food when it has reached the required state of treatment).
- Function F4: allowing control of the process control parameters.
    - C41: food and solution temperature,
    - C42: solution concentration,
    - C43: static pressure of food and solution,

  - C44: agitation.

- Function F5: complying with the appropriate mechanical, electrical and food-related standards.
- Function F6: for industrial equipment, having a reasonable cost of manufactureing.

Table 4.7 Responses of the studied osmotic dehydration principles to the functions and the assessment criteria (Marouzé et al., 2001)

Principles	Operating mode[a]	Functions and assessment criteria[b]						
		F1, contacting						F4, control
		C11	C12	C13[c]	C14	C15	C16	C44
Immersion without solution renew	Batch	*	****	****	***	***	****	No
Immersion+ movement	SB	*	***	****	****	**	****	No
Counter-current percolated bed	C	**	**	**	*	**	***	No
Hydraulic mixing	Batch	****	*	****	*	**	***	Yes
Multi-level drenching	B/SB	****	****	****	***	****	*	No
Continuous flow OD	B	****	****	***	****	****	****	No

[a] Operation mode: batch-batch process, SB-succession of small batches, C-continuous processing.

[b] Responses of the principle to the functions and assessment criteria: * not satisfied, **patially satisfied, ***adequately satisfied, ****fully satisfied.

[c] Treatment time and spread of treatment times for principles: used in the batch processing, ****treatment time fully controlled.

The selected contact modes are compared and shown in Table 4.7, which indicates the extent to which each mode provides the required functions, using a 4-point scale. The lowest rating indicates that the principle fails to provide the required functions and the highest rating indicates that the principle provides the required function perfectly. The ability of osmotic dehydration allowing good contact of food with the osmotic solution was set as the first assessment criteria, as mass transfer is directly linked to this factor. The other functions (F2~F6) are not selected and compared here. Generally, in terms of contacting, it is apparent that the continuous flow osmotic dehydration contactor presents a good response, even though it appears to be hard to adapt to continuous loading and unloading of samples.

4.4 Conclusions

- Fick's equation of unsteady state diffusion can be used to calculate the mass diffusion coefficients during the osmotic dehydration process under continuous flow conditions.
- A continuous flow osmotic contactor was developed to be an efficient process in terms of osmotic dehydration apple cylinders. Being a separate operation unit, the dehydration process and solution management can be done in a more efficient way: by removing the suspension, solutes and other compounds from the solution; maintaining the physico-chemical and hygiene characteristics of the concentrated solution individually without interrupting the dehydration process involved. This process has potential application in osmotic dehydration with some modifications such as the load and unloads the osmotically treated products before further treatment.
- Effectiveness evaluation functions used in this study can be widely applied to the osmotic dehydration system evaluation. Continuous medium flow osmotic dehydration (CFOD) process is more efficient than conventional osmotic dehydration (COD) process in terms of time reaches certain weight reduction (T_w) and moisture loss (T_m).

Preface to Chapter 5

Previously, in Chapters 3 and 4, continuous flow osmotic drying was shown to permit better exchange of moisture and solids between the food particle and osmotic solution than the conventional osmotic drying process. In this study, the effects of process temperature, solution concentration on moisture loss (ML), solids gain (SG) and mass transport coefficients (k_m and k_s) were evaluated and compared under microwave assisted osmotic dehydration (MWOD) versus continuous flow osmotic dehydration (CFOD). Mass transport coefficients in Hawkes and Flink's model (1978) are applied to compare the drying behavior of apple cylinders under two conditions: MWOD vs CFOD.

The objective of this study was to determine the influence of microwave heating on the transfer of moisture and solids during the osmotic dehydration of apple cylinders, and to compare the efficiency of microwave assisted osmotic dehydration (MWOD) with continuous flow osmotic dehydration (CFOD) within the range of experimental study.

In this study, microwave heating is applied to the osmotic dehydration process to improve mass transfer rate during the process. Moisture transfer rates demonstrated an increase and solids gain rate was reduced during microwave assisted osmotic dehydration process. This work would partially fulfill the second, fourth and fifth objectives of this thesis. This would enhance basic knowledge for further study on the osmotic dehydration principle and its application as described in later chapters.

Part of this research has been presented in some conferences and/or published in scientific journals detailed earlier. The experimental work and data analysis were carried out by the candidate under the supervision of professor Dr. H.S. Ramaswamy.

CHAPTER 5

COMBINE MICROWWAVE WITH OSMOTIC DEHYDRATION TO IMPROVE APPLE CYLINDRES MASS TRANSFER RATE DURING OSMOTIC DEHYDRATION PROCESS

Abstract

Continuous flow osmotic drying permits a better exchange of moisture and solids between the food particle and osmotic solution than the batch process. Osmotic drying has been well studied by several researchers mostly in the batch mode. Microwave heating has been traditionally recognized to provide rapid heating conditions. Its role in the finish drying of food products has also been recognized. In this study, the effects of process temperature, solution concentration on moisture loss (ML), solids gain (SG) and mass transport coefficients (k_m and k_s) were evaluated and compared under microwave assisted osmotic dehydration (MWOD) versus continuous flow osmotic dehydration (CFOD). Apple cylinders (2 cm diameter, 2 cm height) were subjected to continuous flow osmotic solution at different concentrations (30, 40, 50 and 60°Brix sucrose) and temperatures (40, 50 and 60°C). Similar treatments were also given with samples subjected to microwave heating. Results obtained showed that solids gain by the samples was always lower when carried out under microwave heating, while the moisture loss was increased. The greater moisture loss strongly counter-acted solids gain in MWOD and thus the overall ratio of ML/SG was higher in MWOD than in CFOD.

Keywords: Microwave, osmotic dehydration, apple, mass transport coefficient, ratio

5.1 Introduction

Osmotic dehydration is a partial water removing process based on the immersion of fruits and other products in a hypertonic sugar solution. The driving force comes from the water and solute activity gradients across the sample and solution interface. Mass transfer rate during osmotic dehydration depends on many factors such as the specific surface area of food pieces, temperature, treatment time, concentration and composition of the solute, mode of phase contacting (solid-liquid phases), pressure, and the product: vs solution ratio (Roult-Wack, 1994). Since the rate of mass transfer during osmotic dehydration is relatively slow, a number of techniques have been tried to improve the mass transfer rate. These techniques include: the application of a partial vacuum (Fito, 1994; Shi, et al., 1995; Rastogi & Raghavarao, 1996), freeze/thaw effects (Lazarides and Mavroudis, 1995), ultra high hydrostatic pressure (Rastogi & Niranjan, 1998; Rastogi., et al, 2000), high intensity electrical field pulses (Rastogi, et al., 1999; Taiwo, et al., 2003; Ade-Omowaye, et al., 2003), supercritical carbon dioxide (Tedjo, et al., 2002) to the material prior to osmotic dehydration treatment; using centrifugal force (Azuara, et al., 1996), ultrasound (Simal, et al., 1998) and microwave (Li and Ramaswamy, 2003) during the osmotic dehydration process.

Compared with the conventional osmotic dehydration process, vacuum treatments increase the water transfer rate, but have no effect on sugar uptake; the treatments are more effective for high porosity sample (Fito, 1994; Shi, et al., 1995; Rastogi & Raghavarao, 1996). Application of high pressure damages the cell structure, leaving the cells more permeable, which affects both moisture transfer and solid transfer rates during osmotic dehydration; however, it can offer better quality in the product (Rastogi & Niranjan, 1998; Rastogi et al., 2000; Ramaswamy et al., 2004). Freezing/thawing does not exhibit a significant change in the rate of water loss during complimentary osmotic dehydration, whereas sugar gain rate increases sharply (Lazarides and Mavroudis, 1995). With centrifugation, solids uptake by the food samples is lower, while the water loss is slightly increased (Azuara et al., 1996). Application of pulsed electric field (PEF) treatment results in increased cell membrane permeability facilitating better water loss and limited sugar uptake during OD process but facilitates higher sugar gain (Tedjo et al., 2002). Applying microwave increases moisture loss and restricts the uptake of solids during the process.

Microwave drying employs a completely different mechanism for heating. Because of the internal heat generated by the microwave field, there is an internal pressure gradient, which effectively pushes the water to the surface. There are many factors that affect the heating of food in a microwave field and this makes the heating process more complex. The heating is accomplished both by the absorption of microwave energy by dipolar water molecules resulting in their rapid rotation as well as polarization of ionic components of the food. The microwave technology offers several advantages such as less start-up time, faster heating, energy efficiency, more precise control and selective heating (Decareau and Peterson, 1986). In food dehydration, microwave is mainly used for products such as pasta and potato chips. Freeze-drying and vacuum drying, in conjunction with microwave energy, also shows promise. Pasteurization of foods by microwave processing has been successfully accomplished for decades, especially in Europe.

The effect of temperature gradient on moisture migration during microwave heating of food materials was studied by Zhou et al. (1994). They found that for high density food material (potato), temperature gradient effect on moisture migration was found to be negligible (less than 5%); while for low density and porous food materials (bread), percentage contribution of moisture movement due to temperature gradient was high (114%). However, the absolute difference of moisture content with and without considering temperature gradient effect was small for the microwave process. The application of microwave to osmotic dehydration with the aim of accelerating mass transfer and reducing solid gain have not been explored previously.

In osmotic dehydration mass transfer consideration, most available models are based on Fick's law of diffusion with simplifying assumptions and use the particular solution given by Crank for unsteady one-dimensional transfers, for instance between a plane sheet and a well-stirred solution, either with a constant surface concentration or with a limited volume of solution. The extent of dehydration and mass transfer coefficient ranges are governed by the equilibrium between the osmotic pressure exerted by the solutes of the food portion on the side of the natural vegetative membrane and that of saturated sucrose solution on the other side. The equilibrium moisture loss and solids gain are generally based on theoretical values or certain assumptions. The resulting apparent diffusivities are correlated with the concentration and temperature of the solution. However, various limitations existing for interpreting the mass transfer phenomenon during the osmotic dehydration process (Raoult et al., 1989). In this study, mass transport coefficients in Hawkes and Flink's model (1978) are applied to compare the drying behavior of apple cylinders under microwave assisted osmotic dehydration (MWOD) vs continuous flow osmotic dehydration (CFOD) conditions.

The objective of this study was to determine the influence of microwave heating on the transfer of moisture and sucrose during the osmotic dehydration of apple cylinders, in order to maximize moisture loss while limiting the solids gain; and to compare microwave assisted osmotic dehydration (MWOD) with continuous flow osmotic dehydration (CFOD) within the range of experimental study.

5.2 Materials and methods

A batch of Idared variety of apples of uniform size and ripeness, and commercial sucrose (sugar) were obtained from the Macdonald Campus Farm and a local supermarket, respectively. The fruits were refrigerated at 2°C-5°C and at 95% relative humidity until being used for the experiments. After cutting the calyx and pedicel ends, apple cylinders were cut vertical to their axis (five cylinders of 2.0 cm in diameter, 2.0 cm in height from each fruit).

5.2.1 Osmotic dehydration procedure

Osmotic dehydration was carried out using four different sucrose solutions: 30, 40, 50 and 60°Brix, at three temperatures: 40, 50 and 60°C. Higher temperatures could not be used without severe negative side effects, *i.e.* tissue softening, enzymatic browning and loss of aroma. On the other hand, lower temperatures would prohibit thorough mixing and satisfactory mass transfer characteristics because of the dramatic increase in viscosity of the osmotic medium. The fruit-syrup mass ratio (R) was kept 1:10 and the osmotic solution was circulated. At the end of 30, 60, 90, 120, 150 and 180 min immersion time, samples were withdrawn out of the solution, quickly rinsed, gently blotted with paper towel to remove adhering osmotic solution and then analyzed. Experiments were run in triplicate both in continuous flow osmotic dehydration (CFOD) or microwave assisted osmotic dehydration (MWOD) system. Both CFOD and MWOD use the same system, however, the difference was in the CFOD operation was that the microwave and cooler system were off, and the solution temperature was maintained by a water bath. During MWOD, microwave power and operation temperature were set to control the process, while the flow rate was fixed. The temperature difference between flow in and flow out was 25°C, which meant that the microwave provided a 25°C temperature increase. A domestic microwave (SANYO EM-563) oven was used for this purpose and a schematic diagram is presented in Figure 5.1. A microwave transparent chamber containing the apple cylinders to be osmotically treated was placed in the oven and the solution was then circulated through. Temperatures of the input and output solution were monitored by thermocouples. The operation temperature was assumed to be the output solution temperature.

5.2.2 Moisture and solids content

The sugar concentration was measured with a portable refractometer (ATAGO, Japan) at ambient temperature. Moisture content of fresh or osmotically treated apple cylinders was determined by the oven method. The moisture content and total solids of fresh and treated apple cylinders were measured based on weight differences after drying in the oven (105°C for 24h). The moisture loss and solid gain were calculated by the equations 5.1-5.2.

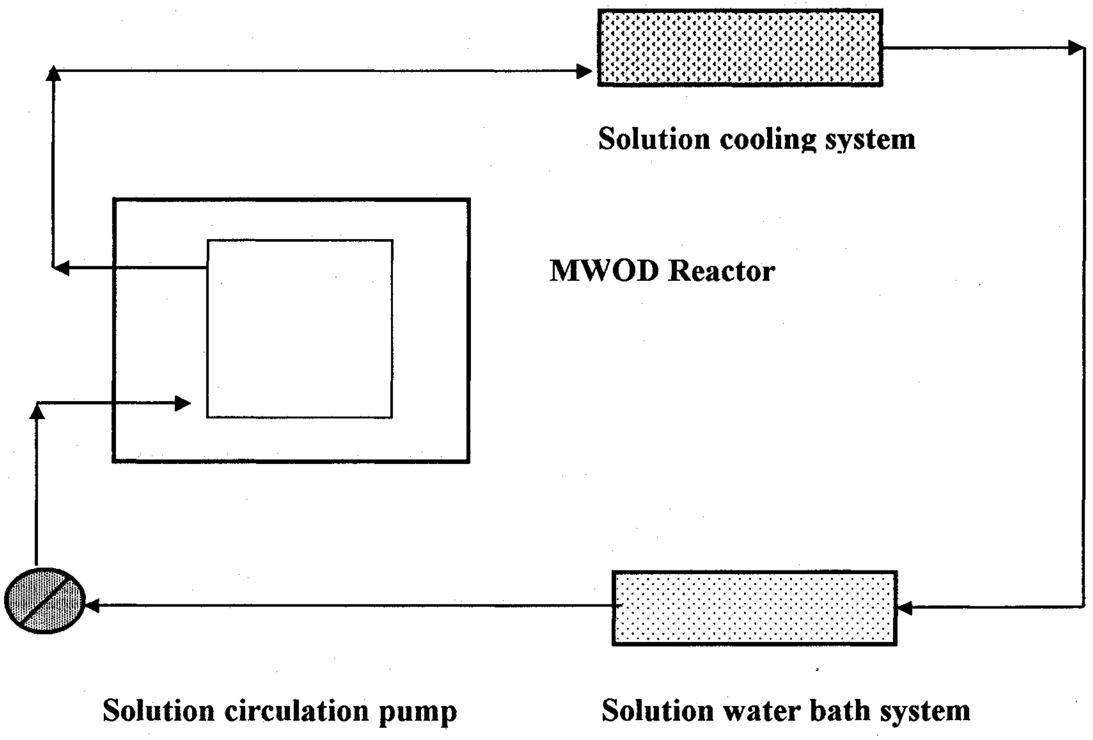


Figure 5.1. Schematic diagram of the microwave assisted osmotic dehydration system

5.2.3 Moisture loss and solids gain

The most important mass transport terminologies used in osmotic dehydration are moisture loss (water loss) and solid gain. The calculations are based on the general balance of concentration driven mass transfer between the liquid and solid phases:

Moisture loss (ML), the net water loss, on an initial sample mass basis:

$$\%ML = 100\frac{(M_0x_0 - M_tx_t)}{M_0} \quad (5.1)$$

Solids gain (SG), the net solids (soluble) transport into the sample, on an initial sample mass basis:

$$\%SG = 100\frac{(M_ts_t - M_0s_0)}{M_0} \quad (5.2)$$

5.2.4 Ratio of moisture loss over solids gain

The ratio of ML/SG was used to describe osmotic dehydration efficiency and calculated with ML over SG.

$$ratio = \frac{ML}{SG} \quad (5.3)$$

5.2.5 Time to get the sample 25% moisture loss (T_m) and 5% sample solids gain (T_s)

The osmotic dehydration time to get the sample moisture loss and solids gain to a given value is used to compare the osmotic drying effectiveness of different conditions. To be able to compare the different runs in the experimental set up, a level of 25% sample moisture loss, and a level of 5% sample solids gain were chosen and times were computed to result in such moisture loss and solids gain using the equations 5.1-5.2.

5.2.6 Mass transport coefficient

Since the equilibrium moisture loss (ML_∞) was difficult to obtain under microwave assisted osmotic dehydration (MWOD) conditions, moisture diffusion coefficients could not be calculated using the conventional procedures. The mass transport coefficients concept was selected instead of the conventional mass diffusion coefficients to compare mass transfer efficiency of the two processes. In order to provide meaningful comparison, the conventional osmotic dehydration data were also treated the same way in this chapter. Sample internal mass concentrations were plotted against square root of processing time, and obtained a line. Mass transport coefficients (k_m and k_s) were calculated from the slope of the line. The coefficients are used as convenient tool to compare the drying behavior of sample under two different treatment conditions not need to consider equilibrium moisture loss and solids gain influence.

$$\%ML = k_m t^{1/2} \qquad (5.4)$$

$$\%SG = k_s t^{1/2} \qquad (5.5)$$

The mass transport coefficients (k_m and k_s) are then related to solution concentration and processing temperature as in the following equations:

$$k_m = A * T^{x_m} * C^{y_m} \qquad (5.6)$$

$$k_s = B * T^{x_s} * C^{y_s} \qquad (5.7)$$

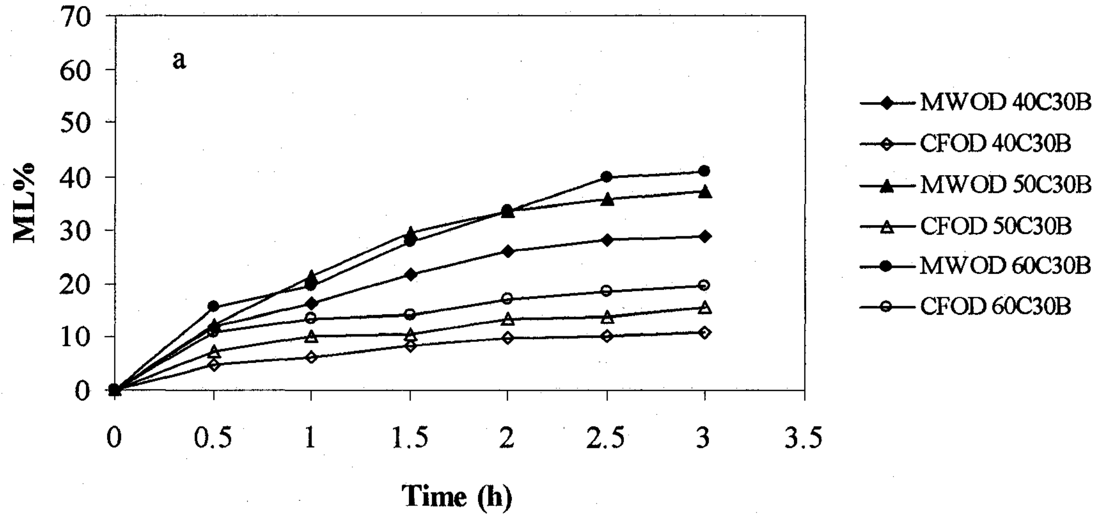
The parameter A, x_m, y_m, B, x_s, and y_x are estimated from the experimental data.

5.3 Results and discussion

5.3.1 Influence of microwave heating on moisture loss (ML)

In this study, apple cylinders were treated in 30-60°Brix at 40-60°C. The moisture loss of 30° and 60°Brix at different temperature conditions are illustrated in Figure 5.2 (a) and (b). The moisture loss (ML%) of apple cylinders was higher under microwave osmotic drying (MWOD) than under continuous flow osmotic dehydration (CFOD), ML% of both CFOD and MWOD was increased with an increasing temperature. This is agreement with Lenart *et al.* (1984), Figen *et al.* (2000) and Ramaswamy *et al.* (2002). Under MWOD at 40°C (Fig.5.3 a), the increase in ML% was 170%, 71%, 46% and 27% for 30, 40, 50 and 60°Brix, respectively; while at 60°C (Fig. 5.3 b), the increased ML% was 108%, 102%, 46% and 30% for 30, 40, 50 and 60°Brix, respectively (Table 5.1). There were no major differences in increased ML% range for the two temperature conditions, especially at the high solution concentration conditions: 40°C-50°Brix was 46%, 60°C-50°Brix was 46%; while at 40°C-60°Brix it was 27% and 60°C-60°Brix, 30%.

In the mean time, with the solution temperature increasing, ML% was increased for both CFOD and MWOD. Under MWOD at 30°Brix, the net increase in ML% after 3h was 170%, 138% and 108% for 40, 50 and 60°C, respectively; while at 60°Brix, the increase in ML% after 3h was 27%, 41% and 30% for 40, 50 and 60°C, respectively. The microwave treatment was thus beneficial in speeding up the moisture diffusion process, especially at low solution concentration conditions. At higher concentrations, 60°Brix, in the first 30min., the ML% for both CFOD and MWOD were almost the same. After that the ML% under MWOD was increased (Figure 5.2). The rapid loss of water in the beginning was apparently due to the existing large osmotic driving force between the dilute sap of the fresh fruit and the surrounding hypertonic solution. Thus the rate of moisture loss in both MWOD and CFOD was the highest at the beginning. However, with the process proceeding, the rate decreased very fast independently of what method was used. But with microwave heating, the internal moisture pressure was increased, thus the overall moisture loss was higher in MWOD than in CFOD (Figure 5.2 and 5.3) under different temperature and concentration correspondents.



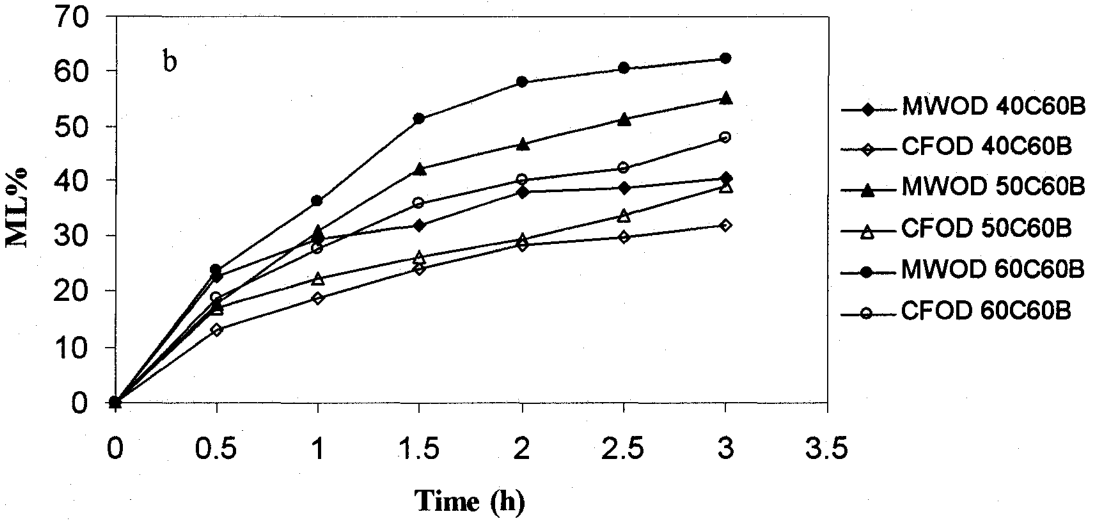


Figure 5.2. Comparison of moisture loss with MWOD and CFOD at same concentration 30°Brix (a) and 60°Brix (b) under different temperatures

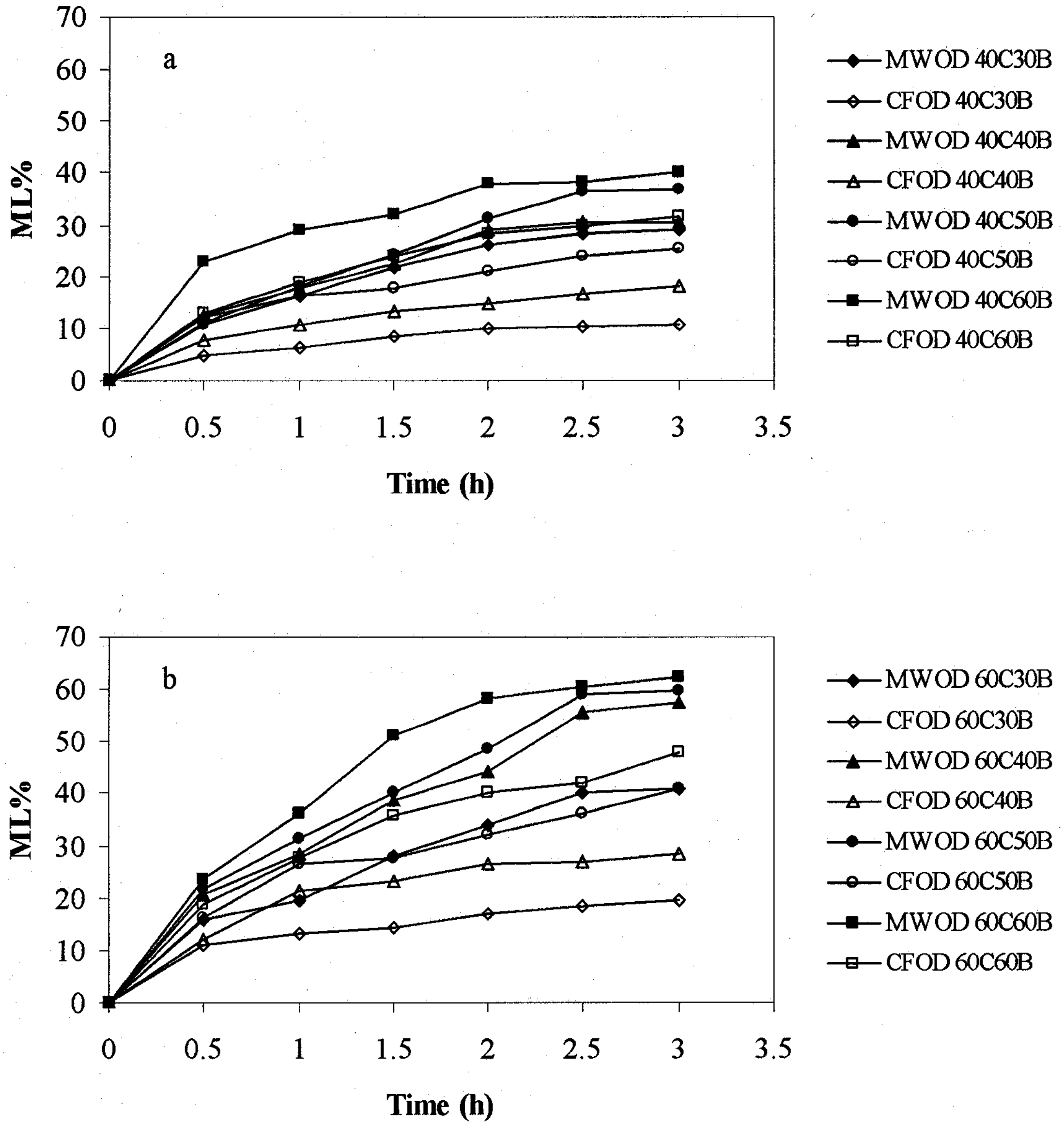


Figure 5.3. Comparison of moisture loss with MWOD and CFOD at same temperature 40°C (a) and 60°C (b) under different concentration

The higher moisture loss during MWOD could be explained by the fast and uniform heating effect of microwave heating on water molecules resulting in sample internal moisture pressure to increase and accelerate the osmosis. The microwave heating thus increased moisture loss, as shown in Figures 5.2 and 5.3. The microwave treatments were thus beneficial in speeding up water diffusion, and speeded up water molecules travel through the fruit tissue (Shi, *et al.* 1995). The resulting osmotic dehydration mechanisms between MWOD and CFOD might be different. CFOD was influenced by external conditions, solution chemical potential and solution temperature, etc.; while MWOD was influenced by both external conditions and internal conditions simultaneously, chemical potential and internal pressure (Baro-dynamic).

Table 5.1. Comparison of moisture loss % (g/g fresh apple) after 3h osmotic dehydration at different conditions

Process conditions	CFOD	MWOD	
	ML%^{a}	ML%^{b}	ΔML%
40°C 30°B	10.8±0.54	29.1±1.10	170
40°B	18.0±0.51	30.7±1.17	71.0
50°B	25.3±2.13	36.9±0.77	45.9
60°B	31.7±1.20	40.2±0.77	26.7
50°C 30°B	15.7±1.76	37.4±1.45	138
40°B	26.3±1.57	39.9±1.25	51.6
50°B	34.8±1.13	49.7±1.45	42.8
60°B	39.0±1.45	55.1±0.66	41.3
60°C 30°B	19.6±1.23	40.9±0.99	108
40°B	28.5±5.92	57.5±1.27	102
50°B	40.8±1.53	59.6±1.14	46.2
60°B	47.8±1.28	62.3±1.26	30.4

Different letter showed the two osmotic dehydration ML% was different (t-test: paired two sample for means at 95% confidence.)

5.3.2 Influence of microwave heating on solid gain (SG)

The evolution of solids gain (SG%) in MWOD and CFOD increased as solution concentration and temperature increased (Figure 5.4 and 5.5). Most solids gain occurred within the first two hours and then tapered off toward the equilibrium. However, under MWOD, the overall SG% was lower than under CFOD. It was interesting to note that the solids gain in MWOD was reduced by 7.3% compared to the same conditions (30°Brix, 50°C) in CFOD (Table 5.2). Under MWOD for low solution concentration, the existing chemical potential difference was low between the sample and the solution, therefore the solids gain rate was lower; and the more the microwave increased the outward diffusion of water, the net result was that the solids gain was even lower (Figure 5.4 a). At higher concentrations (50°Brix) the chemical potential difference was high between the sample and the solution; therefore the solids gain rate was high. The microwave increased outward diffusion of water effect was more obvious compared with low concentration conditions, thus SG% was reduced by 33% at the same temperature (50°C 50°Brix) in MWOD as compared with 7.3% in MWOD under the same conditions (50°C 30°Brix, Table 5.2). At 40°C, the decrease in SG% was 9.9%, 16%, 11% and 15% for 30, 40, 50 and 60°Brix, respectively; while at 60°C, the decrease in SG% was 40%, 20%, 40% and 20% for 30, 40, 50 and 60°Brix, respectively (Table 5.2). That meant that at higher temperatures, SG% under MWOD was reduced much more than with lower temperatures under the same conditions (Figure 5.5 b). The difference of sugar gain between MWOD and CFOD was attributed to the microwave treatment effects. The question is why an increased mass transfer allowed for a much faster moisture loss while reducing the solids gain. There exists a simultaneous interaction between moisture going out and solids coming in. Le Maguer (1996) indicated that sucrose transfer could not be the result of a diffusional phenomenon and the two transfer processes could be interdependent. The microwave heating induces an internal diffusion process. The uptake of solids is counteracted by the massive counter-current water diffusion movement. So the overall result is a sharp gain in moisture loss and a decline in solids gain.

Table 5.2. Comparison of solid gain % (g/g fresh apple) after 3h osmotic dehydration at different conditions

Process conditions	COD	MWOD	
	SG%[a]	SG%[b]	ΔSG%
40°C 30°B	1.62±0.15	1.46±0.16	-9.87
40°B	3.51±0.20	2.96±0.24	-15.7
50°B	4.27±0.35	3.80±0.17	-11.0
60°B	5.26±0.29	4.47±0.24	-15.0
50°C 30°B	1.78±0.22	1.65±0.19	-7.30
40°B	3.56±0.13	3.15±0.11	-11.5
50°B	5.13±0.22	3.43±0.23	-33.1
60°B	6.72±0.28	4.63±0.30	-31.1
60°C 30°B	2.85±0.16	1.72±0.09	-39.7
40°B	4.47±0.48	3.56±0.07	-20.4
50°B	6.69±0.21	4.00±0.12	-40.2
60°B	6.34±0.21	5.05±0.24	-20.4

Different letter showed the two osmotic dehydration SG% was different (t-test: paired two sample for means at 95% confidence.)

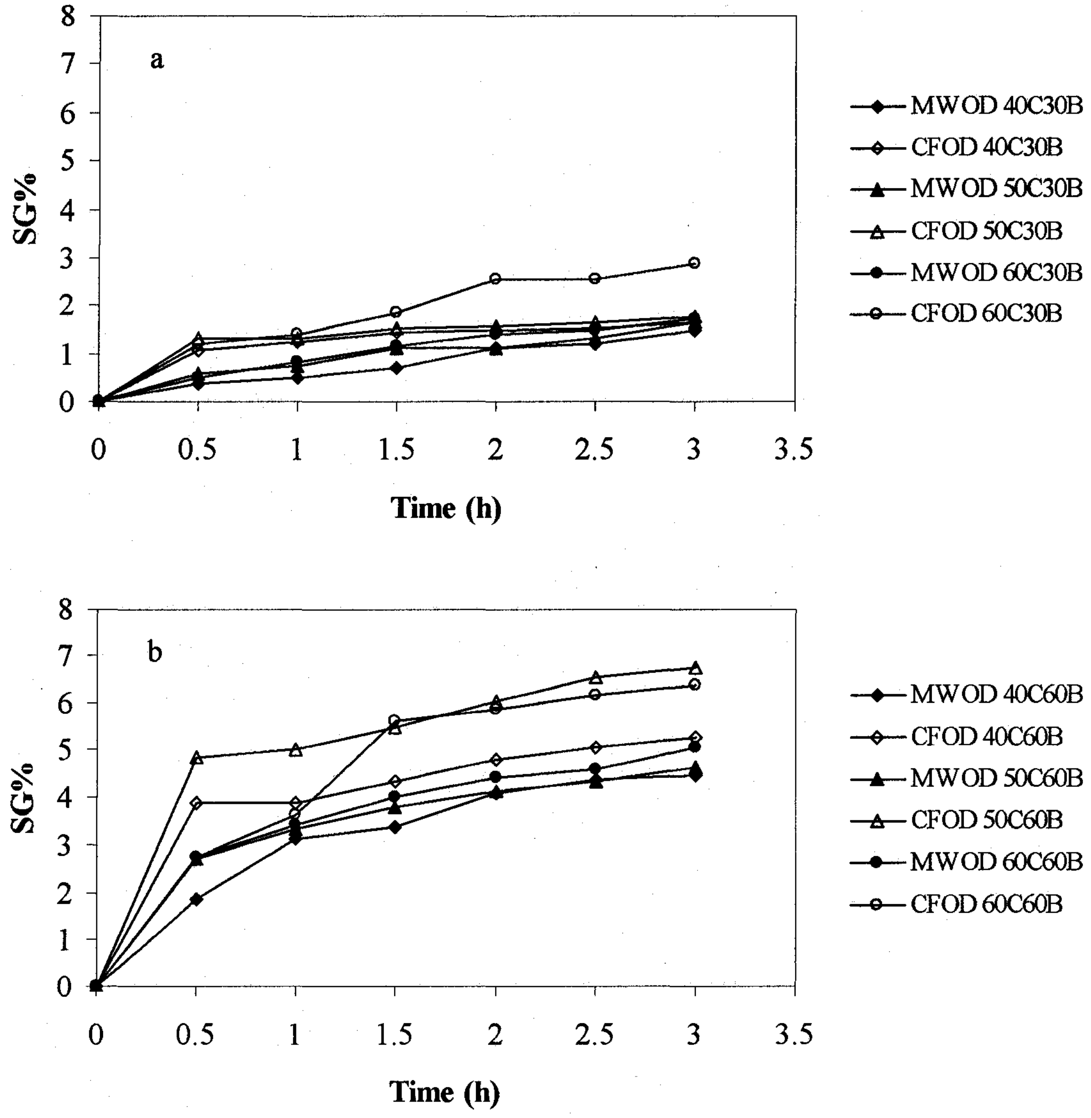


Figure 5.4. Comparison of solids gain with MWOD and CFOD at same concentration 30°Brix (a) and 60°Brix (b) under different temperature

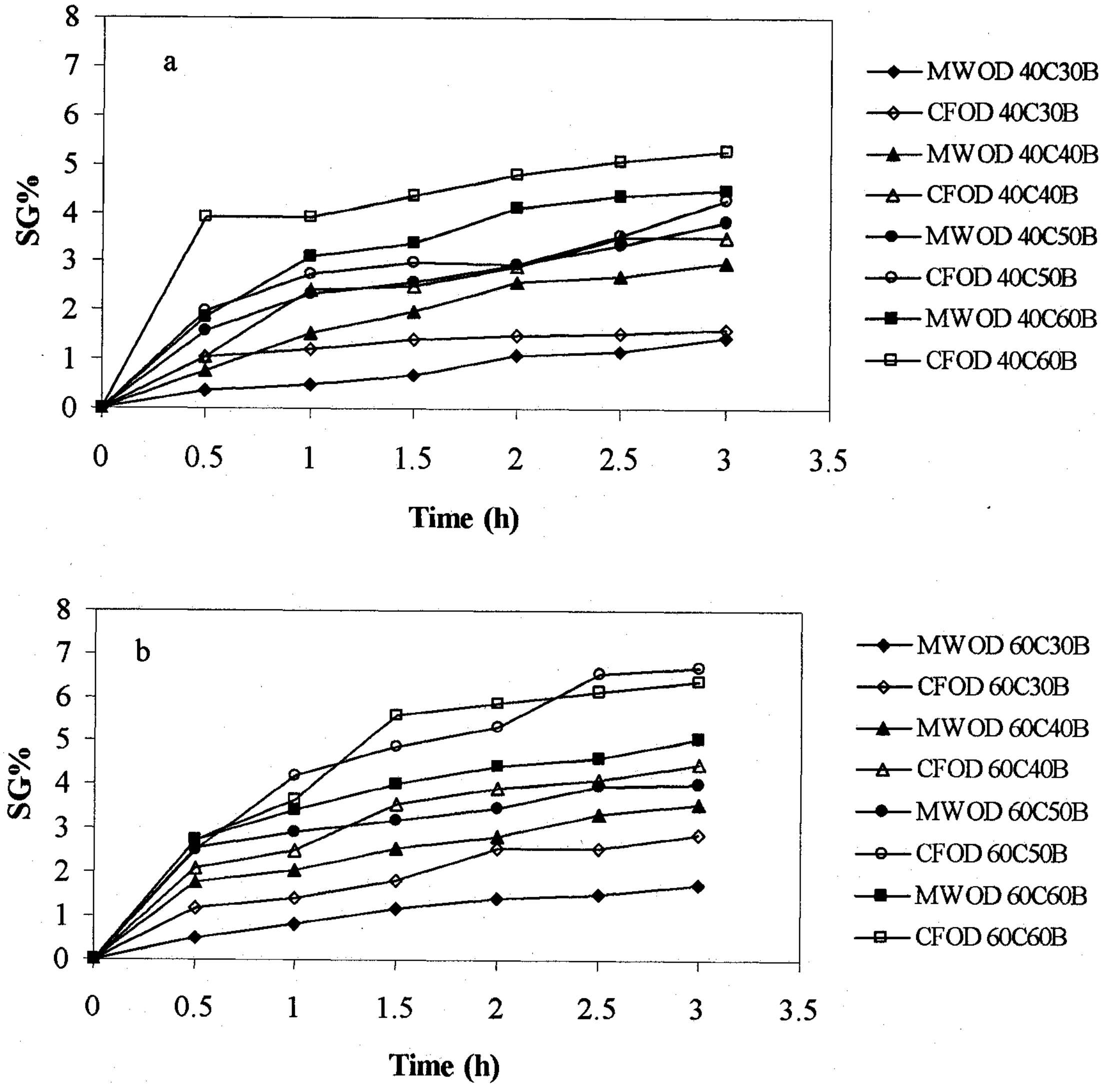


Figure 5.5. Comparison of solids gain with MWOD and CFOD at same temperature 40°C (a) and 60°C (b) under different concentration

5.3.3 ML/SG of MWOD and CFOD

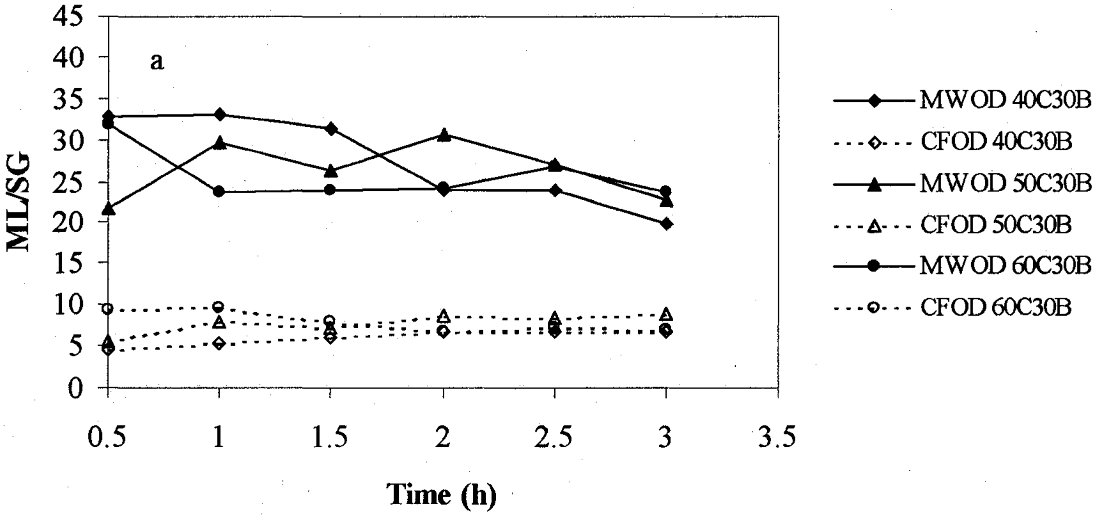
Generally in osmotic dehydration applications, it is desirable to maximize moisture loss and minimize solute gain. The ratio of moisture loss/solids gain (ML/SG) is thus a good indicator of the extent to which a given process succeeded its goal. It was important to note that, in every temperature /concentration combination test, the ratio of ML/SG in MWOD was higher than that in CFOD (Figure 5.6 and 5.7). The difference of the ratio of ML/SG between MWOD and CFOD treatments was quite clear. Especially at low concentration and high temperature conditions, the ratios of ML/SG in MWOD were higher than the ratios of ML/SG in CFOD correspondents.

The rate of water removal was always higher than the rate of osmosis agent penetration which was in agreement with the results of other workers (Lazaridis et al., 1995). Comparative results on ML/SG ratio for all experimental treatments are presented in Table 5.3. The ratio for CFOD decreased with the increasing solution concentration at the same temperature (except at 40°C-50°Brix, 60°C-60°Brix); similarly, the ratio for MWOD decreased with the increasing solution concentration at the same temperature (except at 40^0C-60^0Brix). Thus, depending on the process conditions, large differences in water removal efficiency (in terms of water removal with minimal solid uptake) could exist.

Table 5.3. Comparison of the ratio of ML/SG (fresh apple) after 3h osmotic dehydration at different conditions

Process conditions	CFOD	MWOD	
	Ratio*	Ratio*	Δ Ratio%
40°C 30°B	5.93	27.5	364
40°B	5.40	12.1	124
50°B	6.19	9.27	49.8
60°B	5.26	9.68	84.0
50°C 30°B	7.72	26.4	242
40°B	6.90	12.4	84.6
50°B	5.98	10.8	80.9
60°B	4.77	10.3	116
60°C 30°B	7.91	25.7	224
40°B	6.77	14.9	119
50°B	6.02	12.6	110
60°B	7.00	11.8	68.0

* Ratio was the average ratio during the osmotic dehydration period.



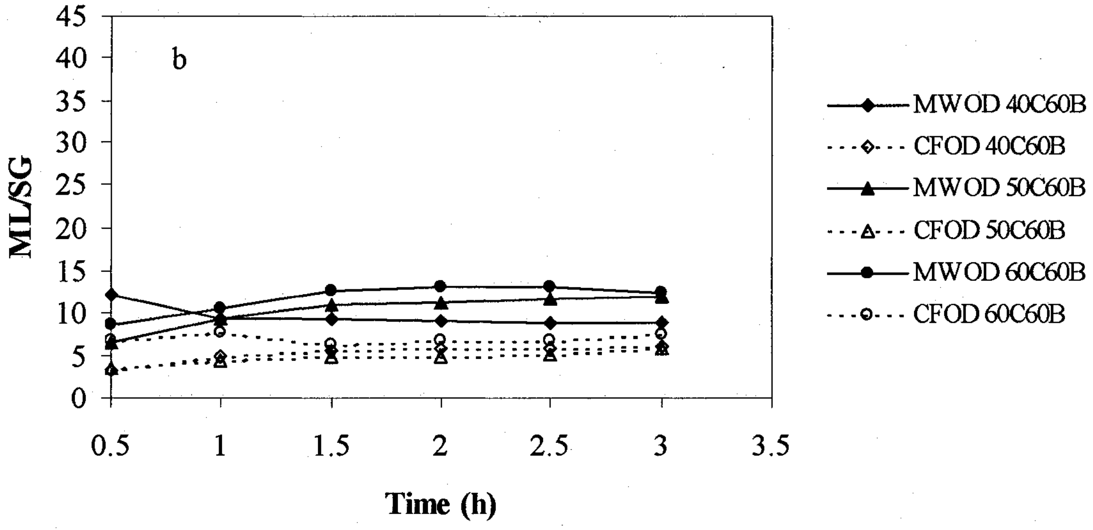


Figure 5.6. Comparison the ratio of ML/SG with MWOD and CFOD at same concentration 40°Brix (a) and 60°Brix (b) under different temperature

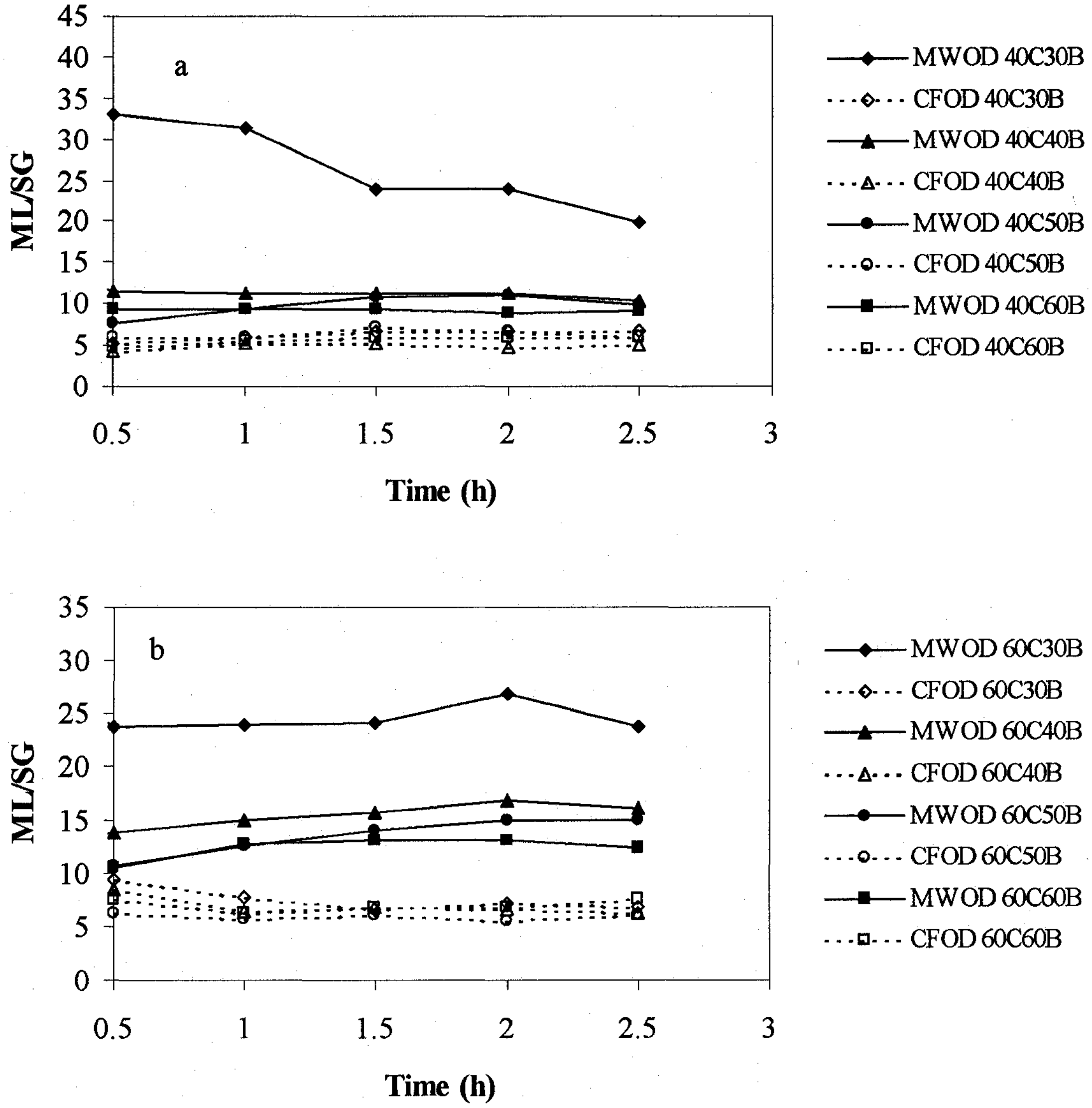


Figure 5.7. Comparison the ratio of ML/SG with MWOD and CFOD at same temperature 40°C (a) and 60°C (b) under different concentration

5.3.4 Time to get the sample 25% moisture loss (T_m) and 5% sample solids gain (T_s)

The dehydration times for each condition were calculated using equations (5.1-5.2). The data for dehydration time with respect to moisture loss (T_m) and solids gain (T_g) are summarized in Table 5.4 for the different conditions. T_m and T_s values in MWOD were smaller than the T_m and T_s values in CFOD conditions. For both systems as expected, the dehydration time decreased with increasing temperature and sucrose concentration. The shortest T_m was 0.59h for MWOD and 0.90h for CFOD at the condition of 60°C-60°Brix, which represented one of the high temperature-high concentration conditions used in this study. The longest T_m was 1.66h for MWOD and 4.65h for CFOD at the condition of 40°C-30°Brix, which represented one of the lowest temperature-low concentration conditions used in this study. In addition the shortest T_s was 1.18h for CFOD at the condition of 60°C-60°Brix and the longest T_s was 4.05h for the condition of 50°C-30°Brix. But for the MWOD process, only the 60°C-60°Brix condition got T_s at 2.63hr. The rest could not get the T_s value. From these observations, we could compare the efficiency of the different conditions with respect to dehydration time for respective moisture loss (T_m) and solids gain (T_g). In terms of faster moisture loss and less solids gain, the MWOD process is a more efficient system compared with the CFOD process.

Table 5.4 Comparison of the time to get the sample 25% moisture loss T_m and 5% sample solids gain T_s under different conditions

Conditions	T_m (hr)		T_s (hr)	
	MWOD[a]	CFOD[b]	MWOD	CFOD
40°C-30°Brix	1.66	4.65	*	3.62
40°C-40°Brix	1.43	3.14	*	3.14
40°C-50°Brix	1.21	3.28	*	2.61
40°C-60°Brix	1.04	1.90	*	2.05
50°C-30°Brix	1.29	4.58	*	4.05
50°C-40°Brix	1.13	2.98	*	3.42
50°C-50°Brix	0.97	2.16	*	2.73
50°C-60°Brix	0.80	1.61	*	2.00
60°C-30°Brix	1.05	3.37	*	3.89
60°C-40°Brix	0.91	2.12	*	3.06
60°C-50°Brix	0.75	1.39	*	2.16
60°C-60°Brix	0.59	0.90	2.63	1.18

Different letter showed the two osmotic dehydration T_m was different (t-test: paired two sample for means at 95% confidence) ($P<0.05$). *: express that sample solids gain did not reach 5% solids gain.

5.3.5 Mass transport coefficient calculation

The relationship between the moisture loss and solids gain vs the square root of time were described by equations (5.4) and (5.5), respectively. Using these equations the moisture and solids transport coefficients were calculated. The results are shown in table 5.5.

Table 5.5a. Comparison of the mass transport coefficients of moisture (k_m) during the osmotic dehydration of apple cylinders under different conditions

Conditions	MWOD		CFOD	
	k_m^a	R^2	k_m^b	R^2
40°C-30°Brix	17.65	0.99	6.44	0.98
40°C-40°Brix	18.99	0.98	10.41	0.99
40°C-50°Brix	22.85	0.97	14.69	0.98
40°C-60°Brix	23.15	0.96	18.92	0.99
50°C-30°Brix	23.22	0.98	8.84	0.96
50°C-40°Brix	24.93	0.97	15.87	0.97
50°C-50°Brix	25.13	0.96	19.03	0.98
50°C-60°Brix	33.36	0.99	21.36	0.99
60°C-30°Brix	24.55	0.98	11.03	0.96
60°C-40°Brix	34.13	0.98	17.04	0.93
60°C-50°Brix	35.96	0.99	23.05	0.99
60°C-60°Brix	38.59	0.98	27.57	0.99

Different letter showed the column values were different (t-test paired two sample for means showed that the diffusivities were different at 95% confidence) ($P<0.05$).

Table 5.5b. Comparison of the mass transport coefficients of solids (k_s) during the osmotic dehydration of apple cylinders under different conditions

Conditions	MWOD		CFOD	
	k_s^a	R^2	k_s^b	R^2
40°C-30°Brix	0.83	0.90	0.90	0.91
40°C-40°Brix	1.82	0.96	2.15	0.96
40°C-50°Brix	2.12	0.99	2.24	0.95
40°C-60°Brix	2.70	0.98	2.85	0.89
50°C-30°Brix	0.90	0.95	0.94	0.84
50°C-40°Brix	1.91	0.98	2.08	0.98
50°C-50°Brix	1.99	0.97	2.98	0.98
50°C-60°Brix	2.61	0.95	3.66	0.90
60°C-30°Brix	1.02	0.98	1.67	0.97
60°C-40°Brix	2.00	0.99	2.60	0.97
60°C-50°Brix	2.24	0.94	3.98	0.99
60°C-60°Brix	2.84	0.97	3.89	0.97

Different letter showed the column values were different (t-test paired two sample for means showed that the diffusivities were different at 95% confidence) ($P<0.05$).

From table 5.5, the values of calculated moisture transport (k_m) coefficients for MWOD conditions are found to be higher than the moisture transport coefficients (k_m) for CFOD conditions; while the values of calculated solids transport coefficients (k_s) for MWOD conditions are found to be lower than the moisture transport coefficients (k_s) for CFOD conditions. The results showed that microwave assisted osmotic dehydration mass transport coefficients are improved compared with continuous flow osmotic dehydration mass transport coefficients.

Based on the influence of temperature and concentration on moisture loss and solids gain, the following equations were developed for the mass transport coefficients:

For MWOD conditions,

$$k_m = 0.0424 * T^{1.1584} * C^{0.5058} \quad R^2 = 0.93 \qquad (5.8)$$

$$k_s = 0.0024 * T^{0.2425} * C^{1.4999} \quad R^2 = 0.91 \qquad (5.9)$$

For CFOD conditions,

$$k_m = 0.0009 * T^{1.1495} * C^{1.3864} \quad R^2 = 0.97 \qquad (5.10)$$

$$k_s = 0.0001 * T^{1.0286} * C^{1.6178} \quad R^2 = 0.90 \qquad (5.11)$$

So the equations of moisture loss and solids gain can be expressed as follows:

For MWOD conditions,

$$\%ML = 0.0424*T^{1.1584}*C^{0.5058}*t^{0.5} \qquad (5.12)$$

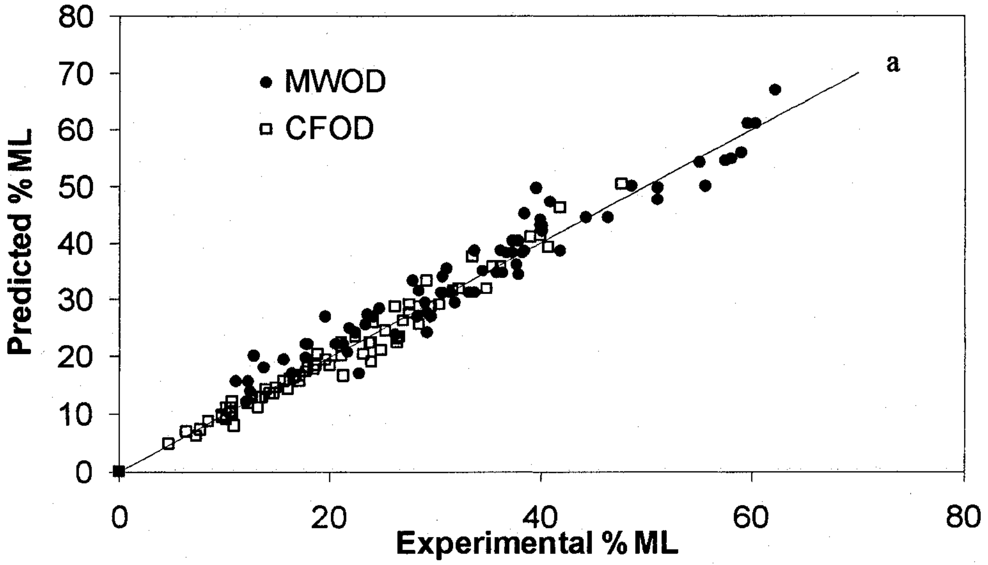
$$\%SG = 0.0024*T^{0.2425}*C^{1.4999}*t^{0.5} \qquad (5.13)$$

For CFOD conditions,

$$\%ML = 0.0009*T^{1.1495}*C^{1.3864}*t^{0.5} \qquad (5.14)$$

$$\%SG = 0.0001*T^{1.0286}*C^{1.6178}*t^{0.5} \qquad (5.15)$$

The root mean square (RMS) deviation of experimental data and from the proposed models was less than 5% and the performance of testing the developed are shown in Figure 5.8.



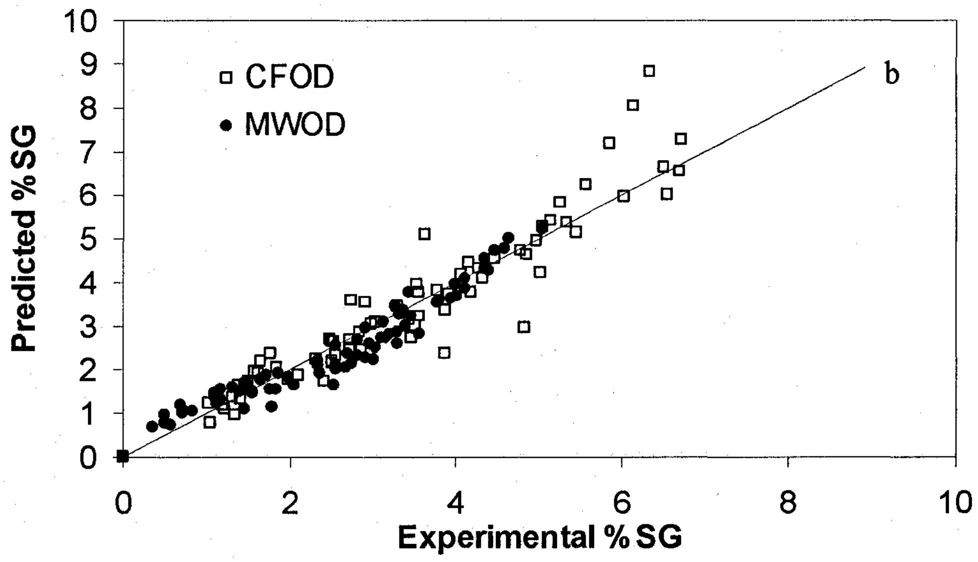


Figure 5.8 Performance of testing the developed model for %ML (a) and for %SG (b).

It is important to realize that the above analysis is limited to the location of processing conditions favoring fast and extensive moisture loss with minimal solid gain; the efforts in this study were concentrated on improving process efficiency and productivity. Besides minimizing solid gain, there are a number of quality factors which needed to be considered in order to reach the desirable final product quality. Such potentially important factors include: taste, texture, shrinkage, rehydration, freeze/thaw behavior, etc. The relative importance of each of these factors mainly depended on the intended application of the final product. Some of the quality related aspects are studied in the following chapters.

5.4 Conclusions

- Microwave heating is applied to the osmotic dehydration process to improve mass transfer rates during the process. Moisture transfer rates demonstrated an increase while solids gain rate was reduced during the microwave assisted osmotic dehydration process.
- Microwave heating has an important effect on water transfer during osmotic dehydration. Osmotic dehydration under microwave heating made it possible to obtain a higher diffusion rate of water transfer at lower solution temperatures. Application of microwave heating to osmotic dehydration process thus would limit the intake of solid and increase the moisture loss of apple cylinders.
- Moreover, it was shown when moisture loss during osmotic dehydration process over equilibrium moisture loss (ML_∞), it should be considered to use other parameters such as: mass transport coefficients instead of diffusion coefficients, to study different osmotic dehydration process efficiency.

Preface to Chapter 6

Osmotic dehydration equilibrium kinetics data (product composition, mass, volume, etc) are the necessary information in modeling osmotic dehydration mass transfer process: to define the driving force, to design equipment and optimize the process, to have high product quality at minimum energy costs. Osmotic dehydration process proceeds in three phases: equilibrium, pseudo-equilibrium and dynamic periods in this study. Pseudo-equilibrium (practical equilibrium) and dynamic period data are necessary for estimating the time of osmotic process, and ultimate mass transport of the solutes and water. This work was carried out for the first and second objectives of this thesis. In the previous chapters 3 and 4, equilibrium moisture loss (ML_∞) and solids gain (SG_∞) were used with experimental data combined with Azuara's model prediction values.

The objectives of this work were: (1) to study osmotic dehydration moisture loss, solids gain relation with equilibrium moisture loss and solids gain with Azuara's model, (2) to evaluate the influence of different process parameters such as temperature and concentration of sucrose syrup on equilibrium *ML*, *SG* and the ratio of *ML/SG* (equilibrium dehydration efficiency, EDE) change, (3) to study sample size influence on equilibrium *ML* and *SG* variance and (4) to investigate sample internal moisture loss and solid gain vary trends during osmotic dehydration equilibration. This would enhance basic knowledge for further study on osmotic dehydration modeling.

Part of this research has been presented in some conferences and/or published in scientific journals detailed earlier. The experimental work and data analysis were completed by the candidate under the supervision of professor Dr. H.S. Ramaswamy.

CHAPTER 6

MASS TRANSFER EQUILIBRIUM CONSIDERATION IN OSMOTIC DEHYDRATION

Abstract

Osmotic drying is a partial drying accomplished by treatment of test products in an osmotic solutions such as sugar syrup. It has been generally credited with offering quality advantages to the final product. Modeling of the mass transfer phenomenon is necessary to optimize osmotic dehydration processes to have high product quality at minimum energy costs. To explain the simultaneous mass-flow in an osmo-dehydration process, evaluation of equilibrium kinetics is important. True equilibrium process is difficult to achieve (a process that may take as many as 60 days); hence, generally a pseudo-equilibrium process is employed. Several methods exist for predicting pseudo-equilibrium conditions and their accuracies vary. Equilibrium moisture loss (ML) and solids gain (SG) data during osmotic dehydration of apple cylinders at different temperature (40°C, 50°C and 60°C) and concentrations (30°Brix, 40°Brix, 50°Brix and 60°Brix) were evaluated in this study. Pseudo-equilibrium achieved depended on product and processing conditions. Higher concentrations increased the equilibrium ML and decreased equilibrium SG. There might exist two kinds of equilibration: one is liquid equilibration, which is reached in about 24h, depending on sample size; the other is solid matrix equilibration, which takes a long time to reach. Solute penetration is a much slowly progressing process during osmotic dehydration equilibration.

KEY WORDS: Osmotic drying, kinetics, equilibrium, moisture loss, solute penetration apple

6.1 Introduction

Osmotic dehydration is a technique for partial removal of water from plant tissues and other materials by immersion in a hypertonic solution. The driving force for water removal is the chemical potential between the solution and the intracellular fluid. The mass transfer mechanisms during the process include osmosis, diffusion, hydrodynamic mechanism penetration (Fito, 1994) and other specific/active mechanisms effective in the temperature range where the tissue is alive (Yamaki and Ino, 1992). In the last several decades, studies have been carried out to better understand the internal mass transfer occurring during osmotic dehydration of foods and to model mechanism of osmotic process from different points of view (Ponting et al., 1966; Conway et al., 1983; Magee et al., 1983; Toupin & Le Maguer, 1989; Marcotte et al., 1991; Azuara et al., 1992; Hough et al., 1993; Rastogi & Raghavarao, 1994; 1995; Le Maguer, 1996; Parjoko et al., 1996; Nsonzi and Ramaswamy, 1998; Fito et al., 1998; Kaymak-Ertekin and Sultanoglu, 2000; Sablani and Rahman, 2003). Only few studies have reported details on the osmotic equilibration. This poses a problem since the modeling of mass transfer processes requires data on the equilibrium status (composition, mass, volume, etc.) of the product to define the driving force for drying (Lenart and Flink, 1984; Fito et al., 1998; Biswal and Le Maguer, 1989). Food engineers depend on theoretical or empirical models for the design of equipment and optimization of processes. Reliable data on the equilibrium properties is necessary in such models involving osmotic dehydration (Gros et al., 2003).

The osmotic dehydration process could be characterized by equilibrium, pseudo-equilibrium and dynamic periods. Equilibrium is the period when both chemical and physical (mechanical) equilibrium are reached with no further changes in sample composition or weight. This true equilibrium (i.e., chemical plus mechanical) is hard to achieve in the osmotic dehydration process. Such equilibrium relationships have not been well established because of system complexity and non-ideal behavior of different phases. Even when no changes either in sample composition or weight occurred, the system might not have reached chemical equilibrium (Barat et al., 1999). In some cases it is also not possible to attain equilibrium due to biological and (or) physical instability (Azuara et al., 1992). Pseudo-equilibrium (practical equilibrium) is the relatively short period of time when compositional equilibrium is achieved, depending on processing conditions. In the dynamic period, the mass transfer rates are increased or decreased till pseudo-equilibrium is reached.

Assuming that the tissue surface is in equilibrium with the contact solution, equilibrium kinetics could be determined by equilibrating the whole tissue in the osmotic liquid. Del Valle et al. (1967) set equilibrium condition as equality of concentration of salt in the brine and in the total water inside the muscle. Favetto et al. (1981) studied beef slices in a sodium chloride glycerol solution and found that the equilibrium condition between beef and external solution was given by the equality of sodium chloride and glycerol concentration in the water of the solution and in the muscle tissue water. Lenart and Flink (1984) reported that 4 to 20 h were required to achieve equilibrium (equal soluble solid concentration and water activity in the product and osmotic solution) in potato cubes (10mm) after osmosis in 10-70% sucrose and NaCl solutions. Biswal and Le Maguer (1989) and Biswal and Bozorgmehr (1991), by considering that fruit solute activities matched those of the osmotic solution at equilibrium, found good agreement between experimental and predicted densities of carrots and potatoes after osmosis in NaCl and ethanol solutions for 16-36 h. Azuara et al. (1992) proposed a model to estimate mass transfer coefficients and equilibrium water loss and solids gain. Rahman (1992) characterized equilibrium kinetics by defining equilibrium constants and dynamic periods. Rastogi et al. (1995) plotted the rate of change of moisture content versus average moisture content, and used the slope define the osmotic dehydration rate and intercept to infer equilibrium moisture and solids contents. Barat et al. (1999) studied the mechanism of equilibrium kinetics during osmosis. They identified two periods in equilibration: first the compositional equilibrium was achieved in a relative short time, depending on conditions. Then a bulk flux of osmotic solution into the fruit tissue occurred due to relaxation of previously shrunken cellular structure. In such a state, differences in both activity and pressure disappeared, and the solid cellular matrix became fully relaxed. Waliszewski et al. (2002) studied equilibrium concentration and water and sucrose diffusivity in osmotic dehydration of pineapple slabs. Sablani et al. (2003) studied the effect of syrup concentration, temperature and sample geometry on equilibrium distribution coefficients during osmotic dehydration of mango.

In spite of the above studies, the application of equilibrium kinetics data in OD process is still very limited because available comparable data are scattered, disconnected or impractical. It is also difficult to establish general rules about the equilibrium kinetics study. Extensive analysis of equilibration osmotic dehydration data has shown that the equilibrium kinetics can take from few hours to 100 days (Barat et al., 1998). Even then only a pseudo-equilibrium state can realistically be achieved. Long time equilibrium kinetics signified the practical end of the osmotic process and sets limit to the range of potential data applications. It presents a challenge to exploit the equilibrium kinetics data to osmotic dehydration process.

The objectives of this work were: (1) to study osmotic dehydration moisture loss, solids gain relation with equilibrium moisture loss and solids gain with Azuara's model, (2) to evaluate the influence of different process parameters such as temperature and concentration of sucrose syrup on equilibrium *ML*, *SG* and the ratio of *ML/SG* (equilibrium dehydration efficiency, EDE) change, (3) to study sample size influence on equilibrium *ML* and *SG* variance and (4) to investigate sample internal moisture loss and solid gain vary trends during osmotic dehydration equilibration. Equilibrium study in this chapter covered the pseudo-equilibrium (practical equilibrium) and dynamic periods.

6.2 Materials and methods

6.2.1 Sample preparation

A batch of Idared variety of apples of uniform size and ripeness were obtained from Macdonald Campus farm and commercial sucrose (sugar) was obtained from a local supermarket. The fruits were refrigerated at 2-5°C and at 95% relative humidity until used for experiments. Three different diameter samples cylinders were cut for osmotic dehydration study, large: 2.0 cm in diameter, middle: 1.0 cm in diameter, small: 0.5 cm in diameter, and 2.0 cm in height for all the samples.

6.2.2 Experimental procedure

Apple cylinders inside the steel cage (60 cm in diameter 60 cm in height) were immersed into sucrose-water solution in a stainless steel pot placed inside a water bath to maintain the required experimental temperature. If necessary during the experiments, a small amount of distilled water was added to the sucrose solution to compensate for the water loss caused by evaporation. The osmotic medium was agitated continuously with a stirrer to maintain the uniform temperatures throughout the experiment and enhance the equilibration process. Temperatures were monitored using digital thermometers within the accuracy of ±0.1°C. Test conditions included: 30, 40, 50 and 60°Brix, 40, 50 and 60°C. The fruit-syrup mass ratio (*R*) was kept very high (1:30), since ideally infinite fruit-syrup mass ration was necessary to avoid the effect of syrup dilution effect during the process. The duration of osmotic drying varied from 0.5 to 48 h depending on process conditions.

After certain time of osmosis treatment, large size samples were cut the two ends layer of the cylindrical sections (0.1 cm thick), and categorized as No. 1. The rest cylindroids were cut into several cylindrical layers (0.1 cm thick) numbered as: 1, 2, 3 and 4, respectively, from outside to center. The schematic explanation showed in Figure 6.1.

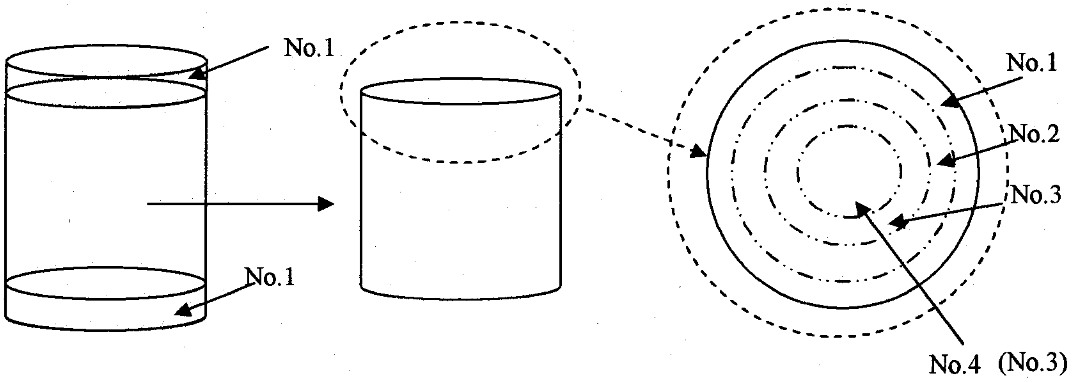


Figure 6.1 Schematic explanation of large size sample sectioning

6.2.3 Analytical methods

Sample soluble solute and solution concentration were measured with a portable refractometer (ATAGO, Japan) at ambient temperature. Moisture content of fresh and osmotically treated apple cylinders was determined by oven method. Initially experiments were conducted to determine the time required to reach equilibration. The moisture content and total solids were measured gravimetrically on apple cylinders after different contact times. The cylinders were quickly rinsed and gently blotted with a paper towel to remove surface water before weighing. For measuring solids content, sample were air dried at 105°C for 24 h. The moisture loss, weight reduction and solid gain were calculated by the equations 6.1-6.3. All experiments were performed at least in triplicate and average values were reported.

6.2.4 Model development

The most common mass transport terminologies used in osmotic dehydration are moisture loss (water loss), solid gain and weight reduction. The calculations are based on the general balance of concentration driven mass transfer between the liquid and solid phases. Moisture loss (*ML*), the net water loss on an initial mass basis was:

$$ML\% = \frac{M_o x_o - M_t x_t}{M_o} \times 100 \qquad (6.1)$$

The corresponding solids gain (*SG*), the net solids (soluble) transport into the sample (again on an initial mass basis), was obtained from:

$$SG\% = \frac{M_t s_t - M_o s_o}{M_o} \times 100 \qquad (6.2)$$

The weight reduction (*WR*), the net mass loss of the sample on an initial mass basis, was:

$$WR\% = \frac{M_o - M_t}{M_o} \times 100 \qquad (6.3)$$

The solids gain (*SG*) was correlated with *ML* and *WR* (Rahman and Lamb, 1990):

$$SG = ML - WR \qquad (6.4)$$

In this study, only dynamic and pseudo-equilibrium (practical equilibrium) period kinetics were evaluated.

6.2.5 Dynamic period

Most theoretical models on moisture loss and solid gain kinetics are based on Fick`s law of diffusion in an unsteady state one-dimension transfer. However, there are some limitations, such as simultaneous mass transfer reduced to a single mass transfer, resulting diffusivities assumed as internal transfers and the biological properties of the cell membrane not be considered. Raoult-Wack (1994) reported that the two-parameter Azuara-kinetic model (Azuara et al., 1992) avoided some of the difficulties of Fick`s diffusion model and found good accuracy to predict the mass transport dynamics of osmotic dehydration. So, the Azuara-model was used to estimate the dynamic period ML_∞ and SG_∞.

$$ML = ML_\infty - MS \qquad (6.5)$$

where ML = fraction of water lost by the food at time t, ML_∞ = fraction of water lost when equilibrium was reached ($t = \infty$), MS = fraction of water that can diffuse out, but remains in the food at time t. In this equation, ML_∞ has a fixed value for the established conditions of temperature and concentration of the osmotic solution. ML increases with ML_∞ increasing, but decreases with MS increasing. Thus, the relationship between ML and MS is:

$$MS = \frac{ML}{K} \qquad (6.6)$$

where: K is a function of time (t) and rate of moisture loss (s). The rate of moisture loss is a function of temperature and initial concentration of the osmotic solution. Most experiments in osmotic dehydration are carried out at constant temperature and at a given initial concentration and, hence, the rate of moisture loss is not noticeably affected during the dehydration process. Based on this, it is possible to propose a simple function for K, time and the rate of water loss:

$$K = s\,t \qquad (6.7)$$

Substituting equation (6.7) into (6.6) and (6.5), and rearranging terms, we obtain:

$$ML = \frac{st(ML_\infty)}{1 + st} \qquad (6.8)$$

This equation associates the moisture loss (ML) with time (t), by means of two constants: s and ML_∞. In order to predict the fraction of water lost by the food at time t in Eq.(6.8), it is necessary to know the values for s and ML_∞. These values can be estimated using a non-linear regression program, or by linear regression, using experimental data and the linearized form of equation (6.9):

$$\frac{t}{ML} = \frac{1}{sML_\infty} + \frac{t}{ML_\infty} \qquad (6.9)$$

Similar equations (6.10) and (6.12) can be written for the weight reduction and solid gain of the products:

$$WR = \frac{s_1 t(WR_\infty)}{1+s_1 t} \tag{6.10}$$

$$\frac{t}{WR} = \frac{1}{s_1 WR_\infty} + \frac{t}{WR_\infty} \quad \text{(Linear form)} \tag{6.11}$$

$$SG = \frac{s_2 (SG_\infty)}{1+s_2 t} \tag{6.12}$$

$$\frac{t}{SG} = \frac{1}{s_2 SG_\infty} + \frac{t}{SG_\infty} \quad \text{(Linear form)} \tag{6.13}$$

where *WR* weight reduction lost by the food at time *t*, WR_∞ weight reduction by the food at equilibrium, s_1 constant related to the rate of weight reduction. *SG* solute solids gained by the food at time *t*, SG_∞ soluble solids gained by the food at equilibrium, and s_2 constant related to the rate of incoming of the soluble solids to the foodstuff.

The goodness of fit of the model was evaluated with the equation for root mean square (RMS):

$$RMS(\%) = 100\sqrt{\frac{1}{N}\sum_{i=1}^{N}\left[\frac{V_e - V_c}{V_e}\right]^2} \tag{6.14}$$

where V_e experiment value, V_c calculate value using the proposed equations and N is the number of experimental data points.

6.2.6 Equilibrium period

Even compositional-chemical potential relationships have not been well established because of system complexity and non-ideal behavior of different phases. Assuming that the tissue surface is in equilibrium with the contact solution, such relationships can be determined by equilibrating the whole tissue in the osmotic liquid (Barat *et al.* 1998). Previous studies have revealed that similar compositions for product and osmotic solution were achieved after relatively long treatment times (about 20 h). Moisture content (*MC*), the net water content on wet mass basis was:

$$MC\% = \frac{M_t - M_d}{M_t} \times 100 \tag{6.15}$$

The corresponding solids content (*SC*), the net soluble solids transport into the sample (again on an initial mass basis), was obtained from:

$$SC\% = \frac{M_d}{M_t} \times 100 \qquad (6.16)$$

where M_t after certain osmotic dehydration treatment, the mass of the sample; M_d after certain osmotic dehydration treatment, the solid mass of the sample.

6.3 Results and Discussion

6.3.1 Dynamic period moisture loss and solid gain relation with equilibrium moisture loss and solid gain

In order to test the applicability of equations (6.8)-(6.9), and (6.12)-(6.13), different time period experimental data were used and compared in Table 6.1. Different time period were selected because they provided a suitable amount of data during a given time. However, Azuara's model is a dynamic model, and hence the predicted equilibrium *ML* and *SG* at 3, 12 and 24 h differed widely. The relative *ML%* difference was 114% for 40°C-30°Brix and 48% for 60°C-60°Brix while the relative *SG%* difference was 381% for 40°C-30°Brix and for 25% for 60°C-60°Brix. That means that simple extrapolation of this model using a 3h data cannot give real equilibrium moisture content results. The equilibrium moisture loss (*ML%*) and solids gain (*SG%*) of apple cylinders in dynamic period increased with increasing contact time, temperature and concentration (Table 6.1), and samples reached pseudo-equilibrium only after 24h (Fig 6.2). The ML% was 64.67%, 64.98% and 65.40% for 24 h, 36 h and 48 h dehydration time, respectively. Thus 24 h can be considered as the equilibrium time for all experiments in this study. The values of *t/ML%*, *t/SG%* and *t/WR%* as a function of time *(t)* at a selected condition are plotted in Fig 6.3 to demonstrate the linearity of the Azuara et al. model. Fig. 6.3 demonstrates the acceptability of the model for mass transport studies in dynamic period.

Table 6.1 Relation of the experimental data and Azuara`s model predicted equilibrium value of osmotic dehydration during dynamic period.

Var.	Conditions (°C °B)	Time interval	Exp.	Calc.	Time interval	Exp.	Calc.	Time interval	Exp.	Calc.
ML_∞	40C30B	3	10.9	12.3	12	17.2	19.6	24	24.6	26.3
SG_∞			2.79	2.94		6.34	7.06		12.5	14.1
ML_∞	40C40B	3	18.2	20.3	12	36.0	37.9	24	50.4	54.0
SG_∞			3.45	4.20		7.37	8.14		11.4	12.7
ML_∞	40C50B	3	26.0	29.3	12	45.2	50.3	24	59.5	62.9
SG_∞			3.68	4.00		5.69	6.31		6.57	6.96
ML_∞	40C60B	3	35.2	37.5	12	61.8	66.7	24	73.0	78.7
SG_∞			5.55	6.25		5.48	5.81		6.10	6.21
ML_∞	50C30B	3	16.2	18.5	12	33.9	41.2	24	36.5	41.7
SG_∞			5.08	5.64		8.02	8.82		14.0	14.5
ML_∞	50C40B	3	31.6	36.2	12	45.0	48.8	24	52.6	55.3
SG_∞			4.42	5.13		8.30	9.30		12.1	13.0
ML_∞	50C50B	3	36.6	41.3	12	53.6	60.2	24	65.2	69.4
SG_∞			3.49	3.72		5.39	5.97		7.73	8.03
ML_∞	50C60B	3	35.1	39.1	12	68.4	76.3	24	73.8	80.6
SG_∞			4.37	5.01		6.20	6.52		7.39	7.63
ML_∞	60C30B	3	19.0	21.6	12	36.2	41.3	24	37.4	41.0
SG_∞			5.88	6.93		9.66	10.8		16.0	16.8
ML_∞	60C40B	3	31.2	36.6	12	50.7	55.0	24	52.7	56.2
SG_∞			6.20	7.07		10.0	10.9		12.4	13.8
ML_∞	60C50B	3	41.0	46.5	12	58.7	62.5	24	68.0	70.4
SG_∞			6.05	6.94		7.75	8.08		8.65	8.89
ML_∞	60C60B	3	48.8	54.6	12	72.8	77.5	24	76.3	80.6
SG_∞			5.77	6.91		7.62	7.87		8.43	8.65

If experimental data would not include equilibrium time, the parameters obtained by linear regression were impossible to fit (Waliszewski et al. 2002). In all cases, the model fitted experimental moisture loss; weight reduction and solids gain quite well with the 24 h experimental data (Table 6.2). Azuara-model permitted the evaluation of mass change at equilibrium with a linear regression equation, if experimental data were calculated long-time trials.

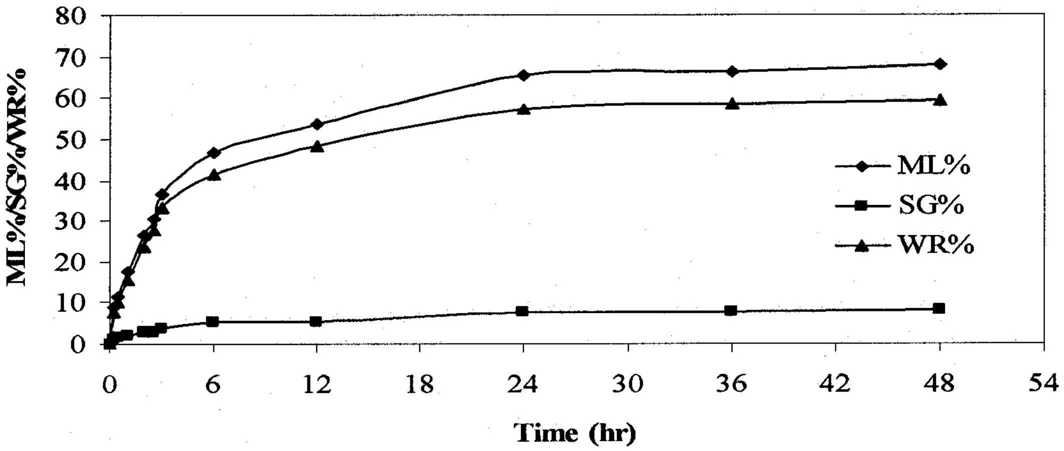


Figure 6.2. Moisture loss, solids gain and weight reduction of apple cylinders as a function of time at 50°C 50°Brix.

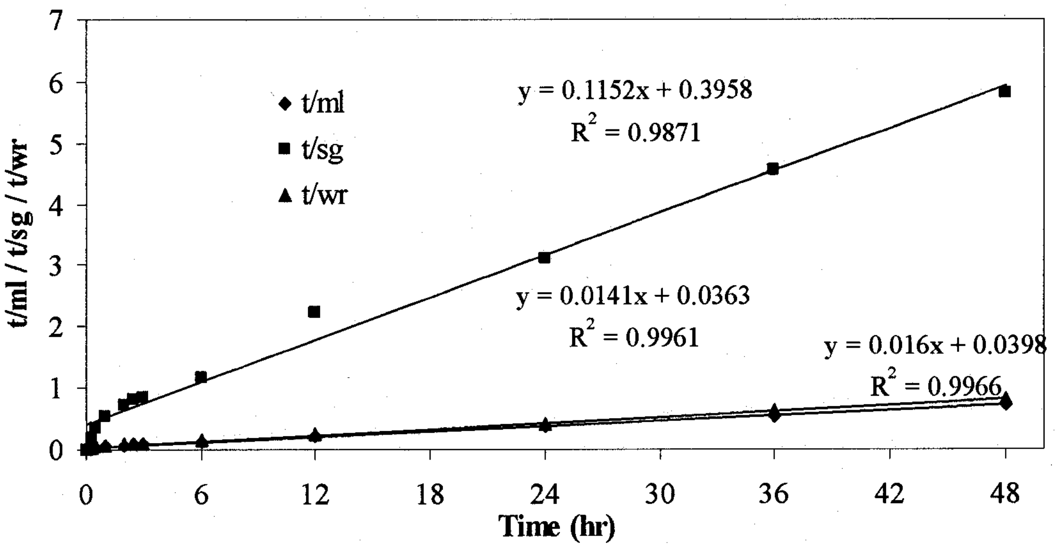


Figure 6.3. Plot of *t/ML / t/SG / t/WR vs t* for osmotic dehydration of apple cylinders at 50°C 50°Brix.

Table 6.2 Relation of Azuara's model predicted equilibrium moisture loss, weight reduction and solid gain with 24h period experiment data

Variables	Conditions	R.M.S. %	Time (h) interval used for prediction	Exp.	Calc.	Constant related to velocity (h^{-1})
ML	40°C	1.52	24	24.6	26.3 (0.96)	0.28
SG	30°Brix	2.84		12.4	14.5 (0.81)	0.13
WR		2.33		12.2	12.9 (0.98)	0.48
ML	40°C	2.46	24	50.4	54.0 (0.90)	0.24
SG	40°Brix	9.41		11.4	12.7 (0.84)	0.46
WR		2.68		39.0	41.7 (0.92)	0.26
ML	40°C	1.92	24	59.5	62.9 (0.96)	0.35
SG	50°Brix	1.53		6.57	6.96 (0.99)	0.50
WR		2.00		52.9	56.2 (0.96)	0.33
ML	40°C	1.94	24	73.0	78.7 (0.96)	0.34
SG	60°Brix	1.23		6.10	6.22 (0.99)	1.17
WR		2.18		66.9	73.0 (0.95)	0.30
ML	50°C	2.72	24	37.3	41.7 (0.97)	0.28
SG	30°Brix	3.17		14.0	14.5 (0.89)	0.25
WR		2.94		23.2	27.3 (0.95)	0.30
ML	50°C	1.50	24	52.6	55.2 (0.99)	0.52
SG	40°Brix	1.98		12.1	13.0 (0.93)	0.25
WR		1.58		40.5	42.4 (0.99)	0.63
ML	50°C	1.42	24	65.2	69.4 (0.98)	0.41
SG	50°Brix	2.33		7.73	8.03 (0.95)	0.35
WR		1.32		57.4	61.3 (0.98)	0.42
ML	50°C	1.87	24	73.8	80.6 (0.98)	0.41
SG	60°Brix	1.69		7.39	7.63(0.98)	0.58
WR		1.96		66.4	73.0 (0.97)	0.39
ML	60°C	2.49	24	37.4	41.0 (0.98)	0.44
SG	30°Brix	2.92		15.9	16.8 (0.91)	0.25
WR		2.42		21.4	23.7 (0.97)	0.66
ML	60°C	1.55	24	52.6	56.2 (0.99)	0.60
SG	40°Brix	2.02		12.4	13.8 (0.96)	0.33
WR		1.48		40.2	42.7 (0.99)	0.71
ML	60°C	1.13	24	68.0	70.4 (0.99)	0.62
SG	50°Brix	6.91		8.65	8.90 (0.99)	0.80
WR		1.26		59.4	61.7 (0.99)	0.59
ML	60°C	0.98	24	76.3	80.6 (0.99)	0.67
SG	60°Brix	1.00		8.43	8.65 (0.99)	0.84
WR		1.12		67.8	71.9 (0.99)	0.65

Numbers in the bracket are the experimental data regression coefficient use Azuara`s model.

6.3.2 Equilibrium moisture loss and solid gain relation with temperature and concentration

As expected, higher concentrations of osmotic solutions gave a higher equilibrium *ML* (Figures 6.4 and 6.5). Equilibrium *ML* (ML_∞) was not a strong function of temperature except for 40°C-30°Brix combination in which case the chemical potential was relatively very low, and thus the *ML* rate was slow and the ML_∞ was probably not completed within the time period. Statistical comparison of the various temperature-concentration treatments is presented in Table 6.3. Concentration effects were significant to ML_∞ ($P<0.05$). As concentration was increased from 30 to 60°Brix, ML_∞ increased 199% for 40°C, increased 100% for 50°C and increased 107% for 60°C. Increasing temperature from 40°C to 50°C, ML_∞ associated at 30°Brix increased by almost 50%, but between 50 and 60°C for 30°B and between 40 and 60°C for all other concentrations, the temperature effect on ML_∞ was not significant ($P>0.05$). The combined increase in ML_∞ from 30°Brix 40°C to 60°Brix 60°C was 207%. Parjoko et al. (1996) also reported that at constant temperature, the equilibrium constants for both water and solids increased with increase in syrup concentration. Waliszewski et al. (2002) found the concentration effects on ML_∞ to have a very positive effect and temperature to have a less obvious effect.

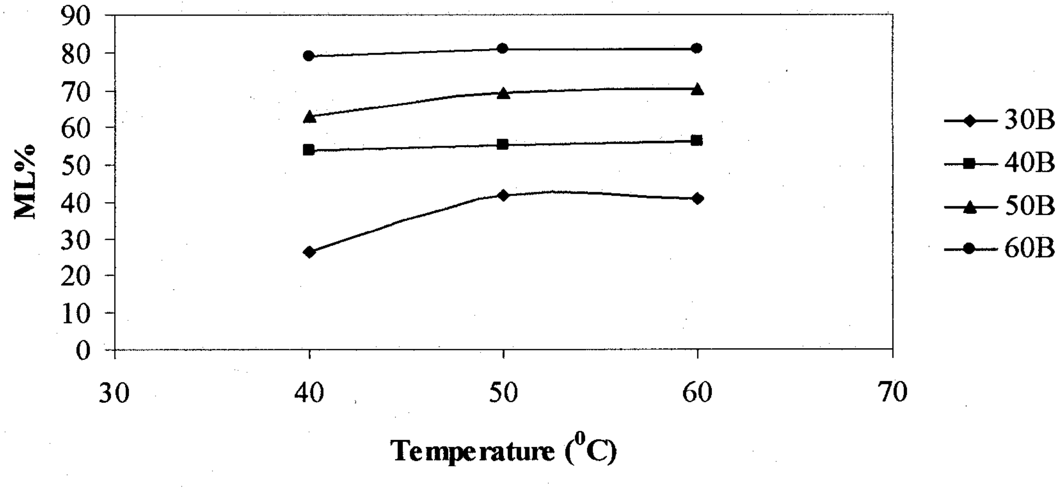


Figure 6.4. Plot of equilibrium *ML%* *vs* temperature for osmotic dehydration of apple cylinders at different concentration

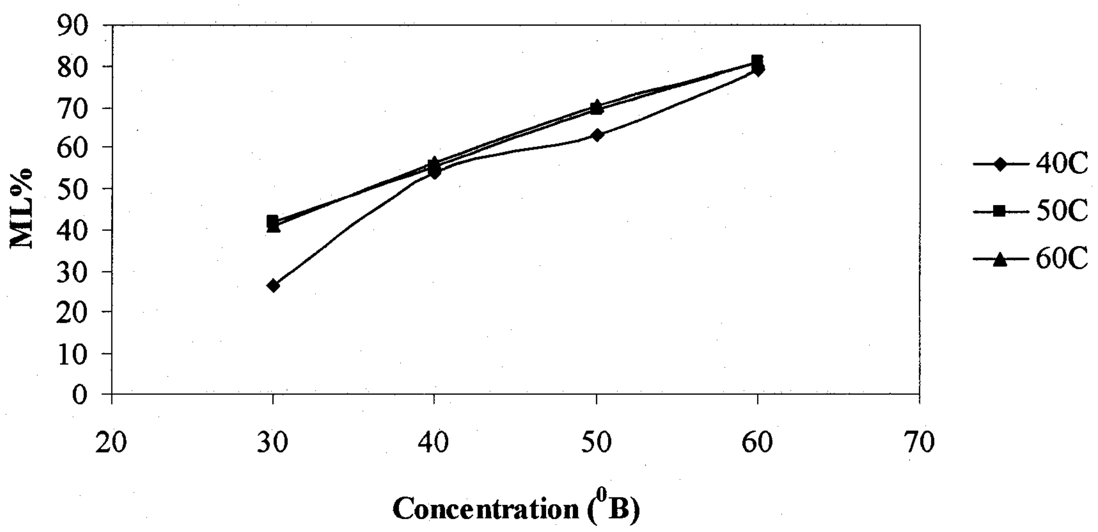


Figure 6.5. Plot of equilibrium *ML%* *vs* concentration for osmotic dehydration of apple cylinders at different temperatures

Table 6.3. Mean values and 95% confidence limits for moisture loss (%) during osmotic treatment of apple cylinders in sugar solution at different concentrations and different temperatures.

Concentration (°Brix)	ML%		
	40°C	50°C	60°C
30	$25.5 \pm 0.86^{a1*}$	38.3 ± 2.98^{a2}	37.8 ± 2.99^{a2}
40	51.9 ± 1.89^{b2}	53.8 ± 1.34^{b2}	54.0 ± 1.90^{b2}
50	60.2 ± 2.40^{c2}	67.0 ± 2.22^{c2}	68.7 ± 1.48^{c2}
60	76.0 ± 2.90^{d2}	76.6 ± 3.56^{d2}	78.2 ± 2.18^{d2}

*Means in columns followed by the same letter or rows followed by same number are not significantly different at the 5% level.

Figures 6.6 and 6.7 show plots of SG_∞ versus temperature and concentration for different concentrations and temperatures. SG_∞ increased with an increase in temperature and decreased with an increase in solution concentration. Statistical comparison of the various temperature-concentration treatments is presented in Table 6.4. Temperature had a positive effect on SG_∞, while concentration had negative effect. All temperature effects were significant ($P<0.05$), while only concentration effects from 30 to 50°Brix were significant ($P<0.05$). Contrary to the observed ML_∞ increase, SG_∞ reduced by 50-55% when solution concentration was raised from 30 to 60°Brix. Waliszewski et al. (2002) reported that sucrose concentration had a positive effect on solids equilibrium and the temperature effect is less evident confirming the results of this study.

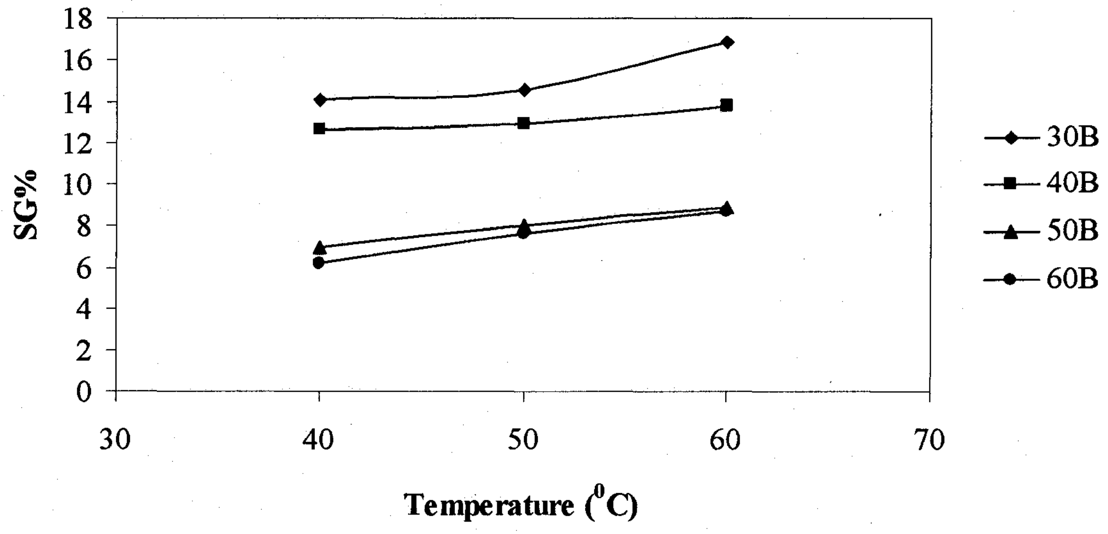


Figure 6.6. Plot of equilibrium *SG%* *vs* temperature for osmotic dehydration of apple cylinders at different concentrations

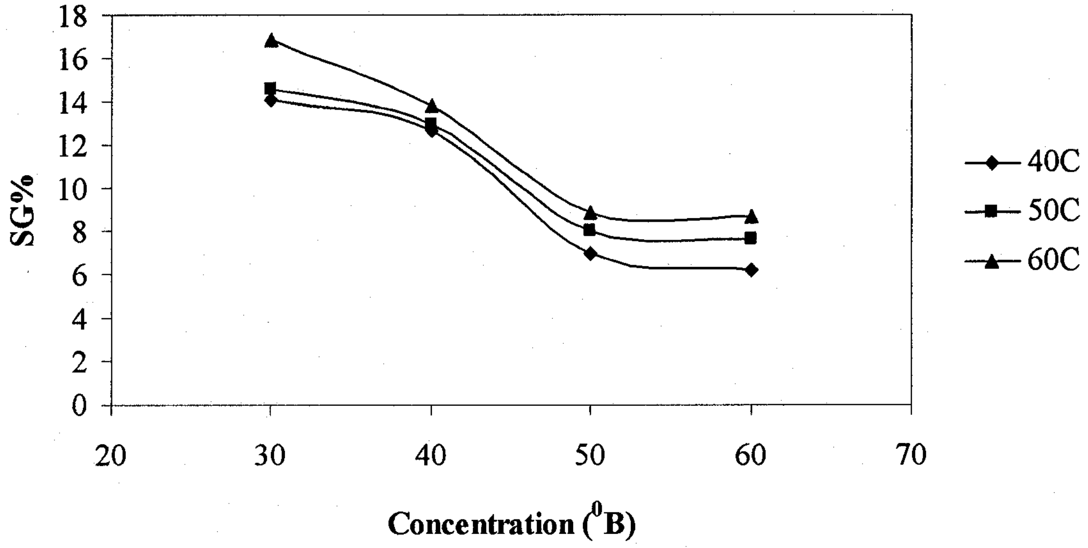


Figure 6.7. Plot of equilibrium *SG%* *vs* concentration for osmotic dehydration of apple cylinders at different temperatures

Table 6.4. Mean values and 95% confidence limits for solids gain (%) during osmotic treatment of apple cylinders in sugar solution at different concentrations and different temperatures

Concentration (°Brix)	SG%		
	40°C	50°C	60°C
30	13.2±0.82^{ad*}	14.4±0.39^{ae}	15.9±0.99^{af}
40	11.9±0.69^{bd}	12.0±1.12^{be}	12.5±1.22^{bf}
50	6.68±0.25^{cd}	7.70±0.46^{ce}	8.50±0.48^{cf}
60	6.13±0.08^{cd}	7.47±0.14^{ce}	8.36±0.33^{cf}

*Means followed by the same letter are not significantly different at the 5% level.

6.3.3 Equilibrium dehydration efficiency (EDE) relation with temperature and concentration

The ratio of *ML/SG* increased with concentration but decreased or remained constant with temperature (Figures 6.8 and 6.9). The highest ratio of *ML/SG* was observed with highest concentration (60°Brix) and at the lowest temperature (40°C). Processing at lower temperatures in higher concentration medium therefore favored better water removal over solute uptake; however, this prolonged the equilibrium time.

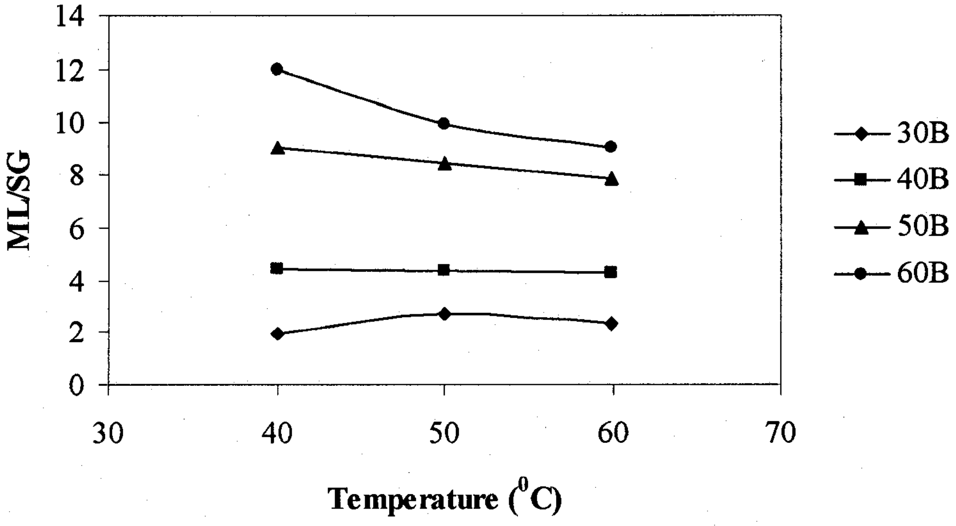


Figure 6.8. Plot of equilibrium ratio of *ML/SG* *vs* temperature for osmotic dehydration of apple cylinders at different concentrations

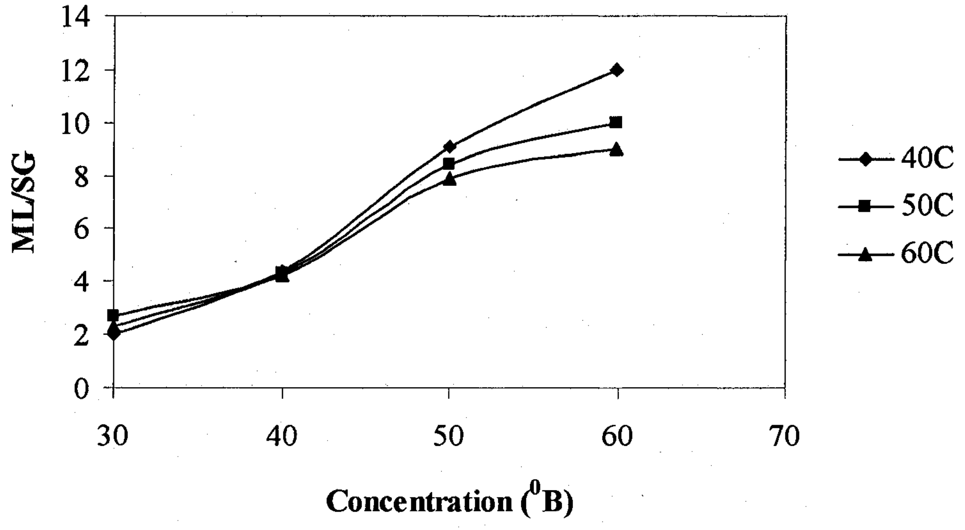


Figure 6.9. Plot of equilibrium ratio of *ML/SG vs* concentration for osmotic dehydration of apple cylinders at different temperatures

6.3.4 Influence of sample size on equilibrium moisture loss and solid gain

Euilibrium moisture loss and solids gain for samples of different size under selected conditions are shown in Figure 6.10. While ML_∞ increased with increasing solution concentration for three different sizes of sample, the SG_∞ decreased with increasing solution concentration increasing. The ML_∞ for large and middle size sample was in same trend and level, the lower ML_∞ for small size sample was due to the same level ML_∞ coming earlier and reducing afterwards (Figure 6.10a). The detailed discussions are presented in another paper. The SG_∞ for large and middle size sample was same, and however, it was different compared with the SG_∞ for small size sample. From these observations, it can be concluded that sample size may not affect equilibrium moisture loss but affect equilibrium solids gain. The possible explanations for these phenomena were both the moisture transfer and solids transfer inside the samples occurred in the progressing way, the moisture transfer was faster than soluble solids transfer, even in pseudo-equilibration period, the equilibrium solids gain was not reached totally.

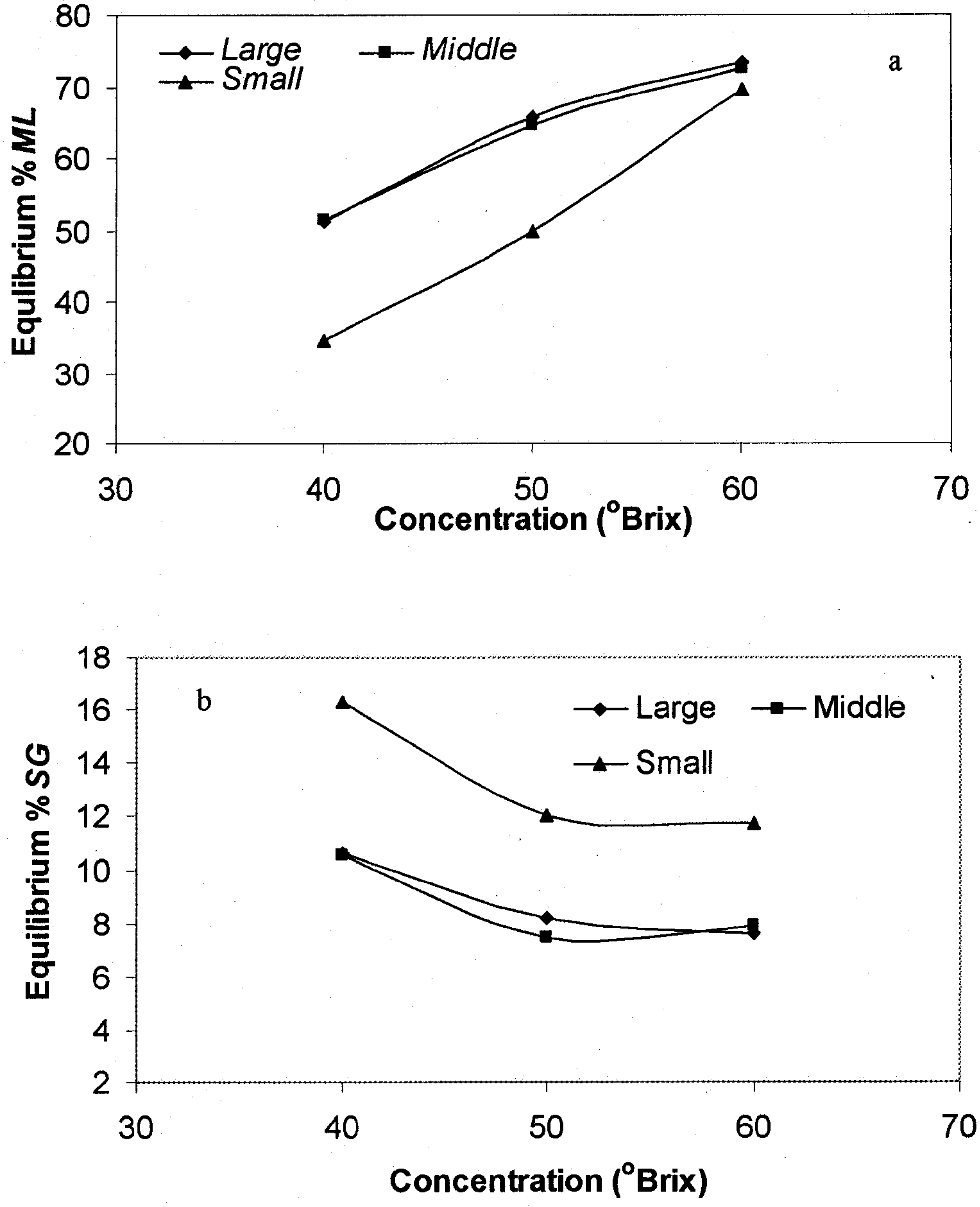


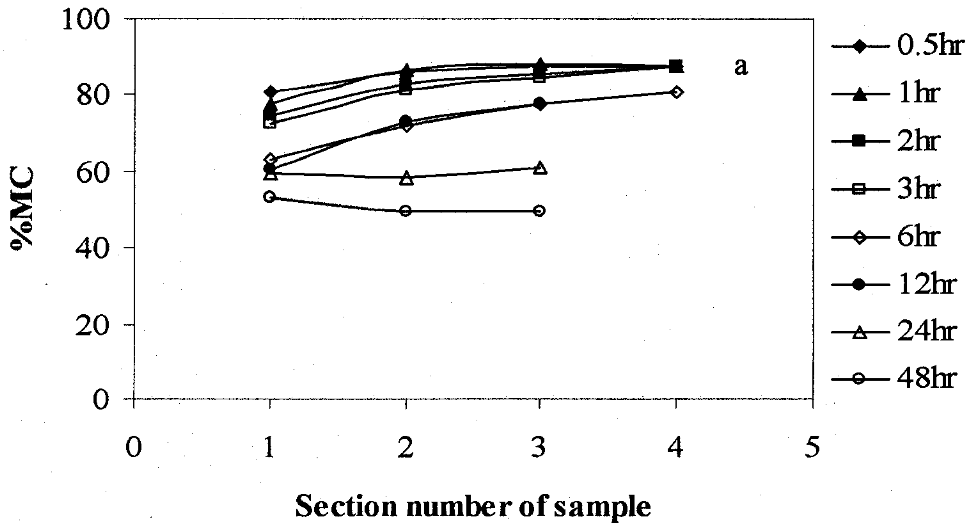
Figure 6.10. Plot of equilibrium ML (a) and SG (b) *vs* concentration for osmotic dehydration of apple cylinders at 50°C 50°Brix 24h for three-size sample

6.3.5 Sample internal moisture transfer and solid transfer variation trend during osmotic dehydration equilibration

In order to study sample internal mass transfer variation, we divided the osmotic treated sample into different sections and measure its moisture content (MC) and solids content (SC). The accuracy of five-time repeat sectioning operation measured MC and SC were 95% compared with control without sectioning. The MC and SC variations with sample positions and osmotic processing time were shown in Figure 6.11.

For short time period (<6h), the MC of different sections increased from outside to inside of the sample, e.g. at the first time period (0.5-3h), the center section moisture content were same as the fresh sample moisture content; even after 6hr osmotic dehydration treatment, the center section moisture content was still higher than that of external solution moisture content 50% (Figure 6.11a). For long time period (>12h), due to the sample shrinkage, the osmotic treated sample can only be separate to three different sections: first layer (No.1), second layer (No.2) and center section (No.3). The MC varied less with position inward to the center with time proceeding. After 24h osmotic dehydration treatment, MC for all the three sections were in same level, even the overall MC for 24h and 48h processing time were different. And more from these observations, we found that sample internal moisture transfer mechanisms for short time (<12h) and long time (>24h) were different. The internal moisture transfer was progressing for short time and simultaneous for long time.

Similarly, short time period (<6h), the SC of different sections decreased from outside to inside of the sample, e.g. at the first 6h period, the center section solids content were same as the fresh sample solids content; even after 12h osmotic dehydration treatment, the center section moisture content was still lower than that of external solution moisture content 50% (Figure 6.11b). For long time period (>12h), due to the sample shrinkage, the osmotic treated sample can only be separate to three different sections: first layer (No.1), second layer (No.2) and center section (No.3). The SC varied less with position inward to the center with time proceeding. After 24h osmotic dehydration treatment, SC for all the three sections were in same level, the slightly low SC for 48h No.1 section was due to the over washing of sample. However, the 48h SC for different sections was still higher than 24h SC for different sections. From these observations, we found that sample internal soluble solids transfer were progressing for short time period (<12h), progressing and simultaneous mixture (12-24h) for middle time period and simultaneously for long time period (>48h).



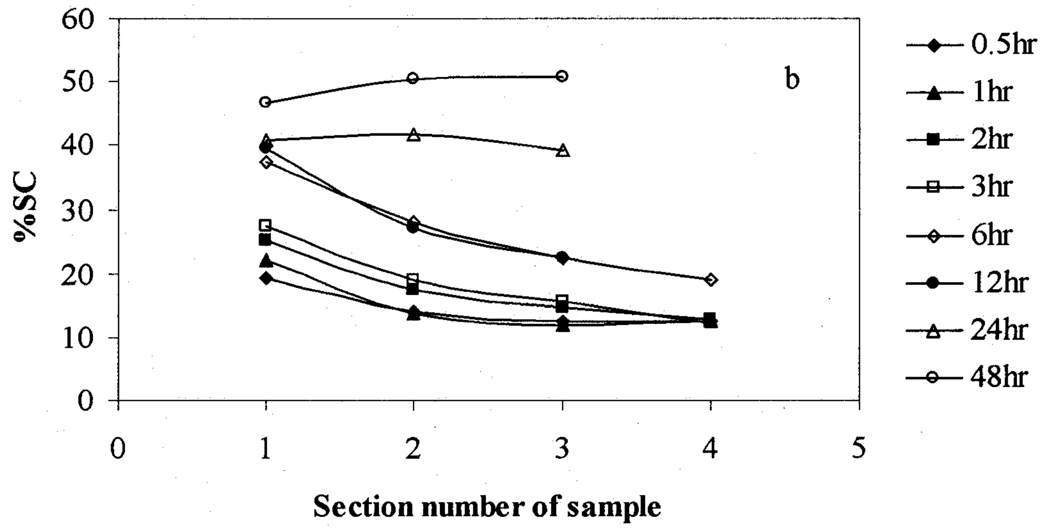


Figure 6.11 Plot of %MC (a) and %SC (b) *vs* sample section number for osmotic dehydration of apple cylinders at 50°C 50°Brix for large-size sample at different time

Further study results showed in Figure 6.12. Sample internal solution soluble solute equilibrated with external solution around 24h for large size apple cylinders. After that time period sample internal solution soluble solute concentration kept stable even after 150h. However, the ML and SG varied over all the experimental time period. The useful information we found were after 24h both ML and SG vary trend were very slow. From this point, it suggested that the pseudo-equilibrium study used instead of true equilibrium (which is impossible to fulfill) provided some necessary information for osmotic dehydration kinetics study, modeling and other related study.

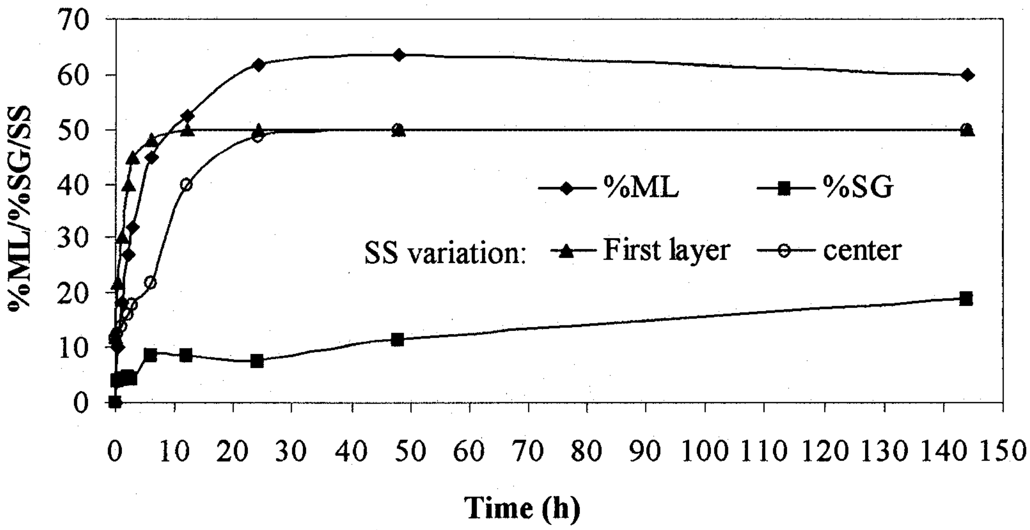


Figure 6.12 Plot of %ML/%SG/ soluble solutes (SS) *vs* processing time for osmotic dehydration of apple cylinders at 50°C 50°Brix for large-size sample

Table 6.5 Sample internal equilibrium water content and solid content

Conditions	X_w	X_s
40°C 30°B	67.7	32.3
40°C 40°B	54.5	45.5
40°C 50°B	52.4	47.6
40°C 60°B	36.4	63.6
50°C 30°B	60.8	39.2
50°C 40°B	53.2	46.8
50°C 50°B	42.9	57.1
50°C 60°B	39.9	60.1
60°C 30°B	59.4	40.6
60°C 40°B	51.8	48.2
60°C 50°B	40.5	59.5
60°C 60°B	30.8	69.2

6.4 Conclusions

- Osmotic dehydration equilibrium kinetics data (product composition, mass, volume, etc) is the necessary information in modeling conventional osmotic dehydration mass transfer process, to define the driving force, to design equipment and optimization of the process.
- Osmotic dehydration process is first time defined as three period: equilibrium, pseudo-equilibrium and dynamic periods in this study. Pseudo-equilibrium (practical equilibrium) and dynamic period data are necessary for estimating the time of osmotic process, and ultimate mass transport of the solutes and water.
- Higher concentrations increased ML_∞ and decreased SG_∞. Temperature effect on result of water loss at equilibrium was less evident. Azuara-model fitted osmotic dehydration kinetics very well up to equilibration. Equilibrium moisture loss and solid gain could be estimated with Azuara-model combined with relatively long time experiment data. The equilibrium estimated here is the initial equilibrium stage without structural relaxation. The equilibrium *ML*, *SG*, ratio of *ML/SG* (EDE) and

other related information could be used as reference to design osmotic dehydration process and equipment for apple products.

- There might exist two kinds of equilibration: one is liquid equilibration, which is reached around 24h; the other is solid matrix equilibration, which takes long time to reach. Solute penetration is not overall just certain depth around 24h osmosis. Solute penetration is not strictly followed diffusion law.

Preface to Chapter 7

Microwave assisted osmotic dehydration combined microwave and osmotic drying together and accelerated the mass transfer during osmotic process. However, the effect of microwave assisted osmotic dehydration (MWOD) pretreatment on sample subsequent air-drying behavior and products color change need to be investigated. During air-drying, fruit slices can undergo enzymatic or non enzymatic darkening process and visual color change is considered a major sensory parameter and acceptability attribute of a food product (Clydesdale, 1993). Osmotic pre-concentration pretreatments may affect the subsequent drying behavior of the sample and product's color profile during the subsequent air drying process. Earlier studies on the osmotic dehydration pretreatment effect have been conducted principally on the subsequent air drying behavior of osmotically treated samples, little has been reported on how the pretreatment conditions are related to the subsequent air drying behavior of the products and their quality aspects-color profile. Therefore, the need for a more in depth qualitative and quantitative study of osmotic pretreatment effect on sample moisture diffusivity and other parameters during subsequent air-drying has been recognized. This work was carried out for the fourth objectives of this thesis. This study would enhance basic knowledge for osmotic dehydration application.

Part of this research has been presented in some conferences and/or being prepared for publication in scientific journals detailed earlier. The experimental work and data analysis were carried out by the candidate under the supervision of professor Dr. H.S. Ramaswamy.

CHAPTEER 7

EFFECT OF MICROWAVE ASSISTED OSMOTIC DEHYDRATION TREATMENT ON THE CONVECTIVE AIR DRYING RATE AND QUALITY CHARACTERISTICS OF APPLES

Abstract

The effect of microwave assisted osmotic dehydration (MWOD) treatment on subsequent air drying behavior and product color change was investigated for apple cylinders. Compared with control samples, osmotically treated samples had lower moisture diffusivity during the subsequent air drying process. The color parameters: L-, a-, b- value during air drying were influenced by MWOD pretreatment conditions. The results presented in this work suggest that the change in L- and b-values were larger as compared to the a-value, and may contribute significantly to the perception of color change. MWOD pretreatment shifted products color profile toward those of the more expensive freeze dried products.

Keywords Moisture diffusivity, pretreatment, drying, microwave, osmotic dehydration, apple cylinders, color.

7.1 Introduction

Being a partial dehydration or concentration step, osmotic dehydration is used as a pretreatment proceeding conventional drying, vacuum drying and freezing for improving fruit product quality. Depending on process conditions, water loss of the sample can extend to 70% of its initial weight, but usually goes up to 30-50% of its initial weight for practical application. The process could be described by at least two simultaneous flows: water moves from the biological tissue to the solution, and solutes migrate into the sample tissue. The selective permeability of water is probably due to the semi-permeable characteristics of biological materials and water physicochemical property specialty.

Previous studies on product drying behavior of osmotically treated materials show that the influence of osmotic dehydration pretreatments differed as the sample properties change from one commodity to another. Hawkes & Flink (1978) noted that with osmotic concentration as a pre-step to freeze drying, the water load to the freeze dryer is significantly reduced, improving drying process economics. Islam & Flink (1982) noted that changes in the composition of food material during the osmotic concentration step can subsequently influence air drying behavior and found that drying rates and water diffusion coefficients were lower for osmotically treated samples compared to non-osmotically treated potato slices. Mazza (1983) found that the air drying rate of osmotically treated carrots was reduced. Rahaman & Lamb (1991) reported that the air drying rates of previously osmotically treated pineapple slices were significantly decreased because of the presence of the infused sucrose, and that the effective diffusion coefficient for water during the air drying step decreased with the increasing solids content of the slices. Karathanos et al. (1995) found that the moisture diffusion coefficient (D_{eff}) decreased significantly for apples pretreated by a concentrated sugar solution due to the lower porosity and other physicochemical factors. Sankat et al. (1996) reported that drying rates fell as the sugar content of banana slabs increased during the osmotic pretreatment. Nieto et al. (1998) noted that moisture transport during the first falling rate period of apple drying was strongly decreased by glucose uptake during the impregnation step. Sugar distribution in the cellular tissue appeared to have a role in drying behavior. Mcminn and Magee (1999) studied the effect of pretreatments on the convective drying of potatoes and reported that the moisture diffusion coefficient was reduced following the osmotic dehydration pretreatment. Lewicki et al. (2002) found that both pretreated with sucrose and sucrose plus $CaCl_2$ reduced moisture transport rates compared to convective drying rate of tomatoes without pretreatments. However, Flink (1980) reported similar dehydration rates for both osmotically treated and non osmotically treated carrot slices when drying rates were expressed as a function of sample original solids, concluding that uptake of solids in the osmosis process does not itself result in significantly lower drying rate. Uddin and Hawlader (1990) reported similar water diffusion coefficients for fresh and sugar osmotically treated pineapples. Ertekin and Cakaloz (1996) reported osmotically treated samples gave much higher drying rate during subsequent air drying compared to non osmotically treated samples.

Previous studies on product quality showed the influence of osmotic dehydration pretreatments on sample quality properties. Ponting et al. (1973) described osmotic concentration processes using sucrose and invert sugar for concentrating fruit pieces prior to vacuum drying and found the products retained a bright, natural color and good flavor, characteristics of fresh fruit. Flink (1975) reported that organoleptic quality of a number of freeze dried fruit products was improved following an osmotic-concentration step in a 60% sucrose syrup. Pretreatment and subsequent drying substantially affected the quality of the product. The color of osmotically treated and subsequently air-dried samples was preserved not only during processing but also during long-lasting storage (Krodia, et al., 2000).

Microwave assisted osmotic dehydration combined microwave and osmotic drying together and accelerated the moisture transfer during the osmotic process (Li & Ramaswamy, 2003; Ramaswamy & Li, 2003). However, the effect of microwave assisted osmotic dehydration (MWOD) pretreatment on sample subsequent air drying behavior and product color change was not investigated. During air-drying, fruit slices can undergo an enzymatic and non enzymatic darkening process and visual color change is considered as a major sensory parameter and acceptability attribute of a food product (Clydesdale, 1993). Osmotic pre-concentration pretreatments may affect sample subsequent drying behavior and product color profile during subsequent air drying process.

The purpose of this study is to investigate the effect of MWOD pretreatment on sample drying behavior and on product color parameter changes during the subsequent drying process.

7.2 Materials and methods

7.2.1 Sample preparation

A batch of Idared variety of apples of uniform size and ripeness, and commercial sucrose (sugar) were obtained from local farm of the campus and local supermarket, respectively. The fruits were refrigerated at 5°C and at 95% relative humidity until they were used for the experiments. Apples were cut into five cylinders of 2.0 cm in diameter, 2.0 cm in height vertically.

7.2.2 Drying equipment and procedure

A domestic MW oven (SANYO EM-563, Japan), with a maximum output of 700 W at 2450MHz was used. The oven has the facility to adjust the power (wattage) supply and the time of processing. The osmotic dehydration process was performed inside this MW oven under a continuous flow circulation condition. The samples were pre-treated by MWOD with different time, concentration and temperature, and were finish dried by conventional hot air drying. The conventional hot air drying experiments were accomplished in a domestic dryer (Equi-Flow Food Dehydrator, Marysville, WA), where cross-flow dehydration was applied using air at 50°C, relative humidity 50% and 0.5 m/s. The end point of drying was 20% (DB) moisture content.

7.2.3 Conventional hot air drying of apple cylinder

Fresh cut apple cylinders were put into an air drier directly and dried to a moisture content of 20% (DB).

7.2.4 Freeze drying of apple cylinder

Fresh cut apple cylinders were immersed into 2% ascorbic solution to protect sample color, were put into a freezer to freeze the sample. FreeZone® Freeze Dry System (Model 79480) was used to dry the frozen sample close to 20% (DB). During the operation, when the collector temperature was less than –40°C and the vacuum was less than 133×10^{-3} mbar, the freeze drying process began. The whole process was controlled by automatic code.

7.2.5 Color measurement

Color measurements were done in a Minolta colorimeter CM-500d using an aperture of 1.2 cm diameter. The exposed area was sufficiently great relative to the illuminated area to avoid any light-trapping effect. The instrument (2°/D65, 2° observer) was calibrated with a standard white tile (L = 77.58, a = -0.27, b = -26.63). The CIELab tristimulus values in terms of L, a and b were measured in two ends of each apple cylinders, and six cylinders were measured for each condition. Standard values considered were those of the fresh cut apple cylinder end areas.

Product color was measured after the sample reached 20% moisture content. The total color difference Eq. (7.1) was calculated from the CIE L-, a-, b-values and used to describe the products color profile change during air drying:

$$\Delta E = \sqrt{(L_o - L)^2 + (a_o - a)^2 + (b_o - b)^2} \qquad (7.1)$$

Where subscript "0" refers to the color reading of a fresh apple cylinder. Fresh apple cylinders were used as the reference and a larger ΔE denotes greater color change from the reference material.

7.2.6 Drying modeling

Food dehydration processes mostly take place in the falling rate period. The experimental data on drying in the period may be analyzed by a diffusion model. The internal temperature during drying may be considered uniform due to the low Biot number for heat transfer usually found for conventional air drying of foods (Alzamora et al., 1979). Thus heat transfer effects in drying analysis may be neglected. The analytical solution to the diffusion equation has been given by Crank (1975) for different regular shape samples. The detailed inferences were explained in Chapter 3. The final formula for a finite cylinder is as follows:

$$M_{mfc} = 0.56e^{-\frac{8.25}{d^2}Dt} \qquad (7.2)$$

where the moisture loss ratio (M_{mfc}) is defined as follows for water transfer:

$$M_{mfcw} = \frac{M_e x_e - M_t x_t}{M_e x_e - M_o x_o} = 0.56e^{-\frac{8.25}{d^2}Dt} \qquad (7.3)$$

where x_t and x_e represent the water content at time 0, t and equilibrium respectively, M_0, M_t and M_e represent the sample masses at time 0, t and equilibrium respectively; D is the apparent moisture diffusivity (m^2s^{-1}), calculated by the slope of straight line $\ln\frac{M_t - M_e}{M_o - M_e}$ *vs* t; *d* is the cylinder radius; M_{mfcw} is selected as larger than 0.2 to get a more accurate moisture diffusivity estimation. Since there is a maximum diffusivity in the region of about 0.2g/g moisture content dry solids (Marousis et al., 1989; Karthanos et al, 1995), beyond this point, the water diffusivity decreases.

Each experiment was triplicate and the average values were used in the analysis.

7.3 Results and discussion

7.3.1 Drying curves

Air drying curves (air temperature 50°C) of apple cylinders without and with MOWD pretreatment in three different conditions (40°C 40°Brix, 50°C 50°Brix and 60°C 60°Brix) are shown in Figure 7.1. During air drying, moisture content decreased logarithmically with drying time, which means that the samples lost greater moisture at the initial stage of drying. The rate of change in moisture content was affected by sample initial moisture content and drying time. The initial point of each curve is different in the moisture content axis (Fig 7.1), obviously due to the different pre-concentration, resulting from the osmotic treatment. The water content of the sample on a dry basis (kg water/kg dry solids fruits) was measured by the oven method. For zero immersion time the initial moisture content was determined to be 6.14 kg water/kg dry solids, for the representing sample of apples used in the experiments (86% water in wet basis).

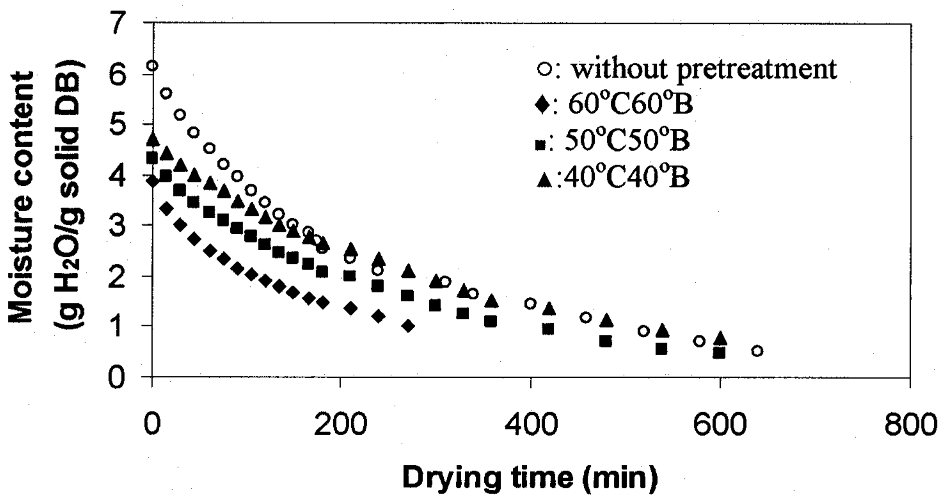


Figure 7.1. Air drying curves of apple cylinders preconcentrated by MWOD at different conditions for 30 min. Air drying at 50°C, air velocity 0.5m/s and RH 50%.

The drying rate curves for air drying of both fresh and osmosed samples under all conditions, showed that drying occurred in the falling rate period (Figure 7.2). The air drying rate was not constant, therefore an internal mass transfer mechanism (diffusion) was assumed to be predominant (Saravacos, 1986; Karathanos et al., 1995). The rates were calculated from weighing moisture content change which occurred in each time interval. Drying rates were highest at the beginning of drying when the moisture content was the greatest. This initial rate is therefore dependent upon the level and state of sample moisture content. In the early period of drying there is a rapid decline in the drying rate for all types of samples. After this period of rapid decline, the drying rate curves continue to decline, but more gradually and in a near linear fashion to equilibrium conditions.

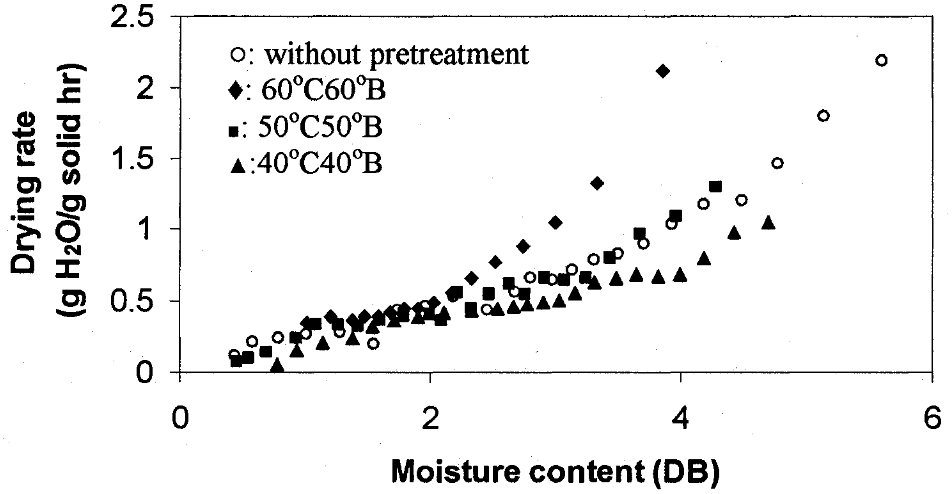


Figure 7.2. Drying rates of apple cylinders osmo-treated by MWOD at different conditions for 30 min. Air drying temperature 50°C, air velocity 0.5m/s and RH: 50%.

For MWOD pretreated samples air drying curve, it is noted that the moisture loss rate (g evaporation water/g solid hr) from osmotically treated apples was affected by pretreatment conditions. Higher temperature and concentration gave higher air drying rate for the same moisture content. Except for the 60°C 60°Brix pretreatment at the beginning, all the air drying rates were similar or lower than that of the untreated samples at the same moisture content (Fig. 7.2). This may be due to the samples being pretreated with higher temperature during air drying still keep higher temperature (60°C) inside the drying oven so as to accelerate the sample moisture diffusion process during the subsequent lower temperature (50°C) drying. However, as the moisture content of the fruit drops during air drying, the drying rate also drops significantly, following the straight line in Fig.7.2. The significance of this figure is that all apple samples, pretreated by various sugar solutions followed the same drying rate/moisture content curve. Similar results were reported by Karathanos et al., (1995).

7.3.2 Moisture diffusivity

The moisture diffusivity D was calculated from the slopes of the straight lines (ln M_r *vs* t) for the region of moisture contents: $0.2 < M_r < 0.6$. From an analysis of the drying curves, the moisture diffusivity during the air drying, with or without osmotic pre-concentration may be found. The sample moisture ratio as a function of drying time under various conditions, with pre-concentration by MWOD and without pre-concentration (fresh) is shown in Figures 7.3-7.6. While calculating the moisture diffusivities, there is a maximum apparent diffusivity in the region of about MC = 0.2 (kg water/kg dry solids). This maximum, which had been found also in past similar experiments (Marousis et al, 1989; Karathnos et al., 1995), is attributed to the porosity increase at the last stage of drying. Beyond that point, although the porosity of the sample may not increase further, the attractive forces of solids/water become stronger, therefore decreasing water diffusivity.

The apparent moisture diffusivities D were calculated using equation 7.3. Calculated average diffusivities for fresh sample was 1.18 x 10^{-9} m^2/s at a range of sample moisture content from 3.51 kg H_2O/kg solid to 1.28 kg H_2O/kg solid. While for 60°C 60°Brix MWOD 10 min treated sample, the average moisture diffusivity was: 0.93 x 10^{-9} m^2/s at the range of sample moisture content from 3.63 kg H_2O/kg solid to 1.43 kg H_2O/kg solid; 30 min treated sample, the average moisture diffusivity was 1.05 x 10^{-9} m^2/s at the range of sample moisture content from 3.33 kg H_2O/kg solid to 1.38 kg H_2O/kg solid; 60 min treated sample, the average moisture diffusivity was 0.98 x 10^{-9} m^2/s at the range of sample moisture content from 2.60 kg H_2O/kg solid to 1.44 kg H_2O/kg solid; 90 min treated sample, the average moisture diffusivity was 0.89 x 10^{-9} m^2/s at the range of moisture content from 2.10 kg H_2O/kg solid to 1.50 kg H_2O/kg solid; 110 min treated sample, the average moisture diffusivity was 0.77 x 10^{-9} m^2/s at the range of moisture content from 2.04 kg H_2O/kg solid to 1.40 kg H_2O/kg solid. Overall, the values of apparent moisture diffusivities in this study are the same order of those compiled by Zogzas et al. (1996), for apples with pretreatments in the range of 0.25 x 10^{-9} m^2/s to 2.2 x $10^{-9}m^2/s$ at 55°C with moisture contents ranging from 0.01 to 5.50 g H_2O/g DM.

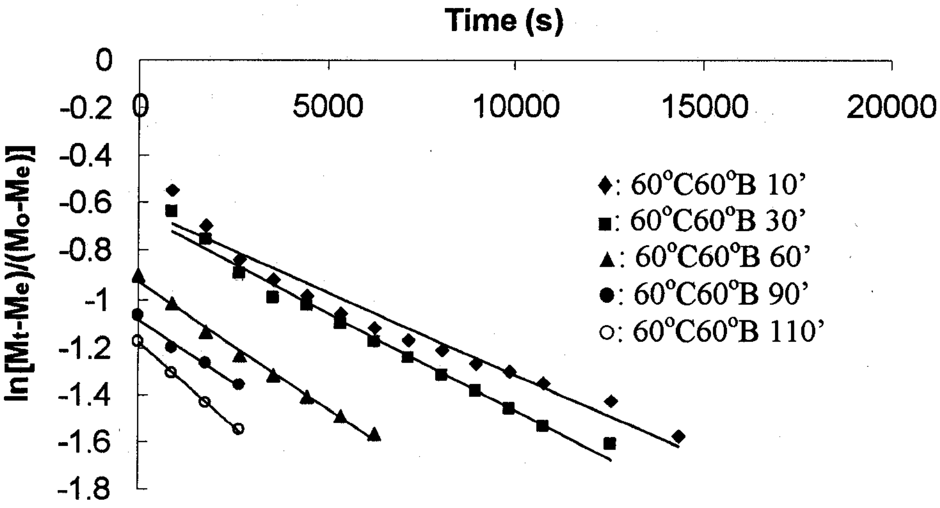


Figure 7.3. 60°C60°B MWOD treated sample residual moisture ratio as a function of time during drying process. Air drying at: 50°C, RH:50% and 0.5m/s

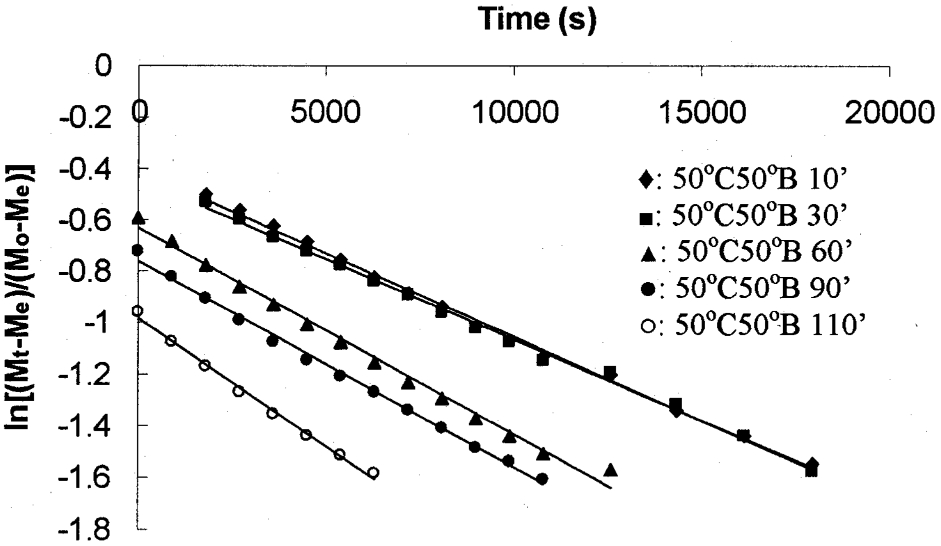


Figure 7.4. 50°C50°B MWOD treated sample moisture ratio as a function of drying time during drying process. Air drying at: 50°C, RH:50% and 0.5m/s

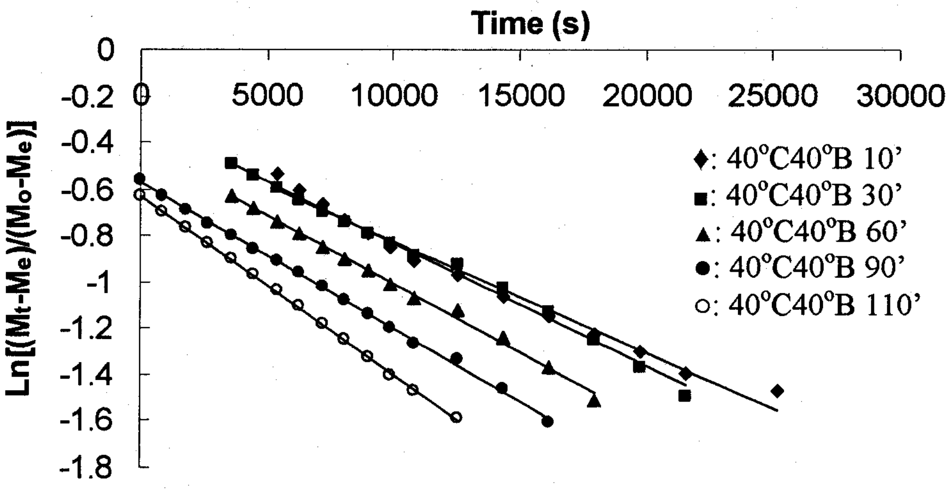


Figure 7.5. 40°C40°B MWOD treated sample moisture ratio as a function of drying time during drying process. Air drying at: 50°C, RH:50% and 0.5m/s

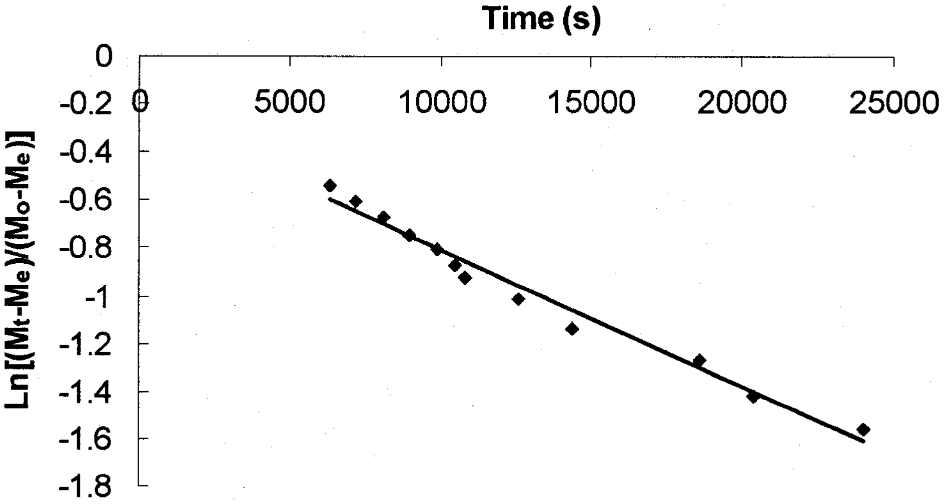


Figure 7.6. Apple cylinders moisture ratio as a function of drying time during drying process. Air drying at: 50°C, RH 50% and 0.5m/s (Control: without osmotic treatment)

Table 7.1 Moisture diffusivities of apple cylinders with or without pretreatment during subsequent air drying under various conditions

Time	Drying parameters					
	60°C60°B		50°C50°B		40°C40°B	
MWOD	D*10^{-9}	R^2	D*10^{-9}	R^2	D*10^{-9}	R^2
10’	0.93	0.96	1.00	0.99	0.89	0.98
30’	1.05	0.98	0.96	0.99	0.92	0.99
60’	0.98	0.99	1.06	0.99	0.99	0.99
90’	0.89	0.94	0.93	0.99	0.85	0.99
110’	0.77	0.99	0.98	0.99	1.07	0.99
Without pretreatment	1.18	0.98	1.18	0.98	1.18	0.98

* Data obtained by drying single layers of samples cabinet dryer, operating at an air velocity of 0.5m/s, 50°C and 50% RH.

Table 7.1 shows that with pretreatment, moisture diffusivities decreased under all conditions. This is an expected behavior since moisture migration becomes increasingly difficult as the physical structure becomes denser and harder during drying. Further, as additional sugar is infused into the samples in the pre-treatment, apparent diffusivities also fall. Similar results were reported by Islam and Flink (1982) who studied osmotic dehydration and its effect on air drying behavior of potato slices. Rahaman & Lamb (1991) concluded that osmotically treated pineapple slices containing the most sucrose had the lowest apparent moisture diffusivities (1.62*10^{-10} m^2/s compared to 12.54*$10^{-10}$$m^2/s$ in the osmotically treated and non-osmotically treated samples, respectively.). Sankat et al. (1996) reported moisture diffusivity of osmotically treated banana slabs by 39°Brix solution was 8.8 x 10^{-10} m^2/s.

The reduction of water diffusivity by treatment with sugars (osmotic dehydration) may have significant applications in the use of dehydrated plant foods, especially mixed with other foods, such as ready-to-eat cereals, since plant foods pretreated with sugars, may exhibit an extended food stability during storage, compared to untreated samples, due to lower water or other substances’ diffusivity, thus retarding several undesirable chemical reactions (Karmas et al., 1992).

7.3.3 Chroma parameters L, a and b

The color specification of a product is simply the specification of a point in a three-dimensional space where visual or mathematical expression of color has become known as a color solid. The experimental values of Lightness (L), redness (a) and yellowness (b) of apple cylinders during hot air drying at 50°C and 50% relative humidity, without or with MWOD pretreatment, and freeze drying are shown in Figures 7.7-7.10, respectively. In each of these figures the color parameters of hot air drying, freeze drying, as well as the samples pretreated by MWOD in sucrose (40°C-40°Brix, 50°C-50°Brix, and 60°C-60°Brix) solutions are presented.

An overall examination of the raw data (shown by symbols) shows that, compared with hot air drying and freeze drying, with MWOD pretreatment, product L values increased and were closer to or higher than freeze dried product L-value (Fig. 7.7). It has been stated that the variation in the brightness of dried samples can be taken as a measurement of browning (Avila & Silva, 1999; Ibarz et al., 1999). Since lightness is a measure of the color in the light dark axis, the increasing value indicates that the samples were turning lighter. The lightness parameter of most of the MWOD treated apple cylinders showed a similar trend over the whole duration of the subsequent air drying (Fig. 7.7). The infusion of sugars and MW treatment in fruits caused a relative increasing of color lightness (L), especially in comparison to air-dried samples, which experienced an extensive browning. This is possibly due to the existence of sugars and MW effect, which cause the relative inactivation of enzymes responsible for the enzymatic browning.

For a-values, with MWOD pretreatments, higher than the a-value of hot air dried product, after 30 min pretreatments, the overall trend of a-value was decreasing and getting close to the hot air drying a-value (Fig.7.8). The redness (a) change for different conditions is shown in Fig. 7.8, the "a" value of MWOD treated air-dried samples increased during hot air drying. This a-value increase probably was due to Maillard condensation of hexoses and amino components and oxidation of ascorbic acid (Barreiro et al., 1997; Lee & Coates, 1999). The increase of the a-value denotes a more red color, which is indicative of the browning reaction. A similar trend was observed by combining hot air with MW finish drying (Maskan, 2001). The increase, compared with hot air drying, was reduced with treatment time increasing. Hot air dried samples showed an a-value (about 11.2) indicating light red and it was observed that the a-value reached the values greater than 11.2 with MWOD treated samples at the first 30 min pretreatment, after that time period, the a-values of all MWOD pretreated sample decreased till close or lower than that of air dried sample a-value, respectively (Fig. 7.8).

The b-value of MWOD pretreated product is close to the freeze dried product b-value, with the pretreatment time increasing, the b-value had a decreasing trend decreasing (Fig. 7.9). This value decreased fast during the first 60 min treatment, then decreased slower after 60 min. The hot air dried sample b-value was 31.1, indicating yellowness, and it was observed that this parameter reduced values to 20.1 after MWOD pretreatment. Therefore, products lost their yellowness to light yellow with MWOD treatment. This may be due to MW inactivate the browning enzyme which might otherwise take action during air drying. Thus the color parameter "b" decreased after all MWOD pretreatment. The decreasing of the b-parameter from the air-dried 31.3 to 20.1, correlated with the visual examination: with MWOD pretreatment, apple cylinders lost their brown yellow color, changing to light yellow and white.

The chroma value indicates the degree of saturation of color and is proportional to the strength of the color. The different behavior of the untreated samples compared to that of MWOD pretreated samples, regarding the color parameters during air drying and freeze drying, showed that MWOD pretreatment affected the sample color change during the air drying process. The MWOD treated samples kept product color light upon subsequent air drying, while untreated samples underwent browning color reactions during subsequent air drying process, which is usually undesirable. A new practical and possible method for color preservation is suggested: the microwave assisted osmotic dehydration. The color preservation may be seen by the relative constant lightness parameter L (almost constant or an increase) and chroma parameters (a, b), which experienced only a small increase, and decrease, respectively. Thus, the MWOD treatment seems to prevent color deterioration during air drying, resulting in products with superior color compared to that of the air-dried ones.

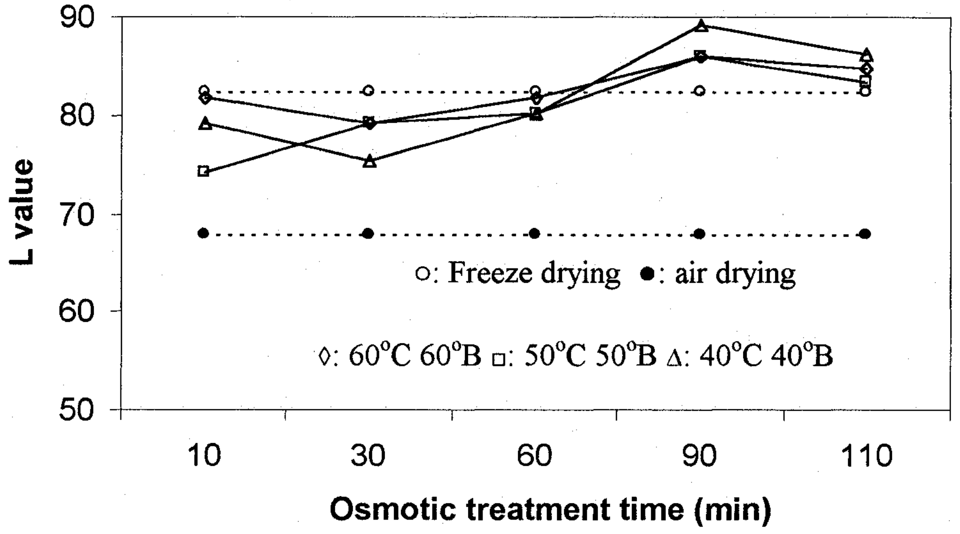


Figure 7.7. Lightness (L) versus MWOD pretreatment time at different conditions. Air drying 50°C.

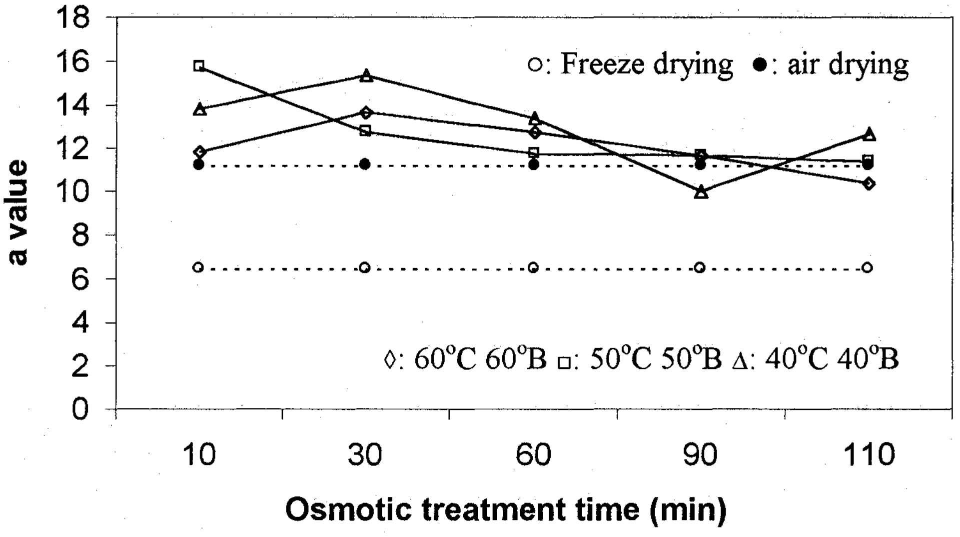


Figure 7.8. Redness (a) versus MWOD pretreatment time at different conditions. Air drying 50°C.

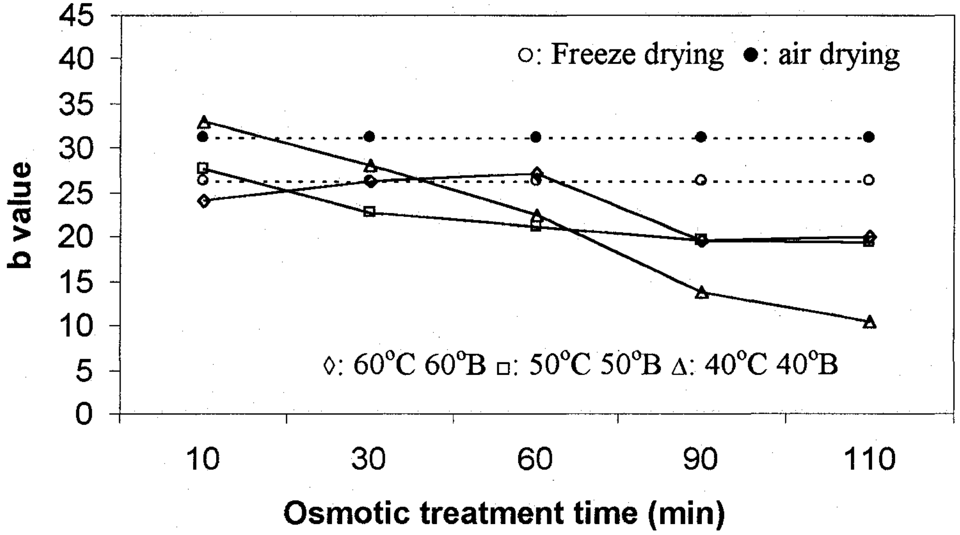


Figure 7.9. Yellowness (b) versus MWOD pretreatment time at different conditions. Air drying 50°C

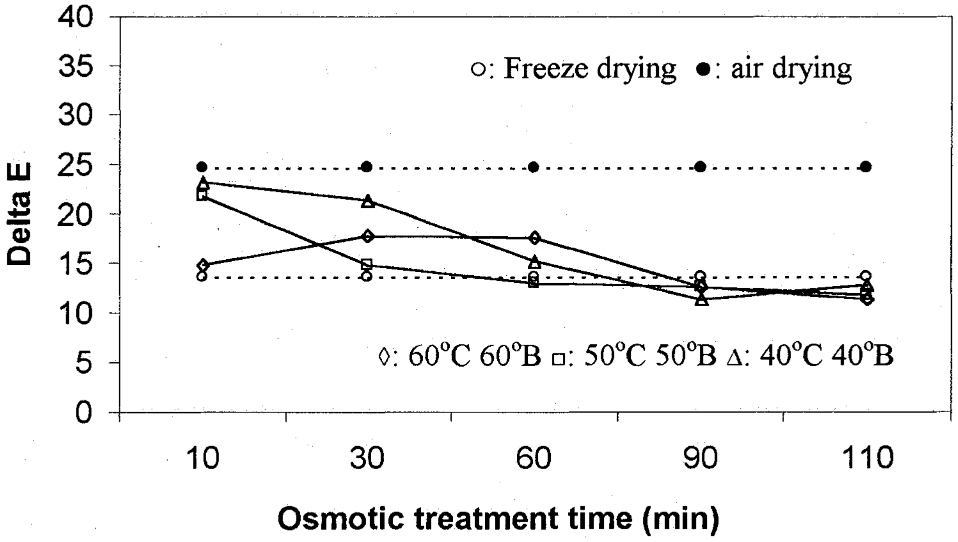


Figure 7.10. Total color difference (ΔE) versus MWOD pretreatment time at different conditions. Air drying 50°C

The total color difference ΔE, a combination of parameters L-, a- and b-values, is a colorimetric parameter extensively used to characterize the variation of colors in foods during processing. ΔE or the total color difference observed from the fresh apple cylinders with different drying methods: hot air drying, freeze drying, and MWOD pretreated with hot air drying were shown in Fig.7.10. As expected, the maximum ΔE was with hot air drying, and the minimum ΔE was with freeze drying, which has a good tendency close to natural color. With MWOD pretreatment, ΔE decreased rapidly; after 60 min the ΔE was close to freeze drying ΔE. The decrease in ΔE observed with MWOD pretreatment was due to a slightly changed a-value, reduced b-value and increased L-value. As it can be seen from Fig. 7.10, MWOD pretreatment reduced the total color difference (ΔE). This might be due to the MW inactivate browning enzyme effects, which is similar to a thermal treatment might prevent color changes during osmosis and this behavior might be related to enzyme thermal inactivation (Guerrero et al., 2002; Rogriguez et al., 2003).

The mechanism of browning of raw fruits is well studied and can be of enzymatic or non enzymatic origin. The formation of darkening pigments via enzymatic browning is conducted by enzyme polyphenol oxidase (EC 1.14.18.10) which catalyzed oxidation of mono- and diphenols to o-quinones that are highly reactive compounds and can polymerize spontaneously to form brown pigments (McEvily et al., 1992). In fresh and undamaged fruits, natural phenolic substrates are separated from the polyphenol oxidase by compartmentalization and browning occurs very slowly (Vamos-Vigyazo. 1980). The most effective method for controlling enzymatic browning is to inactivate polyphenol oxidase, eliminate oxygen from the cut surface or to use antibrowning agents. Thus, MWOD treatment might inhibit nonenzyme browning reaction and inactivate the browning enzyme activity simultaneously.

7.4 Conclusions

- Moisture diffusivities of osmotically treated sample were lower than that of control during subsequent air drying process. Drying rate of osmotically treated sample and control were similar at same moisture content during the subsequent air drying process. The drying characteristics of osmotically pre-concentrated foods are very important in the design, operation and control of industrial dryers.

- The Chroma L-, a-, b- parameters during air drying were more influenced by MWOD pretreatment conditions. The results presented in this work suggest that the change in L- and b-values were larger as compared to the a-value, and may contribute significantly to perception of color change. A color profile shifted towards freeze drying product color after MWOD pretreatment.

Preface to Chapter 8

Knowledge of sorption characteristics is an extremely valuable tool for food scientist, it can be used to predict potential changes in food stability; it can be used for packaging selection and for ingredient selection (Labuza, 1984). Despite the large volume of work on osmotic dehydration, publications on sorption characteristics of osmotic dehydrated products are rather limited (Lerici et al., 1985; Lenart, 1991; Lazarides, et al., 1995). Microwave assisted osmotic dehydration combines microwave and osmotic drying together and accelerates the moisture transfer during osmotic process. However, the effects of microwave assisted osmotic dehydration (MWOD) treatment on products' sorption isotherms have not been investigated. Therefore, the need for a more in depth qualitative and quantitative study of osmotic pretreatment effect on products' sorption isotherms has been recognized.

The main objective was to investigate the possible changes in sorption isotherms of apple cylinders as related to different drying methods. Specially, the influence of osmotic dehydration process time, temperature, and solution concentration on osmo-air dried products' sorption isotherm variation was evaluated. This work was partially to achieve the forth and fifth objectives of this thesis. This study would enhance basic knowledge for osmotic dehydration application.

Part of this research has been presented in some conferences and/or being prepared for publication in scientific journals detailed earlier. The experimental work and data analysis were carried out by the candidate under the supervision of professor Dr. H.S. Ramaswamy.

CHAPTER 8

CHANGES IN SORPTION ISOTHERMS INDUCED BY DIFFERENT CONDITIONS OF OSMOTIC DEHYDRATION OF APPLE CYLINDERS

Abstract

Idared apple variety was vertically cut into 5 cylinders of 2.0 cm in diameter and 2 cm in height. The apple cylinders were first dried using different drying methods and their sorption isotherms were compared. Then apple cylinders were osmotically pretreated in 34°-63°B for different times at 34°-66°C, followed by air drying in a domestic dryer till 20% moisture content (DB), and their sorption isotherms were investigated. All the adsorption isotherms of the products were determined at 20°C, using a gravimetric-static method. Adsorption isotherms data were fitted to the GAB model and were found to be affected by the drying method and osmotic dehydration pretreatment conditions. Adsorption isotherm of osmo-air dried apple cylinders followed type II isotherms (Sigma shaped curve). Changes in sorption curves of osmo-air dried apple cylinders induced by the two different osmotic dehydration treatment: conventional osmotic dehydration (COD) and microwave assisted osmotic dehydration (MWOD), were studied. Monolayer moisture content (M_m) of the osmo-air dried product was reduced. Sorption isotherms of both osmotic dehydrated-air dried products were shifted with respect to control isotherms.

Keywords Sorption isotherms, Osmotic dehydration, Microwave, Apple, GAB model.

8.1 Introduction

Osmotic dehydration is generally used for partially removing moisture from plant tissue and improving product quality. However, it will not make a product of low water activity to be considered shelf stable. Therefore, osmotically treated product should be further processed (dried, frozen, freeze dried and etc.). Overall, the osmosis process minimizes the heat damage on color and flavor, inhibits enzymatic browning and thus limits the use of SO_2 and increases nutrient retention during subsequent air drying (Pointing, 1973; Islam and Flink, 1982).

Since osmotic concentration process results in some solute uptake, the resulting changes in the composition of the food material will influence product's subsequent hygroscopic property. Islam and Flink (1982) reported osmotic dehydration of a pretreated potato with salt changed the product's water sorption behavior. Mazza (1983) reported the equilibrium moisture contents of sucrose osmotic treated and freeze dried carrots decreased with an increase in osmotic solution concentration. Lazarides et al. (1995) found that osmotic preconcentration treated dried product's monolayer moisture content decreased compared with that of control. Ertekin and Cakaloz (1996) reported osmotic dehydrated-air dried peas had a higher moisture content (equilibrium moisture content) compared to the air dried samples. Krokida et al. (2000) found osmotic pretreatment resulted in a shift in sorption isotherm for both apple and banana, the monolayer moisture content (M_m) for the air dried samples was higher than that of osmotic pretreated samples. Falade et al. (2003) reported adsorption isotherms of fresh- and osmo-oven dried plantain slices were affected by variation in sucrose concentration and adsorption equilibration temperature.

Knowledge of sorption characteristics is a valuable tool for food scientist. It can be used to predict potential changes in food stability; it can be used for packaging selection and for ingredient selection (Labuza, 1984). Despite the large volume of work on osmotic dehydration, publications on sorption characteristics of osmotic dehydrated products are rather limited (Lerici et al., 1985; Lenart, 1991; Lazarides et al., 1995).

Our main objective was to investigate the possible changes in sorption characteristics of apple cylinders as related to different drying methods and osmotic dehydration pretreatments. The influence of osmotic dehydration process time, temperature, and concentration on osmo-air dried product's sorption isotherm behavior was evaluated. The difference between conventional osmotic dehydration (COD) and microwave assisted osmotic dehydration (MWOD) pretreatment on product adsorption isotherms was compared as well.

8.2 Materials & Methods

8.2.1 Oven drying

Fresh cut apple cylinders (var. Idared) were put into the oven directly and dried at 105°C for 24h.

8.2.2 Air drying

Fresh cut apple cylinders (var. Idared) were put into the air drier directly and dried to certain moisture content. The conventional air drying experiments were accomplished in a domestic dryer (Equi-Flow Food Dehydrator, Marysville, WA), where cross-flow dehydration was applied using air at 50°C, relative humidity 50% and air velocity 0.5 m/s. The end point of drying was set at 20% (DB) moisture content.

8.2.3 Freeze drying

Fresh cut apple cylinders (var. Idared)were immersed into 0.2% ascorbic solution to protect sample color, then were put into freezer to freeze the sample. The FreeZone® Freeze Dry System (Model 79480) was used to dry the frozen sample close to 20% (DB). During the operation, when the collector temperature was less than – 40°C and the vacuum was less than 133 x 10^{-3} mbar, the freeze drying process would begin. The whole process was controlled by automatic code.

8.2.4 Conventional osmotic dehydration—air drying

Apples (var. Idared) were used as a model fruit, since they provide relatively homogenous flesh structure and convenience in obtaining standardized (in size and shape) samples. Apples were cut into five cylinders of 2.0 cm in diameter, 2.0 cm in height vertically. Sucrose was used as osmotic solutes. The osmotic solution concentration was 34°Brix to 63°Brix, the solution/product ratio was 5:1 with continuous flow (500 ml/min) and the osmotic process was continued for up to 5.5 h at temperatures of 34°C to 66°C. Following preconcentration, apple cylinders were air dried. The conventional air drying experiments were accomplished in the same domestic drier and at 50°C, relative humidity 50% and 0.5 m/s conditions. The end point of drying was set at 20% (DB) moisture content.

8.2.5 Microwave assisted osmotic dehydration—air drying

A domestic MW oven (SANYO EM-563, Japan), with maximum output of 700 W at 2450 MHz was used. The oven has the ability to adjust power (wattage) supply and the time of processing. The microwave assisted osmotic dehydration process was performed inside this MW oven with a continuous flow (500 ml/min) circulation condition. The apple cylinders were pre-treated by MWOD with different times (10 min to 110 min), concentrations (34°Brix to 63°Brix), temperatures (34°C to 66°C), were finish dried by conventional air drying. The conventional air drying experiments were accomplished in the same domestic drier and at 50°C, relative humidity 50% and 0.5 m/s conditions. The end point of drying was set as 20% (DB) moisture content.

8.2.6 Sorption isotherms

Dried samples were stored in desiccators for 7 days to achieve uniform moisture content. Then adsorption equilibration was reached in 10 days by placing them in desiccators containing various saturated salt solutions. During that period, hygrostats were kept in a well temperature controlled environment. Moisture sorption isotherms for osmotically treated sample and control were determined by standard static, gravimetric method at 20°C. Equilibrium moisture contents were tested over the range of a_w: 0.22-0.97. The moisture content of equilibrated samples was determined by oven method, at 105°C for 24 h. The sorption isotherms were obtained by plotting the moisture content of the sample (g water/100g dry matter) *vs* a_w. Each point on the graph represents the mean value of three determinations.

Six glass desiccators were used, each containing a saturated salt solution selected to produce a specific water activity. The following salts were used to give corresponding water activities (in parenthesis): $K(CH_3COO)$ (0.22), $MgCl_2$ (0.32), K_2CO_3 (0.43), NaCl (0.75), KCl (0.84) and K_2SO_4 (0.97).

8.2.7 Isotherm modeling

Numerous mathematical models with two or more parameters can describe the moisture sorption isotherm data. However, models having more than three parameters are too complicated for straightforward interpretation or use (Krokida et al., 2000). Comparative analysis has established that the GAB (Guggenheim-Anderson-de Boer) model best describes sorption isotherms of most foods for the widest water activity range. It has been shown that the GAB equation fits food isotherms better than other equations with four or more terms (van den Berg, 1985).

The GAB equation can be written in the following form, each of the three GAB constants has a specific physical meaning:

$$m = M_m cga_w / [(1 - ga_w)(1 - ga_w + cga_w)] \quad (8.1)$$

where: m is the equilibrium moisture content in g water/g dry solids, M_m is the monolayer moisture content (in g water/g dry solids), c is the Guggenheim constant related to heat of sorption for the first layer, g is a constant related to the heat of sorption for multilayer water, and a_w is water activity.

The parameters of the equation (8.1) were estimated by transforming the equation into quadratic form as

$$\frac{a_w}{m} = Aa_w^2 + Ba_w + Q \qquad (8.2)$$

with

$$A = \frac{g}{M_m}[\frac{1}{c} - 1] \qquad (8.3)$$

$$B = \frac{1}{M_m}[1 - \frac{2}{c}] \qquad (8.4)$$

$$Q = \frac{1}{M_m cg} \qquad (8.5)$$

With SAS software (1999), polynomial regression got the A, B and Q constant, then further calculated the M_m, g and c constant.

The goodness of fit of the models was evaluated with the equation for the mean relative modulus (P_m):

$$P_m = \frac{100}{N}\sum_{i=1}^{N}\frac{|V_e - V_c|}{V_e} \qquad (8.6)$$

where V_e is the experiment value, V_c is the calculated value using the proposed equations, and N is the number of observations.

P_m-values <5.0 indicate an excellent fit, while P_m-values >10.0 are indicate of a poor fit.

8.2.8 Statistical analysis

Variance analysis was carried out using the SAS (SAS Institute Inc. 1999) software package GLM model. Significant differences were determined by Duncan`s multiple range tests. The significance of differences was defined at $P<0.05$.

8.3 Results and discussions

8.3.1 General observations

Sorption isotherms of product dried by three different drying methods are compared in Figure 8.1. The equilibrium moisture contents of apple cylinders were affected by the drying method. At lower a_w (a_w<0.43), air dried sample equilibrium moisture content was higher than those of oven dried and freeze dried samples. With a_w increasing, freeze dried products kept the highest equilibrium moisture content, then followed by air dried products equilibrium moisture content, and oven dried products having the lowest equilibrium moisture content, as expected.

At lower a_w, equilibrium moisture might be adsorbed as a very thin, mono- or polymolecular layer on the external surfaces of the product by molecular forces or as a result of chemical and biochemical reaction, not involved in enhancing solution or plastering processes. Dried product cell structure may also affect equilibrium moisture content. With air drying, the sample cell has a certain reversible shrinkage structure, while with freeze drying and oven drying, the sample cell has an irreversible structure. Freeze dried products had the maximum cell structure. With the cell reversible shrinkage mechanical force and the surface molecular adsorbance force, air dried products had higher equilibrium moisture content at low a_w.

At high a_w, a combinations of actions occurred resulting in a sharp increase in adsorptive capacity for all three different methods dried products. Such actions included solution, new site creation, plastering and water-water adsorption. Equilibrium moisture can be absorbed into internally by colloid substances and remain in a gel as water of swelling due to its dipolar character. In the mean time, dried product cell structure and size could affect absorbed water and moisture adsorption during reconstitution. Based on microstructure studies; good-quality dehydrated products that reconstituted well after rehydration should have the following characteristics (Jen et al., 1989): cells must not be totally collapsed, cell walls must remain intact, and intercellular spaces must be maintained in the dried product. With freeze drying, cell walls were damaged due to being frozen, while the intercellular space were kept at a maximum, allowing capillary action to draw water into the vicinity of the cells at high a_w. For air dried products, cell walls were less damaged, however, the intercellular space was reduced, thus the overall moisture absorption was less. For oven dried products, both cell walls and intercellular space were severely damaged, therefore, the equilibrium moisture content was the least. From Table 8.1, we could come to the conclusion that oven dried product adsorption isotherms were different compared to that of freeze dried and air dried product adsorption isotherms.

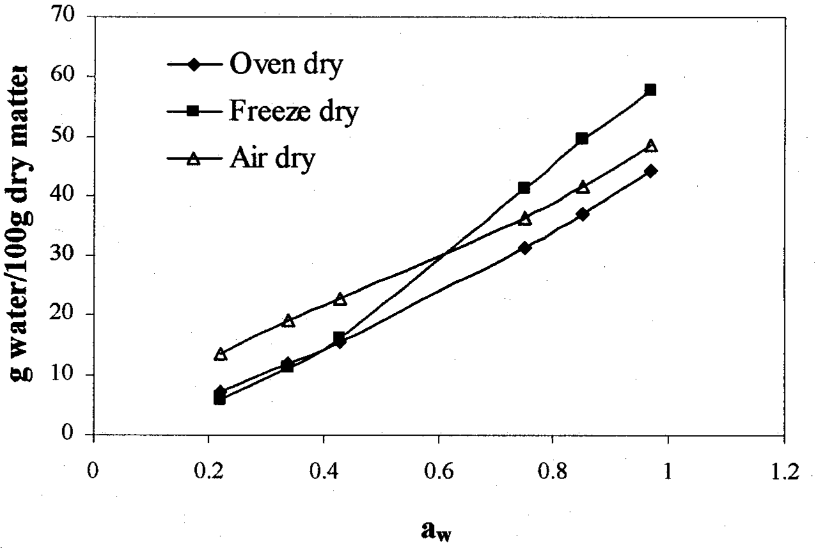


Figure 8.1. Sorption isotherms of oven dried, freeze dried and air dried apple cylinders at 20°C.

Table 8.1 Comparison of equilibrium moisture content of the product with different drying methods

Water activity (a_w)	Oven dry (g/100g dry matter)	Freeze dry (g/100g dry matter)	Air dry (g/100g dry matter)
0.22	7.84 ± 0.25^a	5.79 ± 0.28^b	14.76 ± 0.47^b
0.32	9.54 ± 0.50^a	12.12 ± 0.19^b	18.13 ± 0.24^b
0.43	18.69 ± 0.60^a	16.15 ± 0.13^b	21.32 ± 0.99^b
0.75	29.80 ± 0.69^a	37.36 ± 0.96^b	39.46 ± 0.90^b
0.84	39.60 ± 0.79^a	50.86 ± 1.33^b	42.43 ± 1.24^b
0.97	42.93 ± 0.76^a	59.84 ± 1.47^b	46.34 ± 1.01^b

* different letter showed the adsorption isotherms was different at 95% confidence (t-test compared each two different methods).

Differences among sorption isotherms for osmotically dehydrated-air dried samples are shown in Figure 8.2. Both types of osmotic pretreatments shifted sorption isotherms from that of air dried sorption isotherms. At lower a_w, with both osmotic dehydration pretreatments, the product equilibrium moisture content was lower than those of products without pretreatment. This is probably due to the absorbed sugar on the outside of the plant tissue that covered the active site and hindered the adsorption process. At higher a_w, with microwave assisted osmotic dehydration (MWOD) pretreatments, the product equilibrium moisture content was increased with increasing a_w, a typical characteristic of hygroscopic materials; however, it was still lower than that of products without pretreatments. With conventional osmotic dehydration (COD) pretreatment, with a_w increasing, product equilibrium moisture content increased with the trend closing or higher than those of product without pretreatment. This might be due to two kinds of effects: one was the absorbed sugar dissolution and the other was the sample cell structure difference. At high a_w, dissolution of sugar occurs and crystalline sugar is converted into amorphous sugar (Saltmarch and Labuza, 1980). The amount of water to be absorbed increases greatly after this transition because of the increase in the number of sites upon breakage of the crystalline structure of sugar (Ayranci et al., 1990). According to Saravacos et al. (1986) the slight sigmoid shape of the first part of the isotherms for dried fruits was caused by the water sorption of the biopolymers, and the sharp increase in moisture content at high water activities was due to the sorption by the sugars. Similar results were reported by Lazarides et al. (1995), that osmotic media resulted in shifting and distortion of the sorption isotherm with respect to control. As a result of sugars, composition variance affected water sorption isotherms (Lazarides et al, 1995; Krokida et al, 2000).

Van den Berg (1985) divided sorption/desorption isotherms into three parts. In the first region where water activity was below 0.2, moisture was bound with the material by adsorption and chemi-sorption with the enthalpy of transition from the liquid phase (bound with the material) to the gas phase greater than the heat of evaporation. At low water activities, the moisture molecules were adsorbed on polar components of the material. A further increase in the moisture content results in adsorption on hydrophilic macromolecular components such as proteins and polysaccharides although the processes of dissolution were not activated. The second region (a_w:0.2-0.65) was characterized by polymolecular components adsorption. The enthalpy of transition from the state of a bound liquid into vapor was only slightly higher than heat evaporation for pure liquid. In this range, dissolving and combining of moisture with a material occurred as a result of chemical and biochemical reactions. In the third region, moisture filled up the pores in the material structure. A mechanical character of moisture bonding predominates. Evaporation of this type of moisture did not call for additional energy as it was in the first and second regions. Both osmotic dehydrated treatments might affect all the three regions of adsorption isotherms.

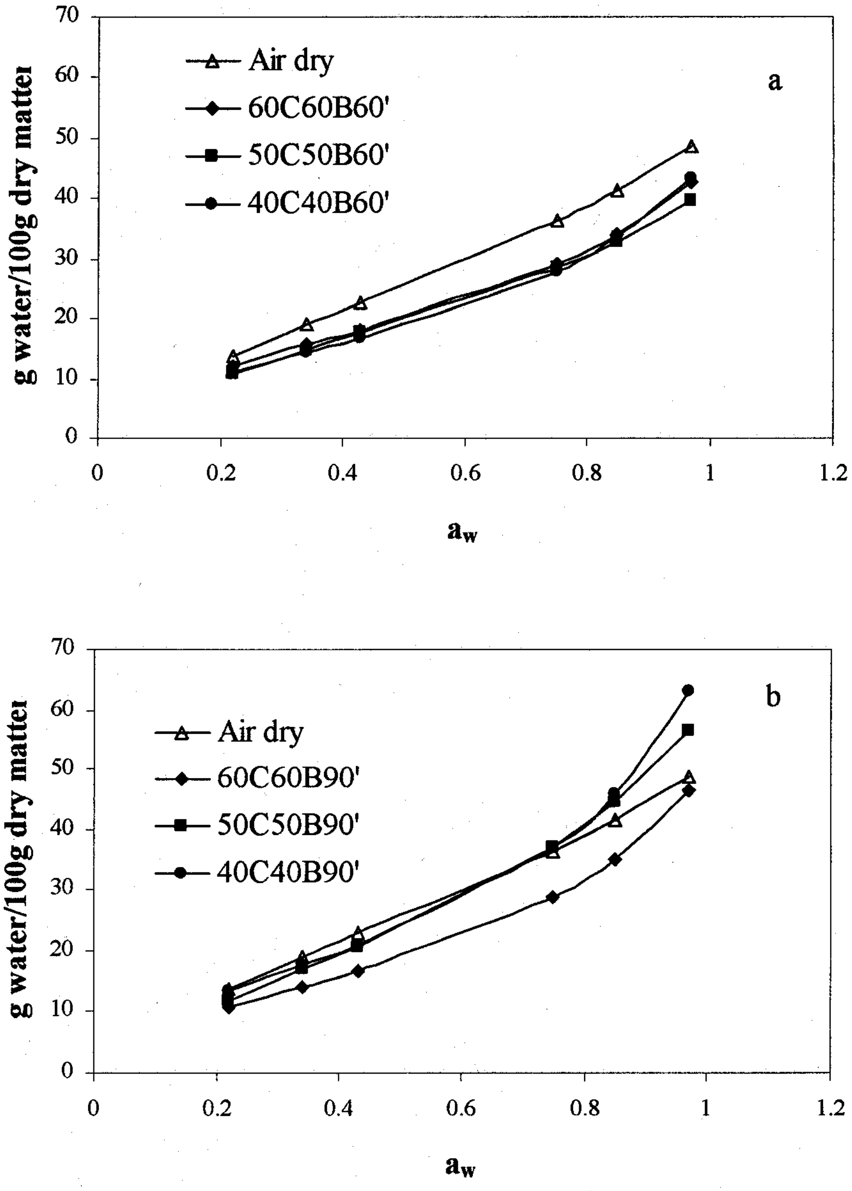


Figure 8.2 Sorption isotherms of air dried apple and osmotic preconcentrated–air dried apple cylinders under different conditions. a: microwave assisted osmotic dehydration (MWOD); b: conventional osmotic dehydration (COD). Pretreatment time 90 min

8.3.2 The GAB model fitting

Sorption isotherm constants and regression parameters dried apple cylinders from different methods and both osmotic dehydrated-air dried apple cylinders give different fit to the GAB model (Tables 8.2 & 8.3). Treatment of sorption data according to the GAB model provided not only the monolayer (M_m) value, but also other information related to the sorption of monolayer and multiplayer. Differences among sorption isotherms were also reflected on certain GAB constants. Due to the fact that drying methods affected dried product cell structure, freeze dried and oven dried product sorption isotherms were only fitted to a polynomial second order equation, but could not get GAB constants. More specifically, the monolayer (M_m) value for air dried samples was higher than most of osmo-air dried M_m values. The GAB constants variation was due to compositional changes and sample cell structure changes that occurred during osmotic preconcentration. The M_m-value decreased with sample solids gain increasing. Similar results were reported by Falade et al. (2003), M_m-value was higher in air dried products than those in osmo-air dried products, as a result of sample sugars composition affecting water sorption isotherms. These results confirmed those reported by other researchers (Mazza, 1983; Lazarieds et al., 1995; Ertekin and Cakaloz, 1996), who noted that osmotic solution resulted in shifting and distortion of the sorption isotherm with respect to the control, and also strongly affected the degree of model fitting. From Table 8.2, MWOD gave the less shift and the less distortion (P_m-value: 2.29—10.51). From Table 8.3, COD gave the wider shift and the larger distortion (P_m-value: 0.82—11.00).

It is concluded that with complex foods such as osmo-air dried fruits or foods with higher sugar content, determining equilibrium moisture content is difficult especially at higher a_w (a_w>0.90), when phase changes involved sugars occurring. Previous studies by other workers who had concluded that the GAB equation was suitable for describing isotherms for a_w values greater than 0.90 had been carried out on less complex foods or food components such as starch, CMC and flour (van den Berg, 1985).

Table 8.2 Results of the experimental data (MWOD-AD) fitting GAB model

Conditions	Time (min)	g	c	M_m	P_m-value
Oven drying		NA	NA	NA	10.53
Freeze drying		NA	NA	NA	4.33
Air drying		0.5170	5.8139	0.2836	5.65
66°C50°Brix	60	0.8162	---	0.0914	3.00
66°C50°Brix	90	0.8245	---	0.0786	4.55
60°C60°Brix	10	0.5453	7.2200	0.2466	6.84
60°C60°Brix	30	0.6213	8.8603	0.1915	6.37
60°C60°Brix	60	0.6690	11.5854	0.1576	6.26
60°C60°Brix	90	0.6999	27.6589	0.1244	7.37
60°C40°Brix	10	0.7270	9.6694	0.1393	7.68
60°C40°Brix	30	0.7792	14.8957	0.1088	10.51
60°C40°Brix	60	0.7996	20.9453	0.0956	8.63
60°C40°Brix	90	0.7900	25.4958	0.0853	5.81
50°C63°Brix	60	0.7163	22.6341	0.1184	5.78
50°C63°Brix	90	0.7602	---	0.0925	2.39
50°C50°Brix	10	0.5166	4.8123	0.2832	3.19
50°C50°Brix	30	0.5672	5.3718	0.2302	4.37
50°C50°Brix	60	0.5986	7.0915	0.1840	3.62
50°C50°Brix	90	0.6409	11.3445	0.1381	4.90
50°C50°Brix	110	0.6403	8.4252	0.1354	4.05
50°C34°Brix	60	0.4971	5.4498	0.2791	6.96
50°C34°Brix	90	0.5525	5.6015	0.2363	8.01
40°C60°Brix	10	0.7487	12.0643	0.1390	6.64
40°C60°Brix	30	0.7616	12.7979	0.1276	6.51
40°C60°Brix	60	0.7792	17.4616	0.1135	5.51
40°C60°Brix	90	0.7761	14.2311	0.1079	5.44
40°C40°Brix	10	0.6895	8.3945	0.1733	3.35
40°C40°Brix	30	0.6954	10.1136	0.1554	2.29
40°C40°Brix	60	0.7050	10.3531	0.1438	2.38
40°C40°Brix	90	0.6847	9.9449	0.1386	2.74
40°C40°Brix	110	0.6943	9.0615	0.1299	3.92
34°C50°Brix	60	0.7351	22.9742	0.1286	5.18
34°C50°Brix	90	0.7293	20.7627	0.1247	5.72

Table 8.3 Results of the experimental data (COD-AD) fitting GAB model

Conditions	Time (min)	g	c	M_m	P_m-value
Oven drying		NA	NA	NA	10.53
Freeze drying		NA	NA	NA	4.33
Air drying		0.5170	5.8139	0.2836	5.65
66°C50°Brix	180	0.8240	28.4845	0.1123	5.08
66°C50°Brix	270	0.8245	57.1970	0.1018	2.19
60°C60°Brix	30	0.7605	6.4948	0.1477	10.07
60°C60°Brix	90	0.7761	8.2306	0.1248	5.26
60°C60°Brix	180	0.7600	7.2958	0.1208	2.94
60°C60°Brix	270	0.7789	7.9496	0.1010	0.82
60°C60°Brix	330	0.8006	8.1339	0.0973	4.18
60°C40°Brix	30	0.5130	5.2427	0.2837	4.34
60°C40°Brix	90	0.6236	8.9541	0.1718	7.17
60°C40°Brix	180	0.5819	8.8935	0.1642	4.16
60°C40°Brix	270	0.6491	11.2779	0.1295	4.17
50°C63°Brix	180	0.7885	30.5171	0.1171	5.75.
50°C63°Brix	270	0.7720	16.6664	0.1222	7.83
50°C50°Brix	30	0.6075	3.6830	0.2950	9.59
50°C50°Brix	90	0.6682	4.8637	0.2217	8.77
50°C50°Brix	180	0.6855	5.1616	0.2015	8.95
50°C50°Brix	270	0.5749	5.2754	0.1985	8.87
50°C50°Brix	330	0.5656	6.6693	0.1855	7.49
50°C34°Brix	180	0.7734	9.2148	0.1591	6.09
50°C34°Brix	270	0.8014	10.1156	0.1434	8.09
40°C60°Brix	30	0.5791	3.9381	0.2833	7.53
40°C60°Brix	90	0.5557	4.3660	0.2644	8.60
40°C60°Brix	180	0.5593	4.3415	0.2502	9.06
40°C60°Brix	270	0.6378	4.7308	0.1924	8.69
40°C40°Brix	30	0.7560	9.6608	0.1785	10.26
40°C40°Brix	90	0.7642	9.7716	0.1692	10.92
40°C40°Brix	180	0.7739	9.3825	0.1601	11.00
40°C40°Brix	270	0.7786	10.3790	0.1515	10.50
40°C40°Brix	330	0.7696	8.5467	0.1539	8.99
34°C50°Brix	180	0.6490	5.9350	0.2287	6.64
34°C50°Brix	270	0.6703	5.9257	0.2054	8.99

8.3.3 Effect of osmotic processing time on adsorption isotherm

The effects of osmotic processing time on the adsorption isotherms of both osmo-air dried apple cylinders at 20°C are shown in Figures 8.3 and 8.4. Longer osmotic dehydrated apple cylinders sorbed more sucrose than those that were osmotic dehydrated for a short period, thus reducing the sorption capacity at the same a_w. The absorbed sucrose might be present in one of several states: crystalline solid, amorphous solid (bound to other food components) and aqueous solution. With less time, the sugar probably went into the amorphous form. In this form, it was very hygroscopic and unstable. The cell structure and the presence of non-sugar fraction in the apple cylinders acted as a support and prevented molecular rearrangement. With more time, the absorbed sugar existed as a crystalline solid inside the sample, which was a more stable state and sorbed very little water until water activity reached approximately 0.8 and the sucrose began to dissolve. Lenart (1991) also found that the longer the osmosis time, the lower the rehydration rate and the longer extended the reconstruction of osmo-convection dried carrots time. Table 8.4 shows that osmotic dehydration time significantly affected osmotic dehydrated-air dried product adsorption isotherms ($P<0.05$). Both MWOD and COD pretreated sample sorption capacity were lower than those of air dried product sorption capacity at lower a_w. At higher a_w however, MWOD pretreated sample equilibrium moisture content was close to air dried sample equilibrium moisture content. While for COD pretreated samples, the equilibrium moisture content was close to or higher than that of air dried sample equilibrium moisture content. This reflected the situation of amorphous sugar changing into an aqueous solution.

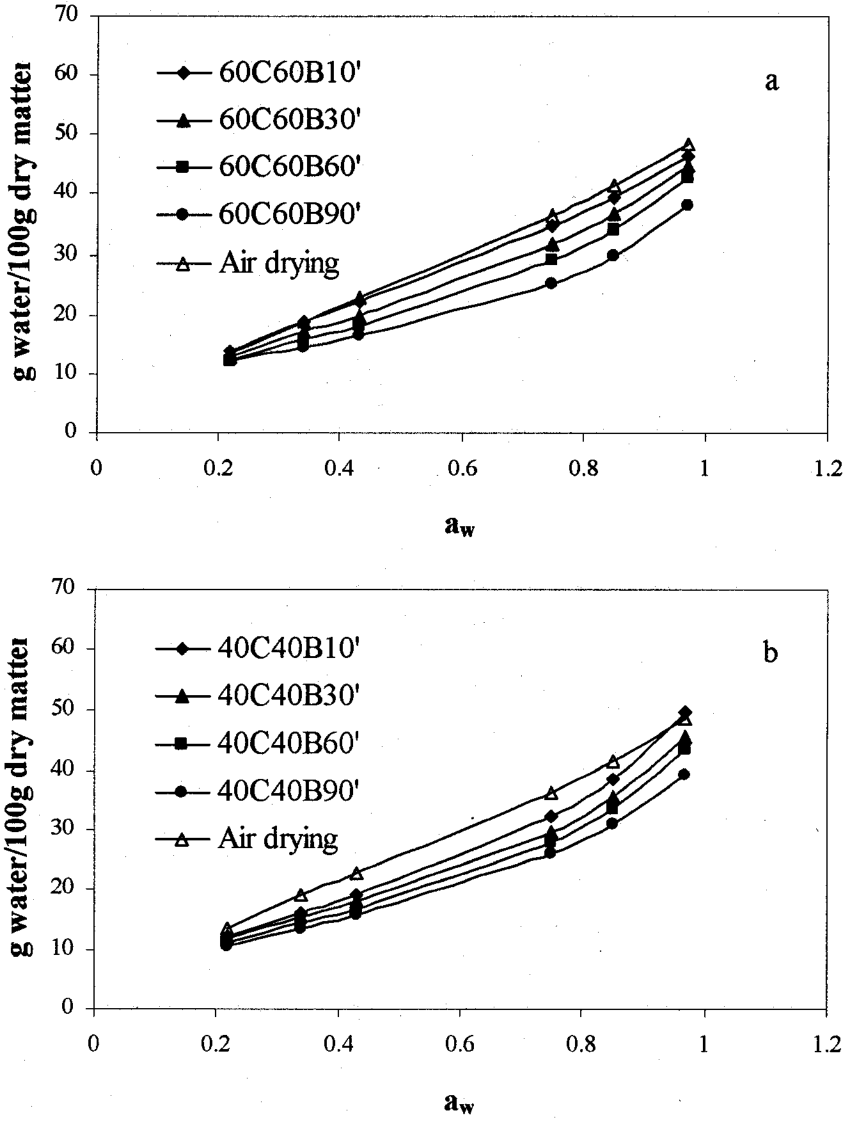


Figure 8.3 Effect of osmotic dehydration time (MWOD) on adsorption isotherms apple cylinders at 20°C. a: 60°C 60°Brix; b: 40°C 40°Brix.

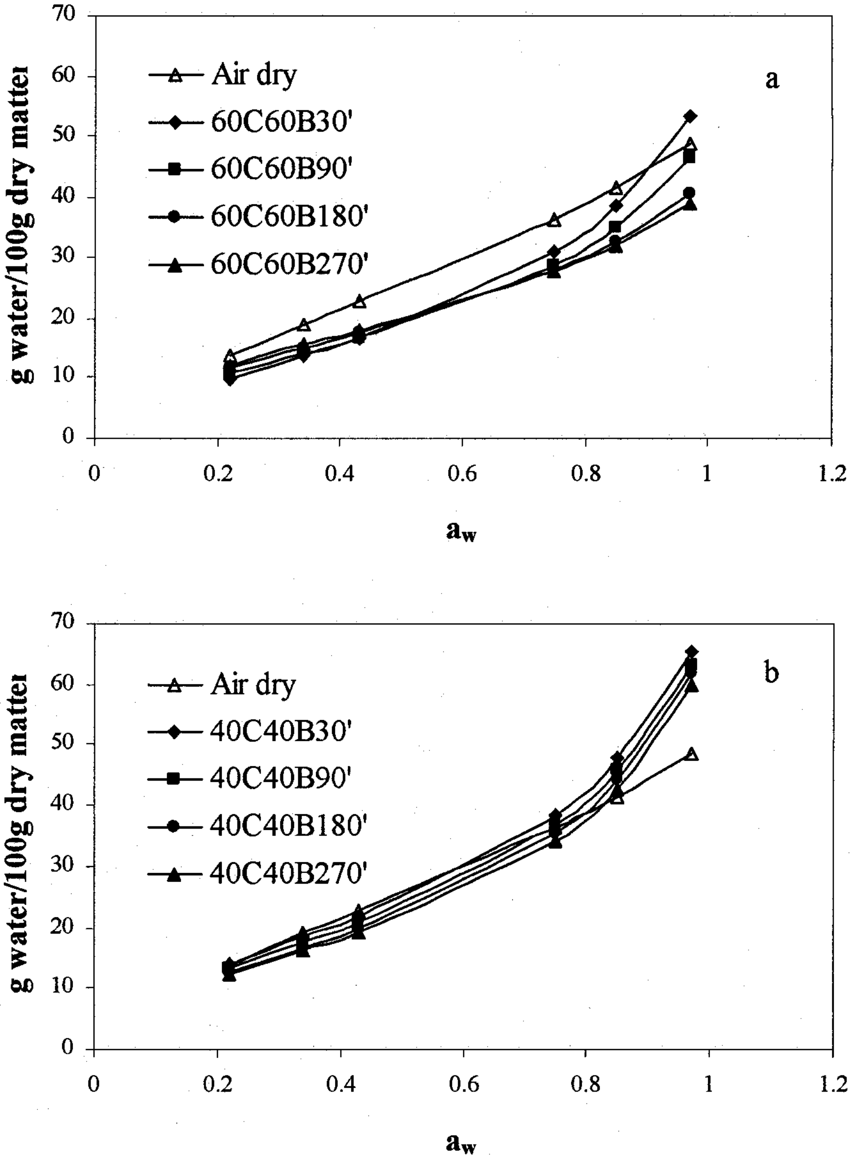
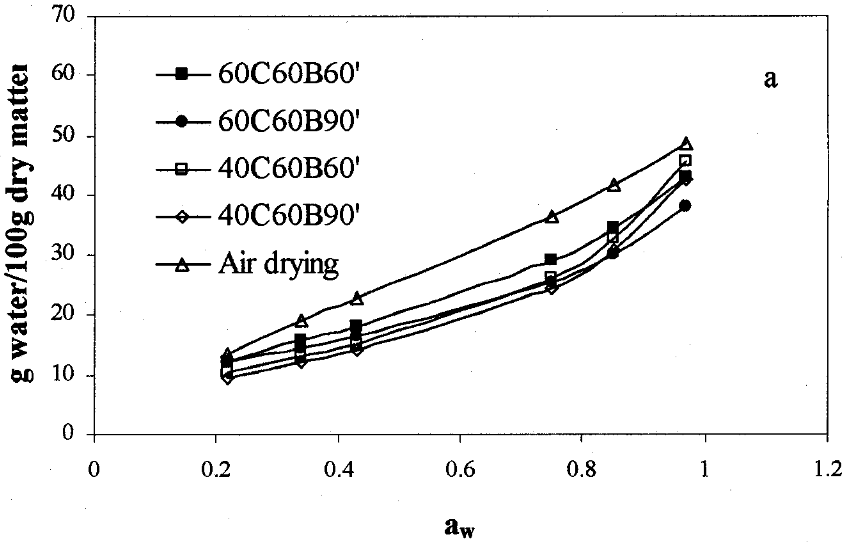


Figure 8.4 Effect of osmotic dehydration time (COD) on adsorption isotherms apple cylinders at 20°C. a: 60°C 60°Brix; b: 40°C 40°Brix.

8.3.4 Effect of osmotic processing temperature on adsorption isotherm

The effects of osmotic processing temperature on the adsorption isotherms of osmo-air dried apple cylinders are shown in Figures 8.5 and 8.6. Equilibrium moisture content was compared with different preconcentration temperatures, except for MWOD, which was pretreated at higher concentration of 60°Brix (Fig. 8.5a) with increasing temperature. Al other treatments decreased the equilibrium moisture content (Figure 8.5b and 8.6). The absorbed sucrose was related to osmotic process temperature, higher temperature accelerated sample sucrose uptake, especially at lower concentration conditions, 40°Brix (Fig 8.5b, Fig 8.6b); whereas at higher concentration process for MWOD, lower temperature benefited sucrose absorption (fig 8.5a). With less absorbed sugar, the sugar probably went into the amorphous form. In this form, it was very hygroscopic and unstable. With more absorbed sucrose, the absorbed sugar existed as crystalline solid inside the sample, a more stable state and sorbed very little water until water activity was high enough and the sucrose began to dissolve. Table 8.4 shows that osmotic dehydration temperature significantly affected conventional osmotic dehydrated-air dried (COD-AD) products adsorption isotherms ($P<0.05$); while not affecting microwave assisted osmotic dehydrated-air dried (MWOD-AD) products adsorption isotherms ($P>0.05$).

It was observed from these sorption isotherms that at low a_w, the higher the pretreated temperature, the lower the sorption capacity of the samples. Both MWOD and COD pretreated sample sorption capacity were lower than that of air dried products sorption capacity at lower a_w. At higher a_w ($a_w>0.75$), however, COD pretreated samples equilibrium moisture content was close to or higher than that of the air dried sample. This also reflects the amorphous sugar changing into an aqueous solution.



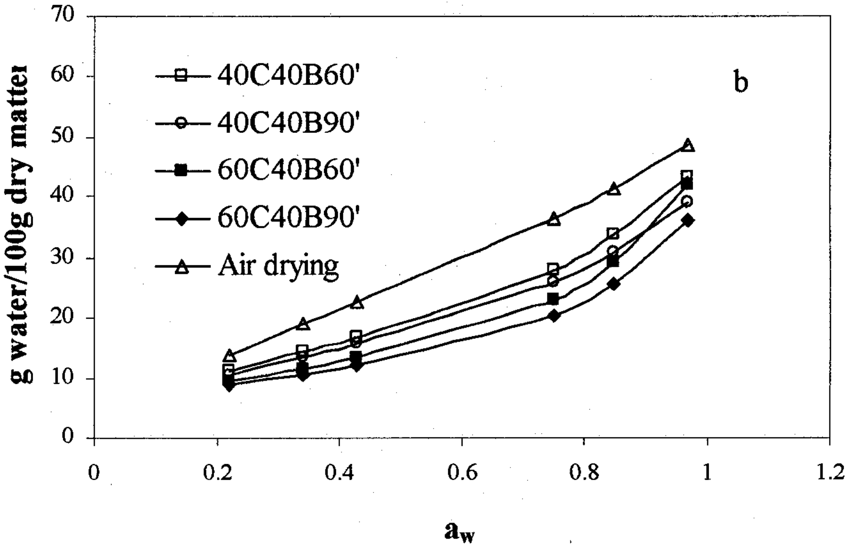
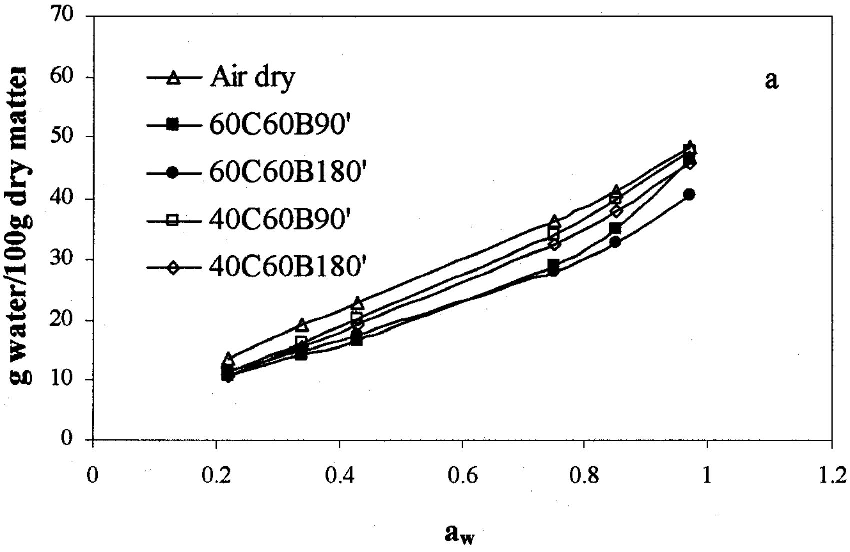


Figure 8.5 Effect of osmotic dehydration (MWOD) temperature on adsorption isotherms apple cylinders at 20°C. a: high concentration 60°Brix; b: low concentration 40°Brix.



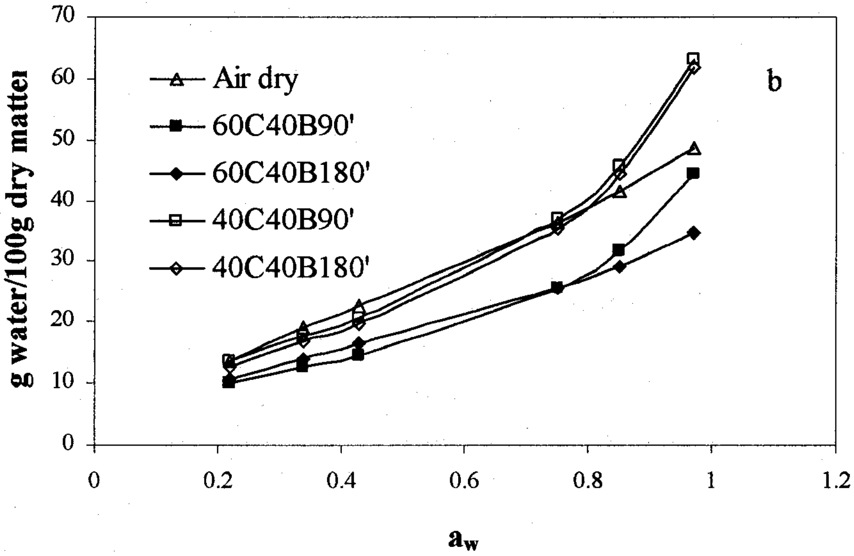


Figure 8.6 Effect of osmotic dehydration (COD) temperature on adsorption isotherms of apple cylinders at 20°C. a: high concentration 60°Brix; b: low concentration 40°Brix.

8.3.5 Effect of osmotic solution concentration on adsorption isotherm

The effects of solution concentrations on equilibrium moisture content are shown in Figure 8.7 and Figure 8.8. For MWOD pretreated at higher temperature 60°C, with an increase in osmotic solution concentration, product equilibrium moisture content was increased (Figure 8.7a). While COD pretreatment osmotic solution concentration effects were not obvious (Figure 8.8). It was observed from these isotherms that at low a_w for different osmotic solution concentrations, both MWOD and COD pretreated sample sorption capacities were lower than that of air dried products sorption capacities. At higher a_w, the equilibrium moisture content of the COD pretreated samples had a trend of closer to (at 60°C, Fig 8.8a; at 40°C 60°Brix, Fig 8.8b) or higher (at 40°C 40°Brix, Fig 8.8b) than that of air dried equilibrium moisture, due to the amorphous sugar changing into a aqueous solution and the crystal sugar dissolution. At the same time, a combination of actions occurred resulting in a sharp increase in adsorptive capacity, as evidenced in experimental isotherms (Figure 8.7 and 8.8). Such actions include solution, new site creation (by swelling), plasticizing and water-water adsorption. Table 8.4 shows that osmotic solution concentration significantly affected MWOD-AD product adsorption isotherms ($P<0.05$); did not affect COD-AD products adsorption isotherms ($P>0.05$).

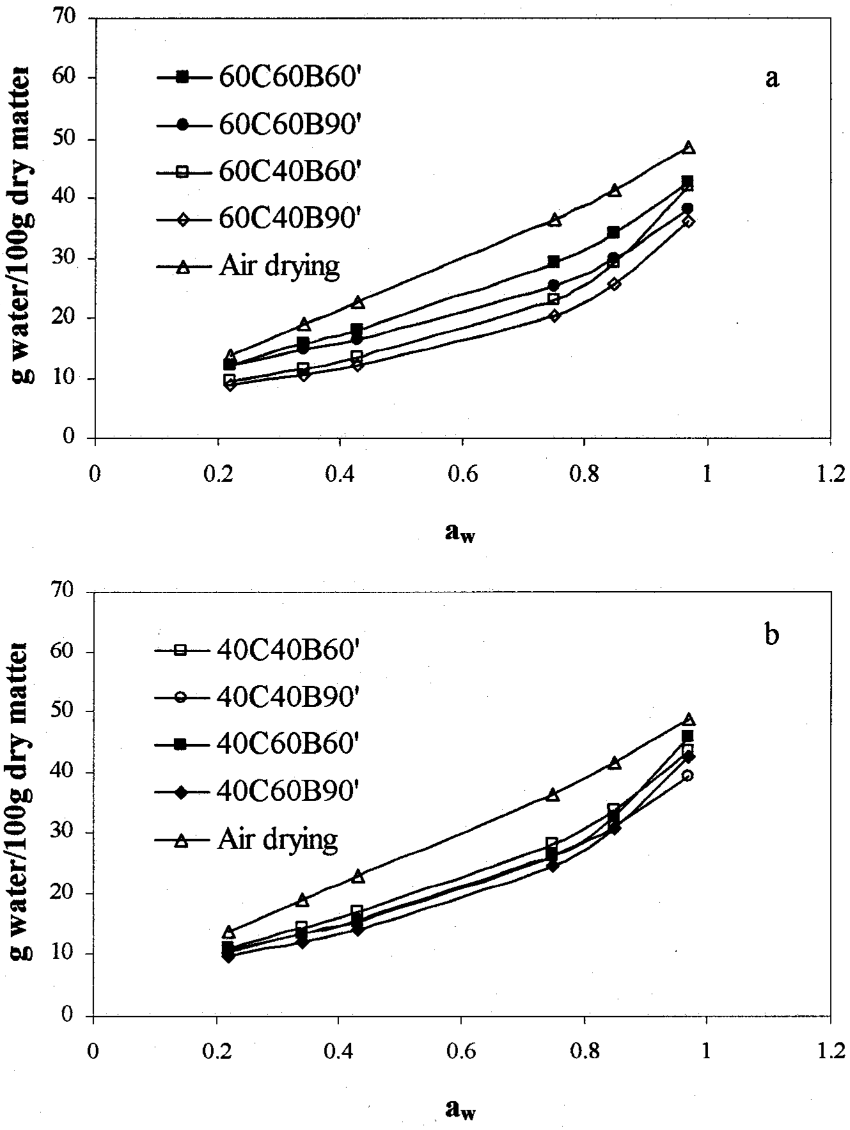


Figure 8.7 Effect of osmotic dehydration (MWOD) concentration on adsorption isotherms apple cylinders at 20°C. a: high temperature 60°C; b: low temperature 40°C.

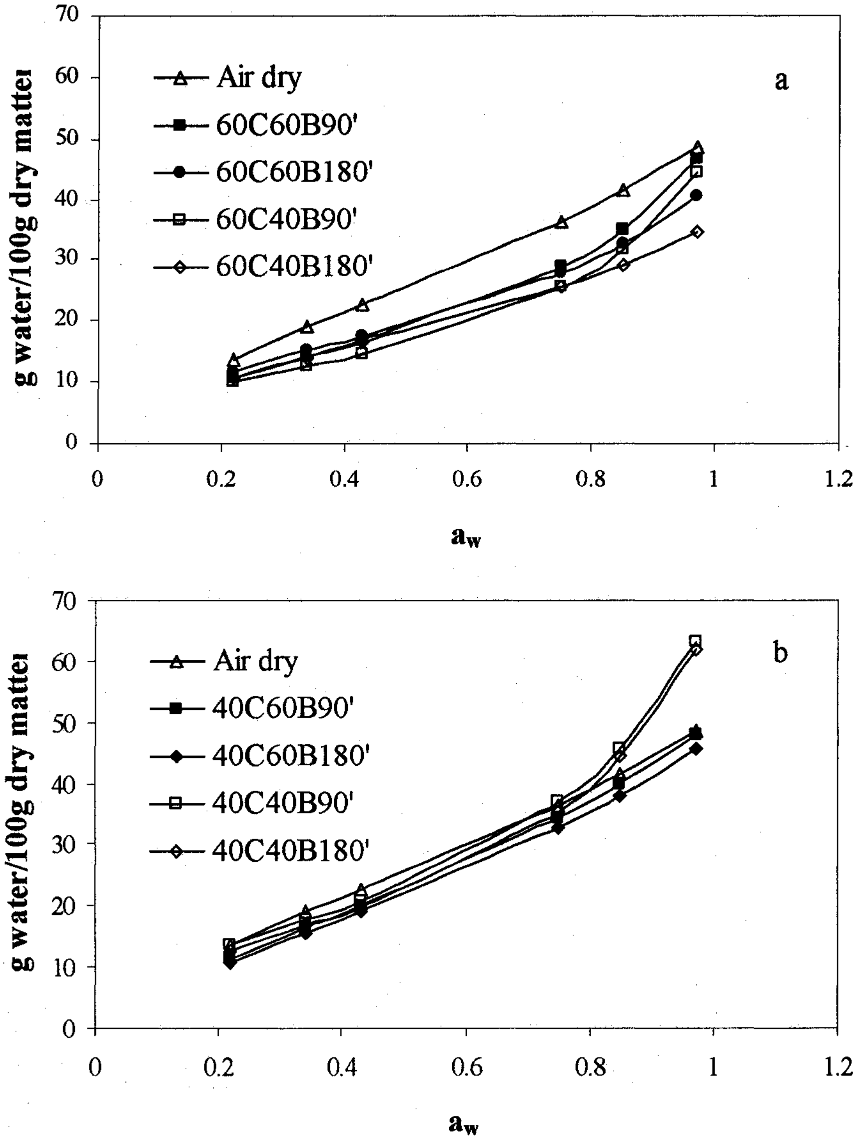


Figure 8.8 Effect of osmotic dehydration (COD) concentration on adsorption isotherms of apple cylinders at 20°C. a: high temperature 60°C; b: low temperature 40°C

8.3.6 Effect of osmotic processing condition variation on monolayer value (M_m)

The monolayer (M_m) value was affected by osmotic processing conditions. Figure 8.9 shows the effect of microwave assisted osmotic dehydration (MWOD) processing effect on product monolayer (M_m) value influences. It was observed that with increased processing time or increased sugar absorption by the sample, the M_m value had a decreasing trend. For higher solution concentration (60°Brix), high temperature (60°C) gave a higher M_m value; for low solution concentration (40°Brix), low temperature (40°C) gave a higher M_m value; at higher temperature (60°C), high solution concentration (60°Brix) had a high M_m value; at low solution temperature (40°C), high solution concentration (60°Brix) had a low M_m value. All these M_m value changes might relate to both the variation in the sucrose amount absorbed by the sample and sample cell structure changes.

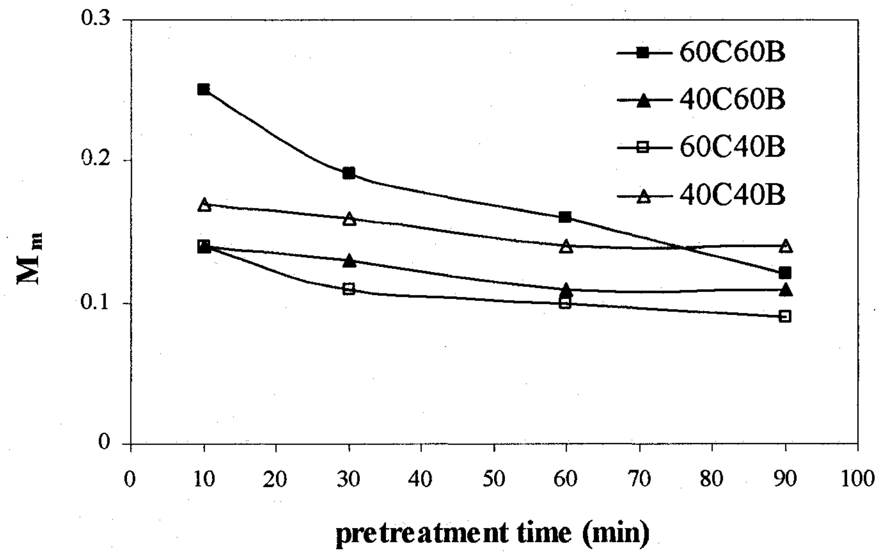


Figure 8.9 Effect of osmotic dehydration (MWOD) variance on adsorption isotherms monolayer value of apple cylinders at 20°C.

Figure 8.10 shows the effect of conventional osmotic dehydration (COD) processing conditions changes on product monolayer (M_m) value influences. It was observed that with increasing processing time or increased sugar absorption by the sample, the M_m value had a decreasing trend. For higher solution concentration (60°Brix), high temperature (60°C) gave a lower M_m value; for low solution concentration (40°Brix), the temperature effect was not obvious except at the first point for 60°C; at higher temperature (60°C), high solution concentration (60°Brix) had a low M_m value; at low solution temperature (40°C), high solution concentration (60°Brix) had a high M_m value. All these M_m value changes might also relate to the amount of sucrose absorbed by the sample and sample cell structure changes. Lararides et al. (1995) reported that following osmotic preconcentration treatments, the monolayer moisture content was decreased compared to that of the control. As a result of sugar composition affecting water sorption isotherms, the monolayer moisture content (M_m) for the air dried samples was higher than that of the osmotic pretreated sample (Krokida et al., 2000).

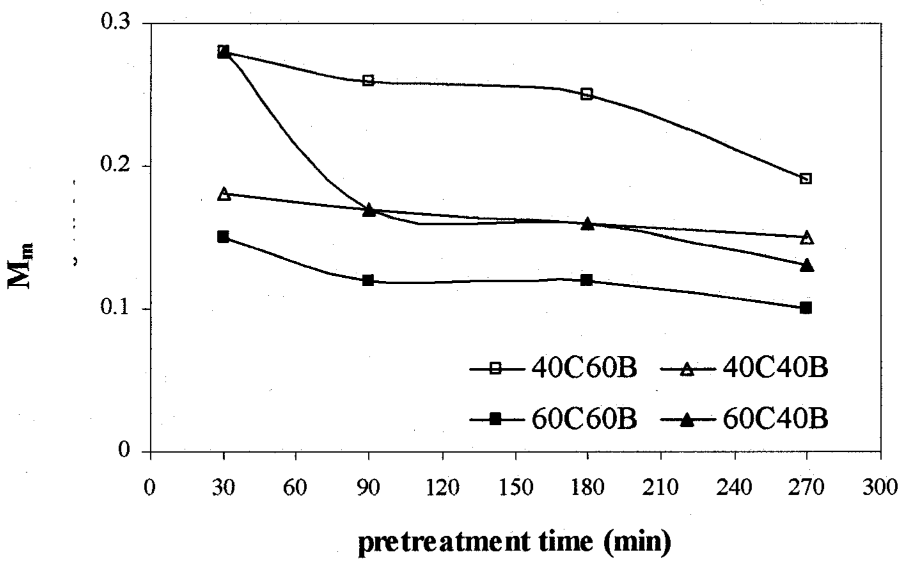


Figure 8.10 Effect of osmotic dehydration (COD) variance on adsorption isotherms monolayer value of apple cylinders at 20°C.

8.3.7 Comparing the difference of the two osmotic processing on adsorption isotherm

Figure 8.11 shows differences between the two osmotic dehydrated pretreatment product adsorption isotherms. At 60°C 60Brix, the difference was not obvious, with prolonged treatment time, both adsorption isotherms had a decreasing trend. At 50°C 50Brix, the overall adsorption isotherms for MWOD-air dried products were lower than the COD-air dried correspondent. At higher a_w, microwave assisted osmotic dehydration (MWOD) pretreated sample equilibrium moisture contents were still lower than that of air dried products equilibrium moisture content; while conventional osmotic dehydration (COD) pretreated sample equilibrium moisture contents were close to or higher than that of air dried products equilibrium moisture content. For MWOD, the absorbed sugar was less compared with the COD process, and the amount of amorphous sugar transferred into the solution during the sorption equilibration was less, thus the equilibrium moisture content was low.

Table 8.4 shows that compared with product adsorption equilibrium moisture content, conventional osmotic-air dried product adsorption isotherms were significantly affected by osmotic dehydration time and osmotic solution concentration ($P<0.05$); while microwave assisted osmotic dehydration-air dried product adsorption isotherms were significantly affected by osmotic dehydration time and osmotic processing temperature ($P<0.05$). The difference of two kinds of sorption isotherms of sucrose- treated samples might be interpreted on the sample cell structure changes difference. During microwave assisted osmotic dehydration, the basic components (protein, starch, cellulose, pectin) and

Table 8.4. Analysis of variance of osmotic dehydration processing conditions change on osmotic dehydrated-air dried products adsorption equilibrium moisture content.

Conditions	COD		MWOD	
	F value	Pr>F	F value	Pr>F
T (min)	3.34	0.0103	4.21	0.0023
C (°C)	5.44	0.0011	0.54	0.6566
B (°B)	1.47	0.2204	2.76	0.0414
Interaction effects				
T*C	0.12	0.9888	0.06	0.9980
T*B	0.08	0.9954	0.02	0.9998
C*B	1.79	0.1814	3.84	0.0506

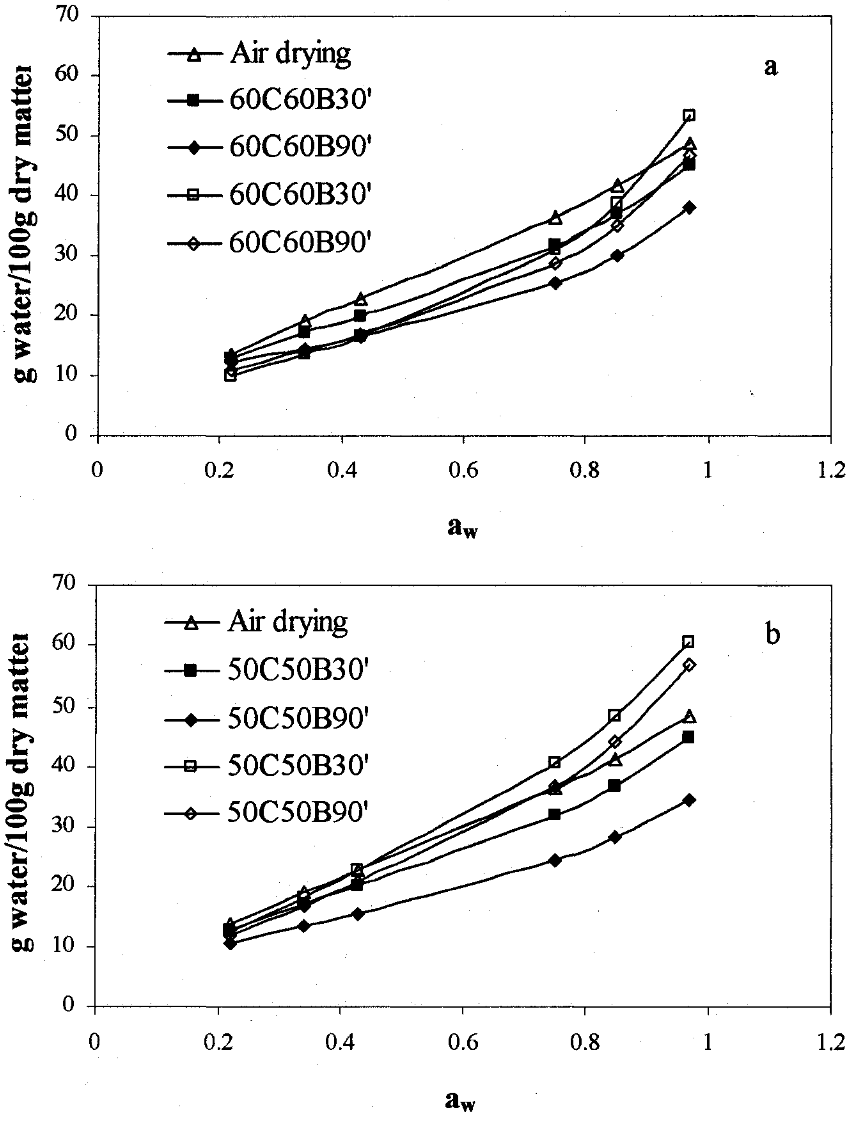


Figure 8.11 Comparison of different osmotic dehydration on adsorption isotherms of apple cylinders at 20°C. a: 60°C 60°Brix; b: 50°C 50°Brix. ■. ♦: MWOD: □. ◊: COD.

soluble solids (sugars, salts, acids) were affected by microwave heating, which may further improve product sorption properties.

8.4 Conclusions

- Isotherms adsorption curves of apple cylinders were affected by the method of drying. Adsorption property of osmo-air dried apple cylinders were affected by variation in solution temperature, concentration and dehydration time. The characteristic shape of isotherms curve of products depended upon the variety and total amount of hygroscopic materials presented in the hydrophilic substances.
- GAB model fitted the isotherms adsorption experimental data properly. Calculated M_m-value was influenced by sorbed sugar content variation, due to the exchange of sugars between products and the osmotic medium. Osmotic-air dried products M_m-value was reduced compared to that of samples treated without osmotic dehydration.
- The physical construction and cell structure of the products affected product sorption behavior and isotherms shape.

CHAPTER 9

GENERAL CONCLUSIONS

The main objective of this study was to develop Microwave Assisted Osmotic Dehydration (MWOD) technique. In order to fulfill MWOD process, related osmotic kinetics study and osmotic treatment effects on products quality influence were investigated. The following research findings were obtained from previous studies:

- The moisture loss (ML) and solids gain (SG) generally increased with increasing treatment time, temperature and concentration of osmotic solution.
- Moisture loss rate (MLR) and sugar gain rate (SGR) were reduced as the process advanced. MLR was always higher than SGR under all experimental conditions. The ratio of ML/SG was an indicator of process efficiency in terms of higher moisture removal relative to solids uptake and depended on the solution concentration and duration of the process.
- Higher process temperature favored faster moisture loss yielding higher ML/SG value; higher sucrose concentrations favored faster moisture loss and slower sugar uptake. Depending on specific process goals one could choose from a range of process conditions to direct treatment towards dewatering, impregnation or a mixed effect.
- Variations in moisture loss rate (MLR) and solids gain rate (SGR), combined with changes in dehydration time (T_w, T_m and T_s) and mass diffusivity (D_m and D_s) could be used for selecting osmotic dehydration conditions.
- At temperature ($T<66^{\circ}C$) and short processing times ($t<30min$), osmosis had a direct effect on dehydration.
- Fick's equation of unsteady state diffusion can be used to calculate the mass diffusion coefficients during osmotic dehydration process under continuous flow conditions.
- A continuous flow osmotic contactor was developed to be an efficient processing equipment in terms of osmotic dehydration apple cylinders. Being a separate

operation unit, the dehydration process and solution management can be done in more efficient way: by removing the suspension, solutes and other compounds from the solution; maintaining the physico-chemical and hygiene characteristics of the concentrated solution individually without interrupting dehydration process involved. This process has potential application in osmotic dehydration with some modifications such as the load and unload the osmosed products before further treatment.

- Effectiveness evaluation functions used in this study can be widely applied to osmotic dehydration system evaluation.
- Microwave heating has been evaluated for first time applied to osmotic dehydration process to improve mass transfer rate during the process. Moisture transfer rates demonstrated to increase and solids gain rate to reduce during microwave assisted osmotic dehydration process.
- Microwave heating has an important effect on water transfer during the osmotic dehydration. Osmotic dehydration under microwave heating made it possible to obtain a higher diffusion rate of water transfer at lower solution temperatures. Application of microwave heating to osmotic dehydration process thus would limit the intake of solid and increase the moisture loss of apple cylinders.
- Moreover, it was shown that some simple models were adequate for comparing MWOD and CFOD processes.
- Osmotic dehydration was defined as a three phase phrases: equilibrium, pseudo-equilibrium and dynamic periods in this study. Pseudo-equilibrium (practical equilibrium) and dynamic period data are necessary for estimating the time of osmotic process, and ultimate mass transport of the solutes and water.
- Higher concentrations increased ML_∞ and decreased SG_∞. Temperature effect on result of water loss at equilibrium was less evident. Azuara-model fitted osmotic dehydration kinetics very well up to equilibration. Equilibrium moisture loss and solid gain could be estimated with Azuara-model combined with relatively long time experiment data. The equilibrium estimated here is the initial equilibrium stage without structural relaxation. The equilibrium ML, SG, ratio of ML/SG

(EDE) and other related information could be used as reference to design osmotic dehydration process and equipment for apple products.

- There might exist two kinds of equilibration: one is liquid equilibration, which is reached around 24 h; the other is solid matrix equilibration, which takes longer time to reach. Solute penetration is not overall just certain depth around 24 h osmosis. Solute penetration is not strictly followed diffusion law.
- Osmotically treated sample moisture diffusivities were lower than that of without pretreatment during subsequent air drying process. The drying characteristics of osmotically pre-concentrated foods are very important in the design, operation and control of industrial dryers.
- The Hunter L-, a-, b- parameters after air drying were more influenced by MWOD pretreatment conditions. The results presented in this work suggest that the change in L- and b-values were larger as compared to a-value, and may contribute significantly to perception of color change. A color profile shifted towards freeze dried product color after MWOD pretreatment.
- Isotherms adsorption curves of apple cylinders were affected by the method of drying. Moisture adsorption property of osmo-air dried apple cylinders were affected by variation in solution temperature, concentration and dehydration time. The characteristic shape of isotherms curve of products depended upon the variety and total amount of hygroscopic materials presented in the hydrophilic substances.
- GAB model fitted the isotherms adsorption experimental data properly. Calculated M_m-value was influenced by sorbed sugar content variation, due to the exchange of sugars between products and the osmotic medium. Osmotically-air dried products M_m-value was reduced compared with that of without osmotic dehydration treatments sample.
- The composition and cell structure of the products affected products sorption behavior and isotherms shape.

RECOMMENDATIONS FOR FUTURE RESEARCH

This research work has demonstrated several important findings. Meanwhile it also showed some areas of interests for future research and development, which could be summarized as follows:

- Microwave assisted osmotic dehydration temperature increasing effect, frequency effect, sample loading effect;
- Osmotic dehydration equilibrium kinetics study, combining with histological anatomy and microscopy analysis techniques;
- Osmotic dehydration process modeling, combining classical physical diffusion model with sample biological material properties;
- Osmotic dehydration solution management, focused on microbiology study inside used osmotic dehydration solution;
- Osmotic dehydration processing effect on subsequent processing step influence: its influence on products sensory quality study, its influence on products shelf life study, etc.

REFERENCES

Ade-Omowaye, B.I.O., Rastogi, N.K., Angersbach, A. and Knorr, D. 2003. Combined effects of pulsed electric field pre-treatment and partial osmotic dehydration on air drying behavior of red bell pepper. Journal of Food Engineering. 60: 89-98.

Akahoshi, R., and Matashige, E. 1990. Drying of sliced potatoes by microwave heating and flowing air. Jap. Soc. For Food Sci. and Techn. 37(8), 581.

Alzamora, S.M. & Chirife, J. 1980. Some factors controlling the kinetics of moisture movement during avocado dehydration. Journal of Food Science. 45:1649-1651.

Avila, I.M.L.B., & Silva, C.L.M. 1999. Modeling kinetics of thermal degradation of color in peach puree. Journal of Food Engineering, 39: 161-166.

Ayranci, E., Ayanci, G., Doğantan, Z. 1990. Moisture sorption isotherms of dried apricot, fig and raisin at 20°C and 36°C. Journal of Food Science. 55: 1591-1593.

Azuara, E., Cortes, R., Garcia, H.S., & Beristain, C.I. 1992. Kinetic model for osmotic dehydration and its relationship with Fick`s second law. International Journal of Food Science and Technology, 27: 409-418.

Azuara, E., Garcia, H.S., Beristain, C.I. 1996. Effect of the centrifugal force on osmotic dehydration of potatoes and apples. Food Research International, 29(2): 195-199.

Bakalis, S.E., Karathanos, V.T., Maroulis, Z.B., Marinos-Kouris, D., Saravacos, G.D., Rudolph, V. (ed). Keey, R.B. Moisture diffusivity in osmotically dehydrated fruits. Drying '94. Proceedings of the 9th International Drying Symposium, Gold Goast, Austrilia. Vol.B: 857-862.

Barreiro, J.A., Milano, M., & Sandoval, A.J. 1997. Kinetics of color change of double concentrated tomato paste during thermal treatment. Journal of Food Engineering. 33: 359-371.

Barat, J.M.E., Chiralt, A. and Fito, P. 1998. Equilibrium in Cellular Food Osmotic Solution Systems as Related to Structure. Journal of Food Science, 63(5): 836-840.

Barat, J.M.E., Chiralt, A. and Fito, P. 1999. Equilibrium in apple tissue in osmotic dehydration: microstructural changes. Drying Technology, 17(7&8) pp125-127.

Bengtsson, N.E. & Risman, P.O. 1971. Dielectric properties of food at 3 GHz as determined by a cavity perturbation technique. II. Measurements on food materials. Journal Microwave Power 6: 107-123.

Beristain, C.I., Azuara, E, Cortés, R. & Garcia, H.S. 1990. Mass transfer during osmotic dehydration of pineapple rings. International Journal of Food Science and Technology. 25:576-582.

Bertolini, D., Cassettari, M. & Salvetti, G. 1983. The dielectric properties of alcohols-water solutions. I. The alcohol rich region. J. Chem. Phys. 78(1): 365-372.

Biswal R.N. and Le Maguer M. 1989. Mass transfer in plant materials in contact with aqueous solutions of ethanol and sodium chloride: Equilibrium data. Journal of Food Engineering. 11: 159-176.

Biswal, R.N., & Bozorgmehr, K. 1991. Equilibrium data for osmotic concentration of potato in NaCl-water soluton. Journal of Food Process Engineering, 14: 237-245.

Biswal, R.N. and Le Maguer, M. 1989. Mass transfer in plant materials in contact with aqueous solutions of ethanol and sodium chloride: Equilibrium data. Journal of Food Processing Engineering, 11: 159-176.

Biswal, R.N., Bozorgmehr, K., Tompkins, F.D. & Liu, X. 1991.Osmotic concentration of green beans prior to freezing. Journal of Food Science. 56: 1008-12.

Biswal R.N. and Bozoorgmehr K.1992. Mass transfer in mixed solute osmotic dehydration of apple rings, Transactions of the ASEA. 35: (1): 257-262.

Box, G.E.P., Hunter, W.G. and Hunter, J.S. 1978. Statistics for Experiments. An Introduction to Design Data Analysis and Model Building , John Wiley and Sons, NY.

Buffler, C.R. & Stanford, M.A. 1991. Effects of dielectric and thermal properties on the microwave heating of foods. Microwave World 12(4): 15-23.

Buffler, C.R. 1993. Microwave Cooking and Processing. Van Nostrand Reinhold. New York.

Calay, R.K., Newborough, M., Probert, D. & Calay, P.S. 1995. Predictive equations for the dielectric properties of foods. Intl. J. Food Sci. Technol. 29(6): 699-713.

Clydesdale, F.M.1991. Color perception and food quality. Journal of Food Quality. 14:61

Clydesdale, F.M.1993.Color as a Factor in Food Choice. Critical Review in Food Science and Nutrition 33 (1): 83-101.

Conway, J.M., Castaigne, F., Picard, G., & Voxan, X. 1983. Mass transfer considerations in the osmotic dehydration of apples. Canadian Institute of Food Science and Technology, 16: 25-29.

Crank, J. 1975. Mathematics of diffusion. 2nd Ed. Clarendon Press. Oxford. P24-25.77.

Datta, A.K., Sun, E. & Solis, A. 1995. Food dielectric property data and their compositionbased prediction. p. 457-494. In: *Engineering properties of foods*. 2nd Ed. Eds. Rao, M.A. & Rizvi, S.S.H. Marcel Dekker, Inc. New York.

Decareu, R. and Perterson, R. 1986. Microwave processing and engineering. Chichester, England: Ellis Horwood.

Decareau R.V. 1985. Microwaves in the food processing industry. Academic press, Inc.

Decareau, R.V. 1975. Developing food products for the microwave oven market. Microwave Energy Appl. Newslett. 8(1): 3-5, 14.

Del Valle, F.R., & Nickerson, J.T.R. 1967. Studies on salting and drying fish. Journal of Food Science, 32: 173-179.

Dibben D.2002. Electromagnetics: Fundamental Aspects and Numerical Modeling. Handbook of Microwave Technology for Food Applications. Marcel Dekker, Inc.

Drouzas, A.E.& Schubert, H. 1996. Microwave application in vacuum drying of fruits. Journal of Food Engineering, 28:203-209.

Ertekin, F K and Cakaloz, T 1996, Osmotic dehydration of peas: I. Influence of process variables on mass transfer. Journal of Food Processing and Preservation, 20: 87-104.

Ertekin, F.K. and Cakaloz, T. 1996. Osmotic dehydration of peas II. Influence of osmosis on drying behavior and product quality. Journal of Food Processing and Preservation. 20: 105-119.

Falade K.O., Adetunji, A.I. and Aworh, O.C. 2003. Adsorption isotherm and heat of sorption of fresh and osmo-oven dried plantain slices. Eur. Food Res. Technol. 217: 230-234.

Farkas D.F. and Lazar M.E. 1969. Osmotic dehydration of apple pieces: effect of temperature and syrup concentration rates. Food Technology. 23: 688-690.

Favetto, G., Chirife, J. and Bartholomai, G.B. 1981 A study of water activity lowering in meat during immersion cooking in sodium chloride-glycerol solutions. I Equilibrium considerations and diffusional analysis of solute uptake. Journal. Food. Technology. 16:609-619.

Figen, K.E. Mustafa, S. 2000. Modeling of mass transfer during osmotic dehydration of apples. Journal of Food Engineering. 46:243-250.

Fito, P. 1994. Modeling of vacuum osmotic dehydration of food. Journal of Food Engineering, 22:313-328.

Fito, P., Chiralt, A., Barat, J., Salvatori, J.D. and Andrés. 1998. Some advances in osmotic dehydration of fruit. Food Science and Technology Internaitonal. 4(5): 329-338.

Fito, P. and Chiralt, A. 1996. Osmotic dehydration. An approach of the modeling of solid food-liquid operations In: Fito P., Ortega-Rodríguez E, Barbosa-Cánovas G.V. (eds), Food Engineering 2000, New York: Chapman and Hall. pp.231-252.

Flink, J.M. 1980. Dehydrated carrot slice: Influence of osmotic concentration on drying behavior on product quality. Food Process Engineering. 1:412-418.

Frank, R.A. and Archambo, G. 1986. Intensity and hedonic judgments of taste mixtures: carbohydrates. Journal Agricultural Food Chemistry. 18(2): 295-297.

Frédéric P., Lilia M.A., Tomas, F., Siw, K., Maud, L. and Ingegerd S. 2001. Effects of combined osmotic and microwave dehydration of apple on texture, microstructure and rehydration characteristics. Lebensm.-Wiss.u.-Technol. 34: 95-101.

Funebo T., and Ohlsson T. 1998. Microwave assisted air dehydration of apple and mushroom. J. of Food Eng. 38: 353-367.

Genina-Soto P.Barrera-Cortes J., Gutierrez-Lopez G., and Nieto E.A. 2001. Temperature and concentration effects of osmotic media on OD profiles of sweet potato cubes. Drying Technology. 19 (3&4): 547-558.

Giangiacomo, R., Torreggiani, D., & Abbo, E. 1987. Osmotic dehydration of fruit. Part I: Sugar exchange between fruit and extracting syrup. Journal of Food Processing and Preservation. 11: 183-195.

Goodshall, M.A. 1990. Use of sucrose as a sweetener of foods. Cereal Foods World. 35(4): 384-389.

Grabowski, S., Mujumdar, A.S., Ramaswamy, H.S. Strumillo, C. 1994. Osmo-convective drying of grapes. Drying Technology. 12(5): 1211-1219.

Gros, J.B., Dussap, C.G. 2003. Estimation of equilibrium properties in formulation or processing of liquid foods. Food Chemistry. 82: 41-49.

Guerrero, S., Campos, C.A., & Alzamora, S. 2002. Development of shelf stable seaweed by a hurdle processing. Food Science and Technology International. 8: 95-99.

Hawkes, J., & Flink, J.M. 1978. Osmotic concentration of fruit slices prior to freeze dehydration. Journal of Food Processing and Preservation, 2: 265-284.

Hough, G., Chirife, J., & Marini, C.A. 1993. A simple model for osmotic dehydration of apples. Lebensmittel Wissenschaft und Technologie, 26: 151-156.

Hoppe, K. 1981. The taste interactions of citric acid with sucrose and sweeteners. Die Nahrung. 25(3): K1-K4.

Hughes, R.E. Chichester, C.O., and Sterling, C. 1958. Penetration of maltosaccarides in processed Clingstone peaches. Food Technology, 12: 111-115.

Islam M.N. and Flink J.N. 1982. Dehydration of potato 2: Osmotic concentration and its effect on air drying behavior. Journal of Food Technology. 17: 387-403.

Ibarz, A., Pagan, J., & Garza, S. 1999. Kinetic models for color changes in pear puree during heating at relatively high temperatures. Journal of Food Engineering, 39: 415-422.

Jason, A.C. & Peters, GR. 1973. Analysis of bimodal diffusion of water in fish muscle. Journal of Physics D: Applied Physics. 6: 512-521.

Jen, J.J. Mudahar, G.S., and Toledo, R.T. 1989. Chemistry and Processing of high-quality dehydrated vegetable products. In: Quality Factors of Fruits and Vegetables. Pp.239-249.

Karathanos, V.T., Kostaropoulos, A.E. and Saravacos, G.D. 1995. Air-drying kinetics of osmotically dehydrated fruits. Drying Technology. 13(5-7): 1503-1521.

Kaymak-Ertekin, F., Sultanoglu, M. 2000. Modeling of mass transfer during osmotic dehydration of apples. Journal of Food Engineering, 46: 243-250.

Kent, M. 1987. Electrical and Dielectric Properties of Food Materials. A Bibliography and Tabulated Data. A COST 90bis production. Science and Technology Publishers. Hornchurch.

Kerkhof, P.J.A.M. 2001. Drying, growth towards a unit operation. Drying Technology. 19(8): 1505-1541.

Kim, M.A. & Toledo, R.T. 1987. Effect of osmotic dehydration and high temperature fluidized bed drying on properties of dehydrated rabbiteye blueberries. Journal of Food Science. 52: 980-989.

Kowalska H., Lenart A. 2001. Mass exchange during osmotic pretreatment of vegetables. Journal of Food Engineering, 49: 137-140.

Krokida, M.K., Karathanos, V.T. and Maroulis, Z.B. 2000. Effect of osmotic dehydration on color and sorption characteristics of apple and banana. Drying Technology. 18(4&5): 937-950

Labuza, T.P. and Hyman, C.R. 1998. Moisture migration and control in multi-domain foods. Trends in Food Science & Technology. 9: 47-55.

Labuza, T.P. 1984. Moisture sorption: practical aspects of isotherm measurement and use. The American Association of Cereal Chemists. 3440 Pilot Knob Road. St. Paul, Minnesota 55121, USA.

Lazarides, H.N., Nickolaidis, A., and Katsanidis, E. 1995. Sorption changes induced by osmotic preconcentration of apple slices in different osmotic media. Journal of Food Science. 60 (2): 348-350, 359.

Lazarides, H.N. Katsanidis, E. & Nickolaidis, A. 1995. Mass transfer kinetics during osmotic preconcentration aiming at minimal solid uptake. Journal of Food Engineering. 25: 151-166.

Lazarides, H.N. and Mavroudis, N.E. 1995. Freeze/Thaw effects on mass transfer rates during osmotic dehydration. Journal of Food Science, 60(4): 826-828, 857.

Lazarides, N.H. and Maroudis, N.E. 1996. Kinetics of osmotic dehydration of a highly shrinking vegetable tissue in a salt-free medium. Journal of Food Engineering. 30: 61-74.

Lee, H.S., Coates, G.A. 1999. Thermal pasteurization effects on color of red grapefruit juices. Journal of Food Science, 64: 344-347.

Le Maguer, M. 1988. Osmotic dehydration: Review and future directions. In Proc. Sym. on Progress in Food Preservation Processes, Brussels, 1:283-309.

Le Maguer, M.1996. Mass transfer modeling in structure foods. Ch. 14 in Food Engineering 2000.Fito P., Ortega-Rodriguez E and Barbosa-Cánovas (Ed). P.253-270. Chapman and Hall, New York.

Lenart A. and Lewicki P.P. 1989. Osmotic dehydration of apple at high temperature. In Drying' 89. A.S. Mujundar and M. Roques (Ed.). p501-508. Hemisphere Publ. Corp., New York.

Lenart, A. 1991. Effect of saccharose on water sorption and rehydration of dried carrot. In Drying'91. A.S. Mujumdar and I.Filkova (Ed.), p.489. Elsevier Science Publ., Amsterdam

Lenart, A., & Flink, J.M. 1984. Osmotic concentration of potato: I. Criteria for end point of the osmotic process. Journal of Food Technology, 19: 45-63.

Lenart, A. & Flink, J.M. 1984. Osmotic concentration of patato: II Saptial distribution of osmotic effect. Journal of Food Technology, 19:65-89.

Lerici C.R., Pinnavaia G., Dalla Rosa M. and Bartolucci L. 1985. Osmotic dehydration of fruit: influence of osmotic agents on drying behaviour and product quality. Journal of Food Science. 50: 1217-1219/1226.

Lewicki, P.P., Le H.V.and Pomarańska-Łazuka, W. 2002. Effect of pre-treatment on convective drying of tomatoes. Journal of Food Engineering. 54: 141-146.

Li, H., Ramaswamy, H.S. 2003. Continuous flow microwave-osmotic combination drying of apple slices. IFT Annual Meeting. 58-4: 141.

Magee, T.R.A., Hassabllah, A. A., & Murphy, W.R. 1983. Internal mass transfer during osmotic dehydration of apple slices in sugar solutions. International Journal of Food Science and Technology, 1: 177-178.

Marcotte, M. 1988. Mass Transport Phenomena in Osmotic Processes. M. Sc. Thesis. University of Alberta.

Marcotte, M., Toupin C.J. and Le Maguer M. 1991. Mass transfer in cellular tissues. Part I: the mathematical model. Journal of Food Engineering. 13: 199-220.Metaxas A.C. and Marouzé, C., Giroux, F., Colligna, A. and Rivier, M. 2001. Equipment design for osmotic treatments. Journal of Food Engineering. 49:207-221.

Marousis, S.N., Karathanos, V.T. and Saravacos, G.D. 1989. Effect of sugars on the water diffusivity in hydrated granular starches. Journal of Food Science. 54: 1496-1500.

Maskan, M. 2001. Kinetics of color change of kiwifruits during hot air and microwave drying. Journal of Food Engineering, 48. 169-175.

Masalve-Gonzalez, A., Barbosa-Ganavos, G.V., & Cavalieri, R.P. 1993, Mass transfer and texture changes during processing of apple by combined methods. Journal of Food Science, 58(5): 1118-1124.

Mathlouthi, M., Reiser, P. 1996. Sucrose properties and applications. 1st Edition. Blackie Academic and Professional. Chapman and Hall, Glasgow, U.K.

Mauro, M.A. and Menegalli, F.C. 1995. Evaluation of diffusion coefficients in osmotic dehydration of bananas (Musa Cavendish Lambert). International Journal Food Science and Technology. 30: 199-213.

Mazza, G. 1983. Dehydration of carrots: Effects of pre-drying treatments on moisture transport and product quality. Journal Food. Technology. 18: 113-123.

McCable, W.L., Smith, J.C., & Harriot, P. 1993. Unit operations in chemical engineering (5th ed. P.301). New York: McGraw-Hill Inc.

McEvily, A.J., Iyengar R. and Otwell W.S. 1992. Inhibition of enzymatic browning in foods and beverages. Critical Reviews in Food Science and Nutrition. 32(3): 253-273.

McMinn, W.A.M. and Magee, T.R.A. 1999. Studies on the effect of surfactant, blanching and osmotic pretreatments on the convective drying of potatoes. Journal of Food Process Engineering. 22: 419-433.

Mead R. & Curnow R.N. 1983. Statistical Methods in Agriculture and Experimental Biology. Chapman and Hall Ltd, New York. USA. P85.

Meredith R.J. Industrial Microwave Heating. Number 4 in IEE Power Engineering Series. Peter Peregrinus Ltd. London, 1983.

Mudgett, R.E. 1995. Electrical properties of foods. p. 389-455. In: Engineering properties of foods. 2 nd Ed. Eds. Rao, M.A. & Rizvi, S.S.H. Marcel Dekker, Inc. New York.

Mujumdar A.S. 2000. Moisture diffusivity in foods-an overview. In: Drying Technology in Agriculture and Food Science. Science Publishers, Inc.

Nieto, A. Salvatori, D., Castro, M.A. & Alzamora. 1998. Air drying behavior of apples as affected by blanching and glucose impregnation. Journal of Food Engineering. 36: 63-79.

Nieuwenhuijzen, N., M.R. Zareifard and H.S. Ramaswamy. 2001 Osmotic drying kinetics of cylindrical apple slices of different sizes. Drying Technology Journal. 19(3-4):525-545.

Nyfors, E. & Vainikainen, P. 1989. Industrial Microwave Sensors. Chapter 2. Artech House.

Nsonzi F. and Ramaswamy H.S. 1998. Osmotic dehydration kinetics of blueberries. Drying Technology. 16 (3-5): 725-741.

Nobel, S.P., 1970. Plant cell physiology. A physicochemical approach. W.H. Freemand and company. U.S.A.

Ohlsson, T. 1989. Dielectric properties and microwave processing. p. 73-92. In: *Food Properties and Computer-aided Engineering of Food Processing Systems*. Eds. Singh, R.P. & Medina, A.G. Kluwer Academic Publishers.

Ohlsson, T., Bengtsson, N.E. & Risman, P.O. 1974. The frequency and temperature dependence of dielectric food data as determined by a cavity perturbation technique. J. Microwave Power 9: 129-145.

Owusu-Ansah, Y.J. 1991. Advances in microwave drying of foods and food ingredients. J. Inst. Can. Sci. Technol. Aliment. 24 (3/4): 102-107.

Parjoko, Rahman, M.S., Buckle, K.A., & Perera, C.O. 1996. Osmotic dehydration kinetics of pineapple wedges using palm sugar. Lebensmittel Wissenschaft und Technologie, 27: 564-567.

Ponting J.D., Walters G.G., Forrey, R.R., Jackson R., & Stanley W.L. 1966. Osmotic dehydration of fruits. Food Technology, 20: 125-128.

Ponting, J.D. 1973. Osmotic dehydration of fruits-recent modifications and applications. Process Biochemistry. 8(12): 18-20

Perry, R.H. 1984. Diffusion coefficients. Perry's Chemical engineer's handbook. McGraw-Hill chemical engineering series.3-285-287.

Qi, H., Le Magure, M. and Sharma, S.K. 1998. Design and selection of processing conditions of a pilot scale contactor for continuous osmotic dehydration of carrots. Journal of Food Process Engineering. 21: 75-88.

Rahman, M.S. and Lamb, J. 1990. Osmotic dehydration of pineapple. Journal of Food Science and Technology, 27:150-152.

Rahman, M.S. and Lamb, J. 1991. Air drying behavior of fresh and osmotically dehydrated pineapple. Journal of Food Process Engineering. 14: 163-171.

Rahman, M.S. 1992, Osmotic dehydration kinetics of foods. Indian Food Industry, 15: 20-24.

Rahman, M.S. 1995. Sorption isotherms. In Food Properties Handbook. Ed by Rahman, S. CRC Press, Inc. p:23-53.

Rahman, M.S., Sablani, S.S. and Al-Ibrahim, M.A. 2001. Osmotic dehydration of potato: equilibrium kinetics. Drying Technology. 19(6): 1163-1176.

Ramaswamy, H.S. and van de Voort, F.R. 1990. Microwave application in food processing. CIFST J. 23(1):17.

Ramaswamy H.S. and N.H. van Nieuwenhuijzen. 2002. Evaluation and Modeling of Two-Stage Osmo-Convective Drying of Apple Slices. Drying Technology. 20(3): 651-667.

Ramaswamy, H.S. Lo, K.V. and Tung, M.A. 1982. Simplified equations to predict unsteady temperature in regular conductive solids. Journal of Food Science. 47: 2042-2047, 2065.

Ramaswamy, H.S.and Li, H. 2003. Osmotic dehydration kinetics of apple cylinders under continuous flow conventional and microwave heating conditions. AIChE Annual Meeting. 111C:124.

Raoult-Wack, A.L., Lafont, F., Rios, G. & Guibert, S.1989 Osmotic dehydration: study of mass transfer in terms of engineering properties. In Drying' 89. A.S. Mujundar and M. Roques (Ed.). Hemisphere Publ. Corp., New York. p487-495

Raoult-Wack A.L., Guilbert S., Le Maguer M. & Rios G. 1991. Simultaneous water and solute transport in shrinking media-Part 1: application to dewatering and impregnation soaking process analysis (osmosis dehydration). Drying Technology. 9: 589-612.

Raoult-Walk, A.L. 1994. Recent advances in the osmotic dehydration of foods, Trends in Food Science and Technology, 5:255-260.

Raoult-Walk, A.L., Lenart, A. and Guilbert, S. 1992. Recent advances in dewatering through immersion in concentrated solutions, in: Drying of Solids, Mujumder, A.S., International Science Publisher, New York.

Rastogi N.K., & Raghavarao K.S.M.S. 1994. Effect of temperature and concentration on osmotic dehydration of coconut. Lebensmittel Wissenschaft und Technologie, 27: 564-567.

Rastogi, N.K., & Raghavarao, K.S.M.S. 1994. Effect of temperature and concentration on osmotic dehydration of coconut. Lebensmittel Wissenschaft und Technologie, 29: 669-672.

Rastogi, N.K., & Raghavarao, K.S.M.S. 1995. Kinetics of osmotic dehydration of coconut. Journal of Food Processing Engineering. 18: 187-197.

Rastogi, N.K., & Raghavarao, K.S.M.S. 1996. Kinetics of osmotic dehydration under vacuum. Lebensmittel-Wissenchaft-Technolotie, 29: 669-672.

Rastogi N K & K S M S Raghavrao. 1997. Water and solute diffusion coefficients of carrot as a function of temperature and concentration during osmotic dehydration. Journal of Food Engineering. 34: 429-440.

Rastogi, N.K., & Niranjan, K. 1998. Enhanced mass transfer during osmotic dehydration of high-pressure-treated pineapple. Journal of Food Science, 63(3): 508-511.

Rastogi N.K., Eshtiaghi M.N., & Knorr D. 1999. Accelerated mass transfer during osmotic dehydration of high intensity electrical field pulse pretreated carrots. Journal of Food Science, 64(6): 1020-1023.

Rastogi, N.K., Angersbach, A. and Knorr, D. 2000. Synergistic effect of high hydrostatic pressure pretreatment and osmotic stress on mass transfer during osmotic dehydration. Journal of Food Engineering. 45: 25-31.

Rastogi, N.K., Raghavarao, K.S.M.S., Niranjan, K. and Knorr, D. 2002. Recent developments in osmotic dehydration: methods to enhance mass transfer. Trends in Food Science & Technology. 13: 48-59.

Risman, P.O. 1988. Microwave properties of water in the temperature range +3 to +140 °C. Electromagnetic Energy Reviews 1: 3-5.

Risman, P.O. 1991a. Terminology and notation of microwave power and electromagnetic energy. J. Microwave Power and Electromagnetic Energy 26: 243-250.

Risman, P.O. 1994. Confined modes between a lossy slab and a metal plane as determined by a waveguide trough model. J. Microwave Power and Electromagnetic Energy 29: 161-170.

Rodriguez, T.V. Rojas A.M., Campos, C.A. and Gerschenson, L.N. 2003. Effect of osmotic dehydration on the quality of air-dried *Porphyra.* Lebensm.-Wiss.U.-Technol. 36: 415-422.

Ryynänen, S. 1995. The electromagnetic properties of food materials: a review of the basic principles. J. Food Eng. 26: 409-429.

Ryynänen, S. 2002. Microwave heating uniformity of multicomponent prepared foods. EKT series 1260. University of Helsinki, Department of Food Technology. 86p. (Dissertation)

Sablani, S.S., Rahman, M.S., Al-Sadeiri, D.S. 2002. Equilibrium distribution data for osmotic drying of apple cubes. Journal of Food Engineering, 52:193-199.

Sablani, S.S., Rahman, M.S. 2003. Effect of syrup concentration, temperature and sample geometry on equilibrium distribution coefficients during osmotic dehydration of mango. Food Research International. 36:65-71.

Saltmarch M., Labuza T.P. 1980. Journal of .Food Science. 45:1231.

Salvatori, D., Andrés, A., A., Albors, A., Chiralt, A. and Fito, P. 1998. Structure and compositional profiles in osmotically dehydrated apple, Journal of Food Science, 63:606-610.

Salvatori, D., Andrés, A., Chiralt, A. and Fito, P. 1999. Osmotic dehydration progression in apple tissue 1: spatial distribution of solutes and moisture content, Journal of Food Engineering , 42:125-132.

Samaniego-Esguerrra, C.M., Boag, I.F. & Robertson, G.L. 1991. Comparison of regression methods for fitting the GAB model to the moisture isotherm of some dried fruit and vegetables. Journal of Food Engineering. 13: 115-133.

Sankat, C.K., Castaigne, F. & Maharaj, R.1996. The air drying behavior of fresh and osmotically dehydrated banana slices. International Journal of Food Science and Technology. 31: 123-135.

Saravacos, G.D., Tsiourvas, D.A., Tsami, E. 1986. Effect of temperature on the water adsorption isotherms of sultana raisins. Journal of Food Science. 51(2): 381-383.

Saurel R., Raoult-Wack A., Rios G. & Guilbert S. 1994. Mass transfer phenomena during osmotic dehydration of apple I. Fresh plant tissue. 1994. International of Journal of Food Science and Technology. 29: 531-542.

Schiffmann, R.F. 2002. Chapter 9: Microwave processes for the food industry. Handbook of Microwave Technology for Food Applications. Marcel Dekker, Inc.

Schiffmann, R.F. 1987. Chapter 10: Microwave and dielectric drying. Handbook of Industrial Drying. Marcel Dekker, Inc.

Shi, X.Q. and Maupoey, P.F. 1993. Vacuum osmotic dehydration of fruits. Drying Technology. 11(6): 1429-1442.

Shi, X.Q., Fito, P. & Chiralt, A. 1995. Influence of vacuum treatment on mass transfer during osmotic dehydration of fruits. Food Research International, 28(5): 445-454.

Simal, S., Benedito, J., Sánchez, E. & Rosselló, C. 1998. Use of ultrasound to increase mass transfer rates during osmotic dehydration. Journal of Food Engineering, 36: 323-336.

Smith, D.S., Mannheim, C.H., and Gilbert, S.G. 1981. Water sorption isotherms of sucrose and glucose by inverse gas chromatography. Journal of Food Science. 46: 1051-1053.

Spies, W.E.L. and Wolf, W.R. 1983. The results of the COST 90 project on water activity. In Physical Properties of Foods. Jowitt et al. (Ed.) p. 65. Applied Science Publishers, London.

Stuchly, M.A. & Stuchly, S.S. 1980. Dielectric properties of biological substances - tabulated. J. Microwave Power 15: 19-25.

Taiwo, K.A., Angersbach, A. and Knorr, D.2003. Effects of pulsed electric field on quality factors and mass transfer during osmotic dehydration of apples. Journal of Food Process Engineering. 26:31-48.

Tedjo, W, Taiwo, K.A., Eshtiaghi, M.N., & Knorr, D. 2002. Comparison of pretreatment methods on water and solid diffusion kinetics of osmotically dehydrated mangos. Journal of Food Engineering, 53(2): 133-142.

Thuery, J. 1992. *Microwaves: Industrial, Scientific and Medical Applications*. Chapter I.3. (Ed. by Grant, E.H.). Artech House, Inc. Norwood.

Tinga, W.R. & Nelson, S.O. 1973. Dielectric properties of materials for microwave processing - tabulated. J.Microwave Power 8: 23-65.

To, E.C., Mudgett, R.E., Wang, D.I.C., Goldblith, S.A. & Decareau, R.V. 1974. Dielectric properties of food materials. J. Microwave Power 9: 303-315.

Torreggiani, D., Forni, E. and Rizzolo, A. 1987. Osmotic dehydration of fruit 2: influence of the osmosis time on the stability of processed cherries. Journal of Food Process Preservation. 12 (1): 27-44.

Torregginni, D. 1993. Osmotic dehydration in fruits and vegetable processing. Food Research International. 26:59-68.

Toupin, C.J. 1986. Osmotically induced mass transfer in biological systems: The single cell and the tissue behavior. Ph. D. Thesis. University of Alberta. Edmonton. Alberta, Canada.

Toupin, C.J., & LeMagure, M. 1989. Osmotically induced mass transfer in plant storage tissues. A mathematical model-Part 2. Journal of Food Engineering, 10: 97-121.

Uddin, M.S., Hawlader, M.N.A. and Rahman, MD.S. 1990. Evaluation of drying characteristics of pineapple in the production of pineapple powder. Journal of Food Processing and Preservation. 14: 375-391.

Valdez-Fragoso, A., Mujica-Paz, Giroux, F. and Welti-Chanes, J. 2002. Pilot plant for osmotic dehydration of fruits: design and evaluation. Journal of Food Process Engineering. 25: 189-199.

Vamos-Vigyazo, L. 1981. Polyphenol oxidase and peroxidase in fruits and vegetables. Critical Reviews in Food Science and Nutrition. 15(1): 49-127.

Van den Berg, C. 1985. Development of B.E.T.- like models for sorption of water on foods, theory and relevance. In Properties of Water in Foods. Ed by Simatos, D and Multon, J.L. NATO ASI Series. p: 119-132.

Van Nieuwenhuijzen N.H., Zareifard M.R. and Ramaswamy H.S. 2001. Osmotic drying kinetics of cylindrical apple slices of different sizes. Drying Technology. 19 (3&4): 525-545.

Videv, K., Tanchev, S., Sharma, R.C., Joshi, V.K. 1990. Effect of sugar syrup concentration and temperature on the rate of osmotic dehydration of apples. Journal Food Science and Technology. 27(5): 307-308.

Vijayanand P., Chand N. and Eipeson W.E. 1995. Optimization of osmotic dehydration of cauliflower. Journal of Food Processing and Preservation. 19: 229-242.

Waliszewski K.N., Cortés H.D., Pardio V.T. and Garcia M.A. 1999a. Color parameter changes in banana slices during osmotic dehydration. Drying Technology. 17(4&5): 955-960.

Waliszewski K.N., Corzo C., Pardio V.T. and Garcia M.A. 1999b. Effect of proteolytic enzymes on color changes in banana chips during osmotic dehydration. Drying Technology. 17(4&5): 947-954.

Waliszewski K.N., Texon N.I., Salgado M.A., and Garcia M.A. 1997. Mass transfer in banana chips during osmotic dehydration. Drying Technology. 15 (10): 2597-2607.

Waliszewski, K.N., Delgado, J.I. and García, M.A. 2002. Equilibrium concentration and water and sucrose diffusivity in osmotic dehydration of pineapple slabs. Drying Technology. 20(2): 527-528.

Weemaes,C., Ooms, V., Indrawati, L. Ludikhuyze, I. Van den Broeck, A. Van Loey and M.Hendrickx . 1999. Pressure-temperature degradation of green color in broccoli juice. Journal of Food Science. 64(3): 504-508.

Yamaki, S. and Ino, M. 1992. Alteration of cellular compartmentation and membrane permeability to sugars in immature and mature apple fruit. J. Amer. Soc. Hort. Sci. 117: 951-954.

Yang, C.D. and Le Maguer, M. 1992. Mass transfer kinetics of osmotic dehydration of mushrooms. Journal Food Processing and Preservation. 16: 215-231.

Zhou, L.M., Puri, V.M. & Anantheswaran, R.C. 1994. Effect of temperature-gradient on moisture migration during microwave-heating. Drying Technology, 12(4): 777-798.

Zagza, N.P., Maroulis, Z.B. & Marinos-Kouris, D. 1996. Moisture diffusivity data compilation in foodstuffs. Drying Technology. 14: 2225-2253.