DEVELOPMENT OF A NOVEL DRYING PROCESS FOR WHOLE CRANBERRIES EMPLOYING MICROWAVE-OSMOTIC DEHYDRATION UNDER CONTINUOUS FLOW MEDIUM SPRAY (MWODS) CONDITIONS AND MICROWAVE-VACUUM (MWV) FINISH-DRYING

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ABSTRACT

Osmotic dehydration is a useful process for producing a high quality intermediate moisture product that requires less time in the more intensive finish-drying processes. While previous work established microwave-osmotic dehydration under spray conditions (MWODS) as a useful means to enhance the moisture loss and product quality while minimizing solids gain, these studies were limited to cut fruit samples which were then hot air finish-dried. Therefore, the current study was focused on applying MWODS to a new product as well as developing a microwave-vacuum (MWV) finish-drying step.

Initial work within this context established the applicability of MWODS to whole cranberries by employing a central composite rotatable design to test the effects of input parameters (temperature, concentration, and contact time) on product quality and drying kinetics. Overall it was found that the MWODS process was well suited to drying of cranberries and was able to overcome the moisture barrier property of the skin. Subsequently the effect of flow rate was also studied. It was found that contact time had the largest effect, where longer processes allowed for higher moisture loss and solids gain but lowered the product quality. Similar effects were found with temperature while increasing concentration preserved anthocyanins. The effect of flow rate was small and appeared to impart some product cooling.

Since MWODS results in a partially dried product, a bench-scale MWV setup was developed for finish-drying the berries. It was found that increasing process intensity reduces drying times and energy use, while product quality was best maintained by lower intensity treatments. Overall, the quality of berries dried via combination power treatments approached that of freeze dried samples in significantly less time.

The properties of recycled osmotic solutions were evaluated and it was found that the solution could be recycled ten times without product quality degradation or microbial build-up. Apple samples that were then treated using the recycled syrup were found to uptake components previously leached from cranberries, indicating a potential application for used syrup.

Overall, the thesis research provided data and insight on the microwave-osmotic-vacuum drying of cranberries and their associated quality changes. The developed novel process was much more rapid than conventional methods and still produced high quality dried cranberries, with further potential to reuse osmotic solutions, indicating promise for commercial production.

RÉSUMÉ

La déshydratation osmotique est un procédé utile pour éliminer la majorité de l'humidité initiale d'un produit et a comme résultat un produit alimentaire de haute qualité avec un teneur en humidité intermédiaire qui nécessite moins de temps durant les procédés de séchage de finition plus intensifs. Des études antérieures ont établis que la déshydratation osmotique par micro-onde (initialement dans une configuration par immersion, ensuite par pulvérisation) est un moyen utile d'accroître la qualité des produits et d'améliorer la perte d'humidité tout en limitant le gain en solides. Parce que le travail précédent a été limité à des échantillons de fruits coupés qui ont été séchés en utilisant le séchage à air chaud pour la finition, ce travail vise à élargir l'utilisation de la déshydratation osmotique sous conditions de flux continu de pulvérisation (MWODS) à un nouveau produit ainsi que d'employer le séchage sous vide aux micro-ondes (MWV) comme la dernière étape de séchage.

Le travail initial a porté sur la création de l'applicabilité des conditions MWODS à des canneberges entières. Pour ce faire, un plan central composite rotatif (CCRD) a été utilisé pour tester de manière indépendante les effets des paramètres d'entrée, soit la température, la concentration et le temps de contact, sur la qualité du produit et la cinétique de séchage. En général, il a été constaté que le processus de MWODS était bien adapté aux canneberges congelées entières et a réussi à dépasser la barrière contre l'humidité de la peau de canneberge, éliminant le besoin de cette étape de traitement supplémentaire. Par la suite, la conception de la CCRD antérieure a été élargie pour inclure le débit en plus de la température, la concentration et le temps de contact. Au total, il a été déterminé que le temps de contact est le processus le plus significativement influencé, où de plus longues durées permettaient une plus grande perte de l'humidité et gain en solides, mais était généralement nuisible à la qualité du produit. Des effets similaires ont été démontrés pour la température tandis que l'augmentation de la concentration tend à protéger les anthocyanes et leur couleur rouge caractéristique. Des débits plus élevés semblent donner un léger effet de refroidissement, bien que les effets fussent peu significatifs.

Parce que le résultat du MWODS est un produit partiellement déshydraté, une installation de séchage sous vide aux micro-ondes (MWV) à l'échelle laboratoire a été assemblée pour terminer le séchage des baies. Divers traitements de séchage de finition ont été examinés et il a été constaté que l'augmentation de l'intensité du processus a permis de raccourcir le temps de séchage et à réduire la consommation d'énergie, mais une étude ultérieure indiquait que les traitements de

faible intensité conservent mieux la qualité du produit. Globalement, le processus MWODS-MWV était capable de produire des canneberges séchées avec des attributs de qualité se rapprochant à celles des échantillons lyophilisés, mais en beaucoup moins de temps.

Enfin, les propriétés et les performances de séchage de solutions recyclées osmotiques ont été étudiées et comparées à celle d'un concentré commercial de jus de canneberge. Il a été déterminé que la solution peut être recyclée jusqu'à 10 fois sans régénération sans changement au produit final ou accumulation de micro-organismes dans le sirop. Grâce à la présence de composés lessivés des canneberges, le sirop osmotique réutilisé modifiait les propriétés sensorielles des échantillons de pommes traités par le MWODS, en leur conférant une couleur rouge et une saveur caractéristique de la canneberge, indiquant une utilisation potentielle pour le sirop osmotique usé.

En général, la recherche décrite dans cette thèse permet de comprendre les effets du nouveau procès « micro-ondes-osmotique-sous-vide » pour canneberges et l'effet sur la qualité du produit final. Le nouveau procédé développé était en mesure de produire rapidement des canneberges séchées de haute qualité en moins de temps que les méthodes conventionnelles, avec un potentiel supplémentaire de réutiliser des solutions osmotiques, indiquant son potentiel économique de production commerciale.

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CONTRIBUTIONS OF AUTHORS

Several parts of this thesis research have been presented at scientific conferences and submitted/prepared as manuscripts for publication. The research was performed in its entirety by the candidate, including design of experiments, experimental work, data analysis, and preparation of manuscripts for publication under the supervision of Prof. H.S. Ramaswamy, who provided input towards framing the research, defining the issue at hand, and reviewing and editing of manuscripts.

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Peer-Reviewed Publications

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Conference Presentations

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Wray, D and Ramaswamy, H.S., 2013. Comparison of Sucrose- and Fruit Juice Concentrate-based Osmotic Solutions for Microwave-Osmotic Dehydration of Cranberries under Continuous Flow Spray (MWODS) Conditions. Institute of Food Technologists Annual Meeting and Food Expo, July 13-16, 2013. Chicago, Illinois.

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CONTRIBUTIONS TO KNOWLEDGE

The work described in this thesis contributes to the expansion of knowledge in the area of microwave-osmotic and microwave-vacuum drying, and their effect on product quality, energy consumption, and drying kinetics. More specifically, the contributions of knowledge from this thesis are as follows:

1. The scope of applications for microwave osmotic dehydration under continuous flow medium spray (MWODS) conditions was expanded beyond cut fruit to include whole cranberries. Moreover, the process was found to be able to overcome the moisture barrier property of waxy fruit skin on small berries, while having a minimal impact on the quality parameters of the fruit during MWODS.
2. A bench-top microwave-vacuum (MWV) drying setup was built and suitable treatments determined for both fresh (frozen-thawed) and MWODS pre-treated berries.
3. During MWV drying, altering duty cycle with constant magnetron power output was recognized as a suitable method to manage product temperature, thereby controlling quality degradation and energy consumption of the process. Moreover, various MWV treatments were found to be capable of producing dried fruit, with quality approaching those of freeze dried berries.
4. A novel drying method was developed by employing MWODS in tandem with MWV, where parametric optimization of the process indicated that the process behaved in much the same fashion as conventional osmotic dehydration, where increasing temperature, concentration, and contact times tended to increase dehydration parameters (ML and SG) while decreasing quality parameters, except in the case of high concentrations which tended to better maintain anthocyanin content.
5. Response Surface Methodology was employed to model the process and independently test the effects of each MWODS input parameter. The calculated model was experimentally validated, indicating its ability to accurately predict the effects of the MWODS-MWV process within the ranges examined in the design space.
6. MWODS pre-treated berries were found to exhibit increased rates of moisture loss in subsequent MWV drying, which was attributed to changes in the cellular structure imparted by the MWODS process. Regardless, the MWODS-MWV process was able to better

maintain cellular structure and overall product quality (texture, color, chemical indices) as compared to the more traditional vacuum, hot air or freeze drying.

7. For MWODS, it was determined that the osmotic solution could be recycled up to ten times with no significant decreases in process effectiveness or end quality of the product. Moreover the recycled solution was found to have some potential for infusing components leached from the initial sample (cranberry) into a new product (apple), indicating potential for use to create novel food products.
8. It was also found that during MWODS, smaller compounds such as organic acids were preferentially leached into the osmotic solution over the larger anthocyanins. Moreover, there was little to no leaching of some components (likely of higher molecular weight) that were present in cranberry juice concentrate.

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NOMENCLATURE

Π	Osmotic Pressure
T	Absolute Temperature (Kelvin)
R	Universal Gas Constant (8.314 J K^{-1} mol^{-1})
V	Volume (m^3)
a_w	Water Activity (dimensionless)
W	Moisture Content (kg H_2O/m^3)
x	Spatial coordinate measured normal to the section (m)
D	Diffusion coefficient (m^2/s)
D_s	Solids Diffusivity (m^2/s)
D_w	Water Diffusivity (m^2/s)
F	Rate of mass transfer per unit area of cross section (kg/m^2)
C	Concentration (w/w)
r	Distance Parameters (m)
t	Time
a	Radius of the sample (m)
M_0, M_t, M_e	Sample mass (kg) at time zero, time t and equilibrium, respectively
x_0, x_t, x_e	Water fractions (kg/kg) at time zero, time t and equilibrium, respectively
s_0, s_t, s_e	Solids content (kg/kg) at time zero, time t and equilibrium, respectively
j	$\sqrt{-1}$
ε^*	Complex relative permittivity
ε'	Dielectric constant
ε''	Loss factor
ε_O	Absolute permittivity of vacuum (8.854188 x10^{-12} F m^{-1})
P	Energy developed per unit volume (W/m^3)
f	Frequency (Hz)
$\|E\|$	Strength of the electric field (V/m)
d_p	Penetration Depth (m)

λ_O	Wavelength of the microwave in free space
EC	Energy Consumption (MJ/kg moisture removed)
t_{on}	Total magnetron power-on time (s)
P_{MW},P_{VP}	Magnetron output and vacuum pump power (W), respectively
M_i	Initial sample mass (kg)
m_i, m_f	Initial and final moisture fractions (kg/kg)
MR	Moisture ratio (dimensionless)
K	Drying rate constant (min^{-1})
k, n	Parameters of Page's Empirical Model
L_0^*, L^*	Lightness of the standard and sample, respectively (dimensionless)
a_0^*, a^*	Chromaticity coordinates (red (+) to green (-)) of standard and sample, respectively (dimensionless)
b_0^*, b^*	Chromaticity coordinates (yellow (+) to blue (-)) of standard and sample, respectively (dimensionless)
$H°$	Hue angle (dimensionless)
Hardness	Newtons (N)
Chewiness	mJ
EC_{VP}, EC_{MW}	Energy input (J) of the vacuum pump and microwave, respectively

ABBREVIATIONS

°B	Degree Brix
AA	Antioxidant Activity by DPPH Method
AD	Air Dried
ANOVA	Analysis of Variance
CCRD	Central Composite Rotatable Design
CFU	Colony Forming Units
CI	Confidence Interval
CJC	Cranberry Juice Concentrate
COD	Conventional Osmotic Dehydration
cyd-3-glu	Cyanidin-3-glucoside
DIS	Dewatering Impregnation Soaking
DPPH	2,2-diphenyl-1-picrylhydrazyl
EM	Electromagnetic
FB	Fluidized Bed
FCR	Folin-Ciocalteu Reagent
FD	Freeze Dried
GAE	Gallic Acid Equivalents
HDM	Hydrodynamic Mechanism
HELP	High-Intensity Electric Field Pulses
HHP	High Hydrostatic Pressure
MFB	Microwave Fluidized Bed
MFD	Microwave Freeze Drying
ML	Moisture Loss
MPSVD	Microwave Vacuum Spouted Bed Process
MSB	Microwave Spouted Bed
MW	Microwave

MWODI	Microwave Osmotic Dehydration under Continuous Flow Medium Immersion
MWODS	Microwave Osmotic Dehydration under Continuous Flow Medium Spray
MWV	Microwave-Vacuum
OD	Osmotic Dehydration
PCA	Plate Count Agar
PEF	Pulsed Electric Field
Pred-R^2	Predicted Coefficient of Determination
PSMFD	Pulse Spouted Bed Microwave Freeze Drying
PVOD	Pulsed Vacuum Osmotic Dehydration
R^2	Coefficient of Determination
RH	Relative Humidity
RHC	Rehydration Capacity
RMS	Root Mean Squared
RSM	Response Surface Methodology
SGA	Sabouraud Glucose Agar
SB	Spouted Bed
SG	Solids Gain
TMA	Total Monomeric Anthocyanins
TP	Total Phenolics
VD	Vacuum Dried
VI	Vacuum Impregnation
VOD	Vacuum Osmotic Dehydration

CHAPTER 1

INTRODUCTION

1.1 General Introduction

Dehydration is one of the oldest methods of food preservation and still is a major player in the food industry for creating shelf-stable products. The main objective of dehydration is to remove moisture to a point where a product is microbiologically and enzymatically stable in order to limit product deterioration during storage and allow its incorporation into different food products (Nijhuis et al., 1998; van Nieuwenhuijzen et al., 2001). Water removal also lowers transportation and storage costs by reducing the weight of the product (Bolin et al., 1983; Rastogi et al., 2002). However, there is increasing consumer demand for higher quality dried products that maintain more characteristics of the fresh product. The primary concerns include loss of flavors and aroma volatiles, deterioration of color and texture, and an overall decrease in nutritional value, mostly to exposure to high temperatures for long periods of time in the presence of air (Nijhuis et al., 1998; Lenart, 1996; Alibas, 2007). Therefore, the key to improving the quality of dried products is to reduce changes to the aforementioned quality characteristics during processing, most often accomplished by using moderate conditions and excluding contact with damaging elements like oxygen. In order to ensure stability while in storage, the water activity (a_w) (which dictates the extent of enzyme and microbial activity) is usually required to be lower than 0.7 (Sunjka et al., 2004).

Traditional hot air drying, still used most widely in food industry, has been shown to be inefficient and lead to excessive quality loss (Grabowski et al., 2002). Case hardening (the over-drying of outer layers of the product) and product shrinkage are the main issues in convective air drying (Nijhuis et al., 1998). Dried fruit, in general, suffers from several disadvantages including loss of juiciness and lignified tissue, both of which result in a harder or chewier product (Lenart, 1996). As such, extensive research has been carried out in recent years in order to find methods of drying food products while maintaining quality. One such technique is freeze drying, which operates below the triple point of water and therefore allows for removal of water without the liquid phase (sublimation), resulting in low drying temperatures and corresponding high product quality. Freeze dried products possess very good structural rigidity which prevents texture collapse

and maintains the porosity of the food matrix, enabling excellent rehydration capacity which is typical of these products (Beaudry et al., 2004). Freeze drying is known to produce the best quality dried product and is generally used as a reference for other drying procedures (Azarpazhooh & Ramaswamy, 2010c). However, this technique is also very expensive and energy intensive, limiting its use mostly to high value products (Nijhuis et al., 1998; Qi et al., 1998; Grabowski et al., 2002).

One way to limit the amount of finish-drying time a product requires is to remove the initial bulk of moisture through a suitable inexpensive and energy efficient operation, before the product is transferred to the primary drying. Osmotic dehydration is a partial dehydration process which addresses both quality and energy concerns. Osmotic dehydration (also known as dewatering-impregnation-soaking, or DIS) comprises placing a solid food product in a solution of high osmolarity which is typically made up of sugar and/or salt solutions (Torreggiani, 1993). Common solutes include low molecular saccharides, sodium chloride, sorbitol, and glycerol, among others (Lenart, 1996). The process is a power efficient means to increase solids content and obtain intermediate moisture foods. OD has been used for a wide variety of fruits such as various berries, pineapple, pear and apple as well as vegetables like potato, onion, and carrot (Bolin et al., 1983; Lenart, 1996; Osorio et al., 2007; Li & Ramaswamy, 2006a; Li & Ramaswamy, 2006b; Li & Ramaswamy, 2006c; Azarpazhooh & Ramaswamy, 2010c; Azarpazhooh & Ramaswamy, 2011b; Azarpazhooh & Ramaswamy, 2011a; Azarpazhooh & Ramaswamy, 2010b; Azarpazhooh & Ramaswamy, 2010a).

Osmotic dehydration has become increasingly popular as a pre-drying step employed because of its high energy efficiency and relatively low impact on product quality (Torreggiani & Bertolo, 2001). Removing moisture by osmotic dehydration has a twofold benefit over that of traditional drying, which are summed up well by Ramaswamy and Tola (2014). First, by removing moisture via diffusion, there is no need to provide the latent heat of vaporization. Second, the removal of moisture in this primary step results in a smaller sample load for finish-drying, shorter drying times, and lower overall operation costs. Additionally, osmotic dehydration will actually increase the solids content of the product and therefore actually yields more product than the starting point (Ramaswamy & Tola, 2014). Moreover, osmotic dehydration is often considered a treatment which is employed to give a higher quality product than traditional techniques can provide (Bekele & Ramaswamy, 2010).

Because of the various quality issues associated with traditional convective hot air drying, researchers in the last 20-25 years have focused on modernizing drying techniques employed to improve efficiency and product quality. Examples of such techniques include those that apply a vacuum or the application of electromagnetic (EM) energy like during microwave based drying techniques. The combination of these two principles is known as microwave-vacuum drying, and is a technique that shows particular promise because of improved drying kinetics and higher product quality (Nijhuis et al., 1998). Microwave-vacuum drying provides several key benefits. First, the boiling point of water is significantly reduced under vacuum and therefore the sample can be maintained at a lower temperature while still evaporating moisture (Beaudry et al., 2004). Second, by heating the product directly via microwave energy instead of relying on air as a heat transfer medium, there is no energy wasted in pre-heating the oven cavity and air to the requisite temperature. Moreover, microwave-vacuum drying allows for faster removal of moisture from within the core of the sample, which is typically the most difficult to remove (Bouraoui et al., 1993). Finally, by drying in a reduced oxygen atmosphere, microwave-vacuum drying limits product degradation that would take place due to exposure to oxygen and high temperatures (Drouzas & Schubert, 1996).

1.2 Research Objectives

With these considerations in mind, the overall objective of this thesis was to develop and evaluate drying of cranberries (*Vaccinium macrocarpon)* produced by a combination drying technique consisting of microwave-osmotic dehydration under continuous flow medium spray (MWODS) conditions and microwave-vacuum (MWV) drying. Specific objectives were:

i. Apply MWODS to cranberries by determining effects of process parameters and the need for skin pre-treatments
ii. Develop a bench-top scale MWV dehydration apparatus and determine suitable treatments for both fresh and MWODS in terms of drying kinetics and energy consumption
iii. Determine the effects of MWV process intensity on quality parameters of fresh and MWODS pre-treated cranberries
iv. Optimize the novel MWODS-MWV drying technique and compare the final product with those dried via other methods
v. Investigate the effect of recycling the osmotic solution on process effectiveness, product quality, as well as potential uses of the spent syrup

CONNECTIVE STATEMENT TO CHAPTER 2

The "Literature Review" in the following chapter aims to provide the reader with background knowledge on the state of dehydration based research, with particular focus paid to osmotic and microwave based techniques. In understanding the concepts and areas lacking thorough investigation, the framework for research presented in further chapters is established. This chapter is spread into 3 main sections, which will address the product itself, osmotic dehydration and methods to enhance mass transfer, and finally the wide range of options for secondary or finish-drying, with an emphasis on microwave based techniques.

A portion of the following chapter has been adapted for publication as follows:

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CHAPTER 2

LITERATURE REVIEW

2.1 Cranberries *(Vaccinium macrocarpon)*

Cranberries represent an increasingly important agricultural crop in North America. Production of cranberries reached an all-time high in Canada in 2012 when nearly 127,000 tonnes of cranberries were produced, representing a 50% increase from the average of the previous three years (FAO, 2014). Botanically, cranberries can be separated into four cultivars of which *Vaccinium macrocarpon* (the Large or American cranberry) is the most important in terms of agricultural production (Leahy et al., 2001). Cranberries are of growing importance in the food industry because of the level of health-positive components found in the fruit. Fresh cranberries have approximately 88% moisture (wet basis) and contain high levels of Vitamin C, phenolics such as flavonoids, anthocyanins and catechins along with organic acids like malic, citric and benzoic acids (Zheng & Wang, 2003). These compounds exhibit a wide range of beneficial effects within the human body including decreased risk of coronary heart disease, stroke, and lung cancer (Hertog et al., 1993; Knekt et al., 1996; Keli et al., 1996; Knekt et al., 1997). Bioactive compounds in cranberries also exhibit a broad anti-oxidant effect by scavenging reactive species such as the superoxide and hydroxyl radicals (Wang & Jiao, 2000). This anti-oxidant activity has an anti-inflammatory effect in the body, thereby reducing the incidence of degenerative diseases generally attributed to oxidative stress including cancers, cardiovascular diseases and neurodegenerative diseases such as Parkinson's or Alzheimer's (Ames, 1983). Additionally, cranberries represent an entirely natural prevention and treatment option for urinary tract infections, supported by significant epidemiological study data (Sunjka et al., 2004; Tracy, 2007).

Cranberries are nearly inedible in their raw form and therefore the bulk of the harvest is processed into sauces, juices or dried products, while the remainder is sold fresh or frozen whole. Cranberries benefit from processing because fresh they are too sour and tart for consumption due to high levels of citric and quinic acids, and are therefore most often transformed into fruit juices and cocktails where sugar is added (Tracy, 2007). Traditionally the shelf life of un-transformed cranberries is extended by freezing, however drying the berries makes them shelf stable and more easily distributed. For dried cranberries, the target moisture content is between 15-20% and water activity (a_w) should be less than 0.7 to limit microbial growth (Sunjka et al., 2004). In identifying

the important properties of cranberries, it can be stated that the optimal drying process for cranberries will minimize losses of these health positive compounds naturally present in the berries, which can be achieved through moderate dehydration conditions.

2.2 Osmotic Dehydration

The alternate name for osmotic dehydration (dewatering-impregnation-soaking) implies a two way transfer of matter involving both 'dewatering' and 'impregnation'. In the context of food, the process involves the simultaneous flux of water and solutes across a differentially-permeable membrane, which in this case is the plant cell wall (Bolin et al., 1983). This results in both reduction of water within the cell as well as an increase of solid matter in the food material as solute is transferred into the cell (Torreggiani, 1993). In addition to the two major fluxes of water out of the cell and the counter-current transfer of solutes from the solution into the cell, there is also a third transfer of low molecular weight substances such as vitamins, minerals or organic acids which also diffuse out of the cell (Lenart, 1996; Torreggiani, 1993). This minor stream has little or no bearing on the overall mass exchange which would be primarily due to exchange of water and solute but it can have a significant impact on nutritional or organoleptic properties of the finalized food product (Lenart, 1996). In the case of anthocyanins in cranberries, it has been shown that the post-osmotic pigment level is on average 10% lower than in the fresh berries due to the effects of this leaching (Grabowski et al., 2002).

When applied to fruits, sucrose based osmotic dehydration (OD) has been shown to reduce browning reactions, retain volatiles and sweeten the product (Osorio et al., 2007). Of particular benefit to food processors is the ability to incorporate different solutes from the osmotic solution in order to create new products (Torreggiani, 1993). This can be quite useful when dealing with a bitter or sour fruit such as cranberries, as the incorporation of sucrose from the solution into the product is necessary for the product to become edible. It is of particular interest that once moisture transfer has effectively stopped, solids uptake by the food product will continue, allowing for a controllable amount of solids gain (Raoult-Wack, 1994). The presence of sugar within the fruit also prevents volatile losses during the required subsequent finish-drying, resulting in aroma retention in osmotically pre-treated dried fruits (Lazarides et al., 1995). Moreover, osmotic dehydration is one of the rare processes that can increase yield (Ramaswamy & Tola, 2014). Osmotic dehydration primarily functions according to the osmotic pressure differential across a

semi-permeable membrane (cell wall), but can also be affected by the tissue structure of the product. Osmotic pressure can be defined as the pressure exhibited by a solution in order to prevent the inward flow of water across a semipermeable membrane. For food products, the osmotic pressure (π) can be expressed as (Azarpazhooh, 2010):

$$\pi = -\frac{RT}{V}\ln(a_w) \qquad (2.1)$$

where V is the molar volume of water, T is the absolute temperature; R is the gas constant and a_w is the water activity of the product.

OD is desirable because of several key factors, including its energy efficiency and low operating costs (Bolin et al., 1983; Raoult-Wack, 1994; Lenart, 1996), reduction of color and texture damage (Torreggiani, 1993; Chen et al., 2001) and suppression of enzymatic browning (Contreras & Smyrl, 1981). Diffusion of water will continue until there is equilibration of the solute on either side of the cell membrane, therefore the final product moisture content is dependent on the initial concentration of solutes in the osmotic solution. However, contact times up to 24 h may be required for a typical ambient temperature pre-drying step (Beaudry et al., 2004). Moreover, in most cases the majority of water loss takes place in the first 2 h of osmotic dehydration (Raoult-Wack, 1994; Biswal et al., 1991; Torreggiani, 1993). Overall then, there is a need for further drying technologies to be applied to the osmotic drying process in order to speed up and finish the drying process without affecting product quality (Rastogi et al., 2002).

After osmotic dehydration, the resulting intermediate moisture food product still has a moisture content of 50% or more and thus still requires further drying to achieve shelf stability. Traditionally this has been achieved by using hot air drying, although full details of various finish-drying methods will be discussed in Sections 2.8 and 2.9.

2.3 Modelling Osmotic Dehydration

While the basic principles are understood, one of the main goals of modern osmotic dehydration studies is to model the process in order to fully understand and predict the influence of process parameters and sample properties on moisture loss and solids gain. Models must take into account process parameters such as temperature, solution concentration and contact time, whereas intrinsic factors comprise the size, shape and nature of food material. Despite increased research into osmotic dehydration in recent years, the exact mechanisms by which mass transfer takes place during osmotic dehydration is still poorly understood (Raoult-Wack et al., 1991; Yao

& Maguer, 1996; Spiazzi & Mascheroni, 1997). It is important to properly model osmotic dehydration in order to minimize energy input while maximizing quality for dried products (Saguy et al., 2005). There are complications because of the complexity of the materials involved, i.e. that membranes used to perform osmosis are complex and of biological origin and are therefore not ideal (Fito, 1994). The mass transfer during osmotic dehydration has been described as a combination of osmosis, diffusion and hydrodynamic mechanism, or HDM (Fito & Pastor, 1994). There are two main approaches used to model conventional osmotic drying (COD), known as the macroscopic and microscopic approaches. Yao and Le Maguer (1996) describe that the macroscopic approach assumes that the food tissue is homogenous and properties of the cell wall, membrane and vacuole are lumped for the purposes of modelling. Conversely, the microscopic approach takes into account the heterogeneity of plant tissues and complex cellular structure and represents them in a simplified conceptual model.

2.3.1 Macroscopic Approach

Lumped models such as the macroscopic approach used for modelling osmotic dehydration often ignore internal resistance to mass transfer (Fasina et al., 2006). Studying concentration profiles over the course of mass transfer processes such as osmo-dehydration in combination with observation of micro-structural features such as changes in intercellular spaces and cell wall deformations can be used to define mass transfer kinetics and mechanisms (Lenart & Flink, 1984). Mathematical modelling provides useful insight into causative relationships with mechanisms taking place during such processes, and several studies have proposed the use of Fick's unsteady state laws of diffusion (Fito et al., 1996; Yao & Maguer, 1996; Nsonzi & Ramaswamy, 1998a; Ochoa-Martinez et al., 2007a) and hydrodynamic mechanisms (Fito, 1994; Fito & Pastor, 1994) in order to model mass transfer during osmotic processes. Hydrodynamic mechanisms were first conceived because the complete effects of vacuum during vacuum osmotic dehydration (VOD) could not be explained using only diffusional and osmotic transport models, so HDM was developed to more completely model the process (Fito, 1994; Fito & Pastor, 1994). More specifically, HDM is a mass transfer mechanism initially developed for the purpose of being able to better predict the effect of vacuum on solute impregnation in order to obtain novel products (Fito, 1994).

When Fick's unsteady state law of diffusion is used to estimate the diffusivity of either

water or the solute in the osmotic solution, boundary conditions are used to overcome assumptions necessary to use Fick's law (Ade-Omoware et al., 2002). Assumptions required to solve Fick's law include: solute concentration is constant; mass transfer is restricted to moisture out of and solids into the fruit; diffusion rate is infinite, allowing for instantaneous equilibration between fruit and syrup; samples are homogenous, of ideal shape and of a uniform size; no product shrinkage; and that the effective diffusivity depends on the conditions of osmotic dehydration alone (Nsonzi & Ramaswamy, 1998a). Despite the difficulty in fulfilling all of these assumptions, studies have shown that that solutions such as Crank's correlate to experimental data in osmotic dehydration (Ochoa-Martinez et al., 2009). The two required parameters for Fick's law are sample dimensions and the effective diffusion coefficient, the latter of which is often determined by calculating the relationship between the slope of the theoretical diffusion curve and that of the experimental mass transfer ratio over time (Ade-Omoware et al., 2002; Rastogi et al., 2002). Crank (1970) developed solutions for long-time and short-time exposures along with a solution for diffusion into a sample within a well-stirred tank for sheets, cylinders and spheres (Ochoa-Martinez et al., 2009). As such Fick's laws can be solved by using various idealized geometric sample shapes, such as infinite slabs and cylinders, spheres, among others (Nsonzi & Ramaswamy, 1998a; Rastogi et al., 2002; Ochoa-Martinez et al., 2009; Crank, 1970). For mass transfer in food dehydration, macroscopic mass transfer studies are typically based on Fick's second law of diffusion, shown below (Rastogi et al., 2002):

$$V\frac{\partial W}{\partial t} = D\frac{\partial^2 W}{\partial x^2} \qquad (2.2)$$

where W is moisture content (gH_20/m^3), x is the spatial coordinate (m); t is time in s; D is the diffusion coefficient (m^2/s) and V is volume (m^3). Fick's second law of diffusion can be used to determine diffusion coefficients for either water loss or solids gain, where mass transfer is assumed to be one-directional and interactions of other components on the diffusion of the solute are considered negligible (Rastogi et al., 2002).

Also employed is Fick's first law, which provides a linear relationship between the flux of a component and the concentration gradient of that component, and is expressed as (Crank, 1970):

$$F = -D\frac{\partial C}{\partial x} \qquad (2.3)$$

where F is the rate of transfer per unit area of cross section (kg/m^2), C is the concentration of

diffusing substance (kg/m^3), x is the space coordinate measured normal to the section (m) and D is the diffusion coefficient (m^2/s) (Ramaswamy & van Nieuwenhuijzen, 2002). Additionally, where the diffusion is radial as opposed to along a plane, the diffusion equation can be expressed as (van Nieuwenhuijzen et al., 2001):

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r}\frac{\partial C}{\partial r}\right) \qquad (2.4)$$

Where D is the diffusion coefficient (m^2/s), C is the concentration (kg/kg), r is the distance parameter (m) and t is time (s). Finally, for spherical food particles, equations for moisture and solids transfer, respectively, can be expressed as (Nsonzi & Ramaswamy, 1998a):

$$\frac{M_t x_t - M_e x_e}{M_0 x_0 - M_e x_e} = \frac{6}{\pi^2} e^{\left(-\frac{D_m \pi^2}{a^2}\right)} \qquad (2.5)$$

$$\frac{M_e s_e - M_t s_t}{M_e s_e - M_0 s_0} = \frac{6}{\pi^2} e^{\left(-\frac{D_s \pi^2}{a^2}\right)} \qquad (2.6)$$

where D_m and D_s are water and solids diffusivity coefficients respectively (m^2/s) and a is radius of the sample (m), and M_0, M_t and M_e are the sample mass (kg), x_0, x_t and x_e are the water fractions (kg/kg) and s_0, s_t and s_e are the solids content (kg/kg) of the samples at time zero, t and equilibrium conditions, respectively (Ramaswamy & van Nieuwenhuijzen, 2002).

Although Crank's solutions to Fick's laws are widely used, more recent work has shown that Azuara's model fits solids gain data better and also provides adequate fit to moisture loss, and should therefore be favored (Azuara et al., 1992). This model also has the capability to determine equilibrium values of moisture loss and solids gain (Ochoa-Martinez et al., 2007a). Azarpazhooh and Ramaswamy (2010a) demonstrated that the Azuara model provided good fit for both moisture loss and solids gain of apple pieces during microwave osmotic dehydration and allowed for the calculation of equilibrium values of both moisture loss and solids gain without waiting for real equilibration to occur. The same authors noted that the actual values deviated from predicted values at short treatment times (less than 30 min), so the model may fit better with longer treatments (Azarpazhooh & Ramaswamy, 2010a).

Recent studies have also focused on the application of artificial neural networks (ANN) in modeling osmotic dehydration (Chen et al., 2001; Ochoa-Martinez et al., 2007b). ANN is a powerful data modeling tool that has the ability to learn linear and non-linear relationships between variables directly from a data set, and allows for these relationships to be applied to unlearned data (Ochoa-Martinez et al., 2007b). The optimal configuration of ANN is obtained by varying the main

parameters, namely: transfer function, learning rule, number of neurons and layers, and number of learning runs (Chen et al., 2001). This method is particularly effective when the system has more than three input parameters (Chen et al., 2001; Basheer & Hajmeer, 2000). Training of the network is required in order to achieve a set of connection weights between neurons in order to calculate outputs that are satisfactorily close to actual example data. As such, a properly trained network is expected to produce outputs that are very close to actual outputs (Chen et al., 2001).

Ochoa-Martinez et al. (2007b) aimed to develop useful models in order to predict effective diffusivity (D_e) and moisture loss at a given time as well as at equilibrium during osmotic dehydration of fruits by combining Crank's solution and ANN as a function of the following ten process variables: temperature, concentration, contact time, water and solids content of the sample, porosity, surface area, characteristic length, solution ratio, and agitation level. The authors (Ochoa-Martinez et al., 2007b) developed models that were easy to implement for design and control of osmotic dehydration processes in order to predict and effectively optimize the process. Moreover, the models do not require experimental results to predict process parameters. Overall, because the ANN models fit well and were built upon a wide variety of data, it is likely that they can be very useful in practice for a wide variety of products (Ochoa-Martinez et al., 2007b). Similarly, Chen et al. (2001) found that using ANN to predict quality changes during osmo-convective drying of blueberries yielded much better performance than traditional mathematical models indicating that it is feasible to use ANN for prediction and optimization of this process. Furthermore, ANN models were able to predict optimal processing conditions for individual quality parameters (Chen et al., 2001).

2.3.2 Microscopic Approach

The microscopic approach to studying mass transfer is based on the fact that many of the macroscopic changes seen in osmotically dried food materials are based on changes at the microscopic level, such as cell shrinkage or lysis, which in turn affects sample porosity and texture (Barat et al., 1999). Additionally, color changes are caused by compositional changes through degradation or loss of pigments (Krokida et al., 2000; Chiralt & Talens, 2005). Increasing porosity due to cell shrinkage, for instance, will affect mass transfer due to hydrodynamic mechanisms and capillary action which pulls osmotic solution into the sample, representing an increase in non-diffusional driving forces that will contribute to mass transfer (Fito, 1994; Chiralt & Talens, 2005).

This is common in osmotic dehydration of plant materials, as the middle lamella typically detaches from the cell wall, leading to loss of cell turgor, increased intercellular space, and change in sample size and shape (Chiralt & Talens, 2005). Understanding these micro-structural changes will help predict corresponding changes at the macroscopic level and therefore allow for creation of better osmo-dehydration processes.

2.4 Effect of Process Parameters on Osmotic Dehydration

Many factors affect mass transfer during osmotic dehydration including temperature, concentration and type of osmotic agents, particle size, surface area, food tissue make-up, solution-to-solid ratio, contact time as well as agitation of the solution (Raoult-Wack, 1994; Rastogi et al., 1999; Ochoa-Martinez et al., 2007b). In this section, the effects of these individual parameters on the outcome of the process will be discussed.

2.4.1 Osmotic Agent Selection and Recycling

At the industrial scale, one of the main issues with osmotic dehydration is the management of the spent solutions. In many cases osmotic solutions are discarded, creating substantial amounts of industrial waste and substantially increasing overall costs for the operation (Garcia-Martınez et al., 2002). Moreover, as the resulting spent osmotic syrup can be considered an industrial waste, recycling the solution is one way to make the process both economical and environmentally friendly (Aachary & Prapulla, 2009). In fact, it was determined long ago that the regeneration and reuse of the syrup is critical for the economic feasibility of the process (Bolin et al., 1983).

One of the main issues is that the water removed from the sample dilutes the osmotic solution and limits the effectiveness of the solution in subsequent re-uses by slowing the mass transfer rate (Garcia-Martınez et al., 2002). As a result, the solution is typically regenerated by either concentration (evaporation) or by adding solute to restore the original concentration (Valdez-Frugoso et al., 1998). Multi-effect evaporators similar to those used in sugar cane processing allow for good conservation of energy and more efficient restoration of the syrup. Bolin et al. (1983) showed that with repeated (5) regeneration cycles, the syrups underwent definite physicochemical changes, most notably the darkening of the syrup which took place almost linearly with the number of times the syrup had been regenerated. Acidification led to further darkening of the syrup, which would be exacerbated when treating a high acid fruit. Tests showed that repeated heating cycles alone led to no change in syrup color, leading to the conclusion that acids or other components

leaching from the fruit were causing the syrups to change color. Acids in the osmotic media also enhance the rate of sucrose hydrolysis, leading to an alteration of the osmotic syrup. The same study (Bolin et al., 1983) showed that osmo-dehydration with high fructose corn syrup (HFCS) led to similar changes in sugar concentration over repeated regeneration cycles, although to a smaller extent. Even with changes to the syrup over the course of five regenerations, it was shown that there was little to no effect on final product quality when graded visually or by an untrained taste panel evaluation. With more cycles it is possible that the solutes in the syrup could be detrimental to product quality, although the effect could be minimized in industry by adding small amounts of fresh syrup for each batch (Bolin et al., 1983). Despite the changes to the osmotic syrup, various studies have found that over the course of 10-20 reuses (with or without evaporative regeneration), there is little to no effect on the quality or sensory attributes of the treated products, and the solutions tend to be microbiologically stable for long periods due to their high osmolarity (Garcia-Martınez et al., 2002; Peiró et al., 2006; Bolin et al., 1983; Osorio et al., 2007; Valdez-Fragoso et al., 2002; Valdez-Frugoso et al., 1998). In the case that microbial growth is found to be an issue, it has been suggested that either a filtration or pasteurization step could be incorporated every few cycles in order to alleviate this concern (Valdez-Frugoso et al., 1998).

Beyond reusing the syrup, it has been suggested that discarding the solution without further use (recycling or use in a new product formulation) can result in loss of valuable natural substances such as vitamins and minerals (Garcia-Martınez et al., 2002). This is because while the main mass transfers that take place during osmotic dehydration are the flow of moisture and solids from and to the product, respectively, there is also a more minor flow of solutes naturally present in the food product into the osmotic solution (Torreggiani & Bertolo, 2001). The leaching of health positive components from fruits during osmotic dehydration takes place to such an extent that it has been proposed that the solutions be used as a natural additive to food or pharmaceutical products (Morales et al., 2005). These concepts are particularly typical with products like cranberry, as they contain various health positive components subject to leaching including flavonols, flavan-3-ols, anthocyanins, tannins, and phenolic acid derivatives (Côté et al., 2010b). Another approach has been to further treat the syrups in order to transform them into value added products, where the use of spent osmotic syrups was a viable starting point to enzymatically produce fructooligosaccharides, which have widely recognized uses as low calorie prebiotics (Aachary & Prapulla, 2009).

While the main solute employed in osmotic dehydration is sucrose (with salt to a lesser extent), the best choice of osmotic medium likely depends on the product type. For instance, Bolin et al. (1983) showed that when both were treated with identical sucrose solutions, apricots were liked more than apples and that high acid foods are more compatible with sucrose-based osmotic dehydration. Moreover, HFCS migrated into the food product to a much larger extent than sucrose, especially after contact times of 3 h or more. Therefore after a given contact time the moisture content of a HFCS-treated sample will be lower than for those treated with sucrose, where the increased solids uptake will also results in a sweeter product (Bolin et al., 1983). This effect is due to the fact that the migration speed and ease of movement across the cell membrane is enhanced with a smaller sized solute like HFCS or salt as compared to that of a disaccharide like sucrose (Bolin et al., 1983; Biswal et al., 1991; Qi et al., 1998). Lazarides et al. (1995) showed that osmotic dehydration done with corn syrup instead of sucrose resulted in lower solids gain under the same experimental parameters. This corresponds with earlier conclusions made by Raoult-Wack (1994), in which smaller molecular weight solutes are described as better for impregnation, while larger solutes are better suited for dewatering the food.

Qi et al. (1998) investigated the potential for having two solutes in the osmotic solution, otherwise known as a ternary solution (for example water/sugar/salt) and found that the optimal solution for maximizing moisture loss while minimizing solids gain was a combination of the two, which represented an improvement over either of the two alone. The same authors (Qi et al., 1998) showed that increasing salt content in the osmotic syrup also increased sugar uptake, most likely due to either the NaCl lowering the viscosity of the syrup or the salt altering the cell membranes permeability making it easier for sucrose to enter. Viscosity of the osmotic syrup comes into play with the power required during pumping (circulation) of the syrup and agitation of the vessel (Bolin et al., 1983) as well as the ability of the syrup to penetrate into the fruits (Qi et al., 1998). Bolin et al. (1983) found that there was so significant change in viscosity over the course of several regenerations of the syrups. However, the viscosity will definitely depend on choice of osmotic agents and should be taken into account.

There has also been some research into using fruit juice as the osmotic solution instead of mixing a solution directly from solutes and water. One study in particular used grape must to infuse cryoprotectants into granny smith apple samples via vacuum impregnation, or VI (Chiralt et al., 1998). While the focus of this study wasn't on dehydration per se, the water content was measured

before and after the VI process, where grape must at 35, 50 and 65°B reduced the moisture content (wet basis) of the apples from 85% (fresh) to 78, 75 and 72% (wb) after 30 min, respectively, showing the effectiveness of a concentrate based osmotic solution. Another study using grape juice for dehydration of kiwi fruit found that the grape juice provided more rapid mass transfer kinetics than those given by sucrose, even with a lower concentration of 63°B for the grape juice versus 65°B for the sucrose syrup (Escriche et al., 2000). This can be largely attributed to the presence of smaller monosaccharides in the fruit juice, an effect which also promoted softer samples when apple cubes were osmotically dried in apple juice concentrate (Torreggiani, 1993). This latter study also partially attributed the softer texture to the fact that the juice produced samples had a higher relative water content at a given a_w value than the syrup produced samples. Furthermore, it has been shown in previous studies that acidified osmotic solutions further increases the moisture loss of the product (Moy, 1978). Therefore, the use of fruit juices with their lower pH values could provide additional benefit with regards to moisture loss during the process.

2.4.2 Contact Time

Contact time with the food product is critical towards determining both the final moisture content as well as the solids gain by the product. Longer contact times allow for more time for the various processes that are taking place to develop. However, while many studies show that the majority of moisture loss by the food product takes place within the first 1.5-2h of contact time (Torreggiani, 1993; Raoult-Wack, 1994; Biswal et al., 1991; Fasina et al., 2006), Qi et al. (1998) found that 75% of moisture loss was complete within the first 16 min of contact for a combination sucrose/salt osmotic syrup. Beyond that time the rate of moisture loss decreases with time while solids gain will continue at roughly the same rate (Nsonzi & Ramaswamy, 1998a). This is most likely due to the fact that as drying progresses and solute are taken into the sample, a high-sugar subsurface layer is formed which impedes both moisture removal and solid uptake, and as contact time progresses, this barrier provides higher and higher resistance, resulting in slower moisture removal as the process proceeds (Li & Ramaswamy, 2006a).

Li and Ramaswamy (2006a) and van Nieuwenhuijzen et al. (2001) found that solution contact time had the largest influence on moisture loss when compared with other process parameters such as solution concentration and temperature. Li and Ramaswamy (2006a) showed that contact time was also the most significant factor in determining solids gain, where the most

significant solids gain took place within two hours of contact time. Additionally, for a sugar based osmotic solution it was found that for short contact times the solids gain by the product was independent of the concentration of sucrose in the solution, whereas for a smaller molecule like salt (NaCl), solids gain was directly proportional to the concentration over the entire course of contact time (Qi et al., 1998). Contact time was also found to have the most significant effect on the moisture loss and solids gain of apple cylinders during microwave-osmotic dehydration (Azarpazhooh & Ramaswamy, 2010b).

2.4.3 Temperature and Concentration

Studies show that moisture loss increases in response to increases in temperature and concentration (Rastogi et al., 2002; Li & Ramaswamy, 2006b; Li & Ramaswamy, 2006c; Li & Ramaswamy, 2006a; Azarpazhooh & Ramaswamy, 2010b). Moreover, it has been stated that the effects of both temperature and concentration increases on moisture loss can be observed regardless of particle size (van Nieuwenhuijzen et al., 2001). Furthermore, Li and Ramaswamy (2006a) described osmotic dehydration as temperature dependent, where higher temperatures and concentrations both promote higher moisture loss. Higher temperatures cause molecules to move faster, allowing water to leave the sample at a faster rate (van Nieuwenhuijzen et al., 2001). While other studies have confirmed this relationship, temperatures over 60°C are generally not recommended as this can cause permanent tissue damage resulting in a lower quality final product (Lazarides et al., 1995). Nsonzi and Ramaswamy (1998b) noted that moisture diffusion was influenced more by increasing temperature than by higher concentration of the syrup, while solids diffusivity was affected by both temperature as well as solute concentration. Overall, higher sugar concentrations will increase the osmotic pressure between the solution and the fruit, thereby increasing moisture loss and solids gain.

Additionally, studies by Sereno et al. (2001), Li and Ramaswamy (2006a), and Ito et al. (2007) suggest that increased temperatures favor mass transfer of moisture and solutes by reducing solution viscosity, increasing cell membrane permeability due to swelling, and promoting moisture diffusion within the sample. Qi et al. (1998) found that increasing concentration of either salt or sucrose in the osmotic solution caused a corresponding increase in the uptake of these solutes into the product. Ito et al. (2007) found the inverse to be true, as an increase in the concentration of the osmotic solution decreased the solids gain when dehydrating mango slices. It is important to note

that the effect of temperature and concentration of the osmotic syrup will vary according to product. A study by Biswal et al., (1991) showed that when dehydrating fresh green beans at 40°C with long contact times, moisture loss was less than at 20°C, indicating that 40°C was too high a temperature for use with this product. However, it was also shown in this study that at suitable temperatures (8-20°C), moisture loss and solids gain increased with temperature. It has been shown that when temperatures exceed suitable range for a product, destructive changes in cell structure can occur resulting in the loss of the ability of the cell wall to be selectively permeable to the point where both moisture loss and solids gain would be affected. As such, it is important to keep cells intact so that osmosis remains the driving force for moisture transfer into the intercellular spaces and the overall cause of water removal from the plant tissue (Li & Ramaswamy, 2006a). Biswal et al. (1991) also showed that increased concentration of the osmotic solution resulted in higher moisture loss, indicating that osmotic dehydration should be conducted at near-saturation concentrations in order to obtain maximum results. However, as seen with temperature there is a maximum observable effect as beyond 65% increasing sucrose concentration has no effect on final moisture content (Ponting et al., 1966).

Solids gain was also found to be increased as a function of temperature and concentration as well as contact time (Li & Ramaswamy, 2006a). In this study, solids gain response to increases in temperature and concentration was shown to be exponential. However, at high concentrations (60°Brix), solids gain was less than at lower concentrations (50°Brix). A similar effect was seen by Nsonzi and Ramaswamy (1998a), in which the effective moisture diffusivity increased with increasing temperature and sucrose concentration, except for at 40°C where the 70°Brix solution showed lower moisture loss than the 60°Brix solution. This was most likely due to the rapid creation of a dense superficial layer in the sample which would block solid mass transfer (Nsonzi & Ramaswamy, 1998a; Li & Ramaswamy, 2006a). The formation of this surface layer of solute may promote crystallization of sugar and hinders mass transfer of both moisture out of and solute into the cell (Nsonzi & Ramaswamy, 1998a). This effect may explain results obtained by van Nieuwenhuijzen et al. (2001), in which rates of solids gain by apple samples decreased with increasing concentration. However, it was also found that both temperature and concentration had a highly significant effect on the moisture loss and solids gain of apple cylinders (Azarpazhooh & Ramaswamy, 2010b).

There is also an impact of osmotic process parameters on subsequent drying steps. For instance, Ramaswamy and Nsonzi (1998) also found that for finish-drying of osmotically pre-treated blueberries both temperature and solute concentration had a statistically significant effect on the air drying kinetics. Increases in either concentration or temperature promoted moisture loss during osmotic dehydration, thereby decreasing the amount of water necessary to be removed during the finish-drying stage and therefore the time necessary to complete the operation. Contact time showed a similar trend, only not to the degree where it was shown to be statistically valid. The exact effects for a given sucrose concentration depended on temperature, showing significant interaction between the two parameters. At 50°C, increasing concentration beyond 55°Brix led to increasing air drying time, most likely due to alterations to tissue structure or composition of the sample, thereby reducing permeability and delaying drying (Ramaswamy & Nsonzi, 1998). A similar effect was found in the case of microwave-osmotic treatments of apple cylinders, where moisture diffusivity during finish-drying was found to be significantly increased by increasing contact time and temperature (Azarpazhooh & Ramaswamy, 2011a).

2.4.4 Plant Tissue

Typical tissue parameters of interest include cell packing and porosity, membrane permeability surface-to-volume ratio, which are in turn generally dictated by product cultivar and ripeness (Chiralt & Talens, 2005). Because of the relative complexity of the structure of plant cells, the osmotic dehydration cannot simply be described as a process that takes place across a semi-permeable membrane. In fact, there are three major pathways for mass transfer in a biological material during osmotic dehydration: (1) the movement of material within extracellular volume towards the cell membrane (apoplasmic transport), (2) the transport of material between neighbouring cells through plasmodesmata and (3) the trans-cell membrane flux (Marcotte & Maguer, 1991). Initially, the solution will penetrate into the materials pores due to capillary pressure (Fito, 1994). The porous structure allows for spaces between cell (intercellular spaces) or voids created by collapsing cells creates a capillary action, drawing the osmotic solution into contact with the cells inducing the action of hydrodynamic mechanisms (HDM), an effect that will be more pronounced in more porous plant tissues (Fito, 1994; Fito & Pastor, 1994; Chiralt & Talens, 2005). Furthermore, loss of water from a cell reduces cell volume and causes the membrane to pull away from the cell wall, which in turn deforms the middle lamellae, a structural material which

permanently attaches cells to one another (Alzamora et al., 2000). The subsequent increase in intercellular spaces due to water loss results in changes in internal pressures further promoting of HDM (Chiralt & Talens, 2005). This is in turn the main driving force for the progressive impregnation of solute into the sample as the osmotic process progresses (Barat et al., 1999; Chiralt & Talens, 2005). Moreover, while initial work on osmotic dehydration considered that as an input the plant tissues structure is fixed, recent studies have focused on the effects of various techniques employed to alter the cellular structure of the product; these techniques will be examined in depth in Section 2.6.

2.4.5 Agitation

Agitation has proven to be a key factor in both increasing rate of dehydration as well as limiting liquid-side mass transfer effects (Rastogi et al., 2002). Carcel et al., (2007) found that OD performed while the solution was well agitated obtained higher moisture loss in apple samples when compared to static tests. Agitation ensures proper contact of the solution with the fruit material and also ensures that the concentration and temperature of the solution remain homogenous throughout the process, allowing for the osmotic pressure differential to remain constant at the interface between the solution and the sample (Nsonzi & Ramaswamy, 1998a). Most often low speed agitators are used to ensure proper mixing while minimizing turbulent flow. In the case of a spray based osmotic setup, agitation is analogous to flow rate, where previous work has found flow rate to be of minimal importance in determining the results of an MWODS procedure (Azarpazhooh & Ramaswamy, 2010b). This is likely because even at the lowest flow rate the solution is adequately mixed and distributed.

2.4.6 Solution Ratio and Sample Size

The solution-to-sample ratio is particularly important because it determines the extent to which the concentration changes as water extracted from the product dilutes the syrup, which can result in a decrease in the driving force (osmotic pressure) of the osmo-dehydration process. This can be counteracted by ensuring that there is an initial solution-to-solid ratio of 20:1 or higher (Rastogi et al., 2002). Determination of Fick's law of diffusion depends on the concentration of the osmotic solution being a constant, leading to issues modelling the process mathematically if this assumption cannot be made (Ade-Omoware et al., 2002). Studies based on microwave osmotic dehydration have typically used a solution to sample ratio as high as 30:1 to ensure the water

addition from the sample is negligible (Azarpazhooh & Ramaswamy, 2012; Azarpazhooh & Ramaswamy, 2011b; Azarpazhooh & Ramaswamy, 2011a; Azarpazhooh & Ramaswamy, 2010a; Azarpazhooh & Ramaswamy, 2010c; Azarpazhooh & Ramaswamy, 2010b). Industrially, there is also an interest in reducing the solution-to-sample ratio as employing less syrup translates to lower costs both in terms of smaller quantities of solute required initially and smaller volumes of water to be removed (evaporated) during re-concentration, which by extension reduces energy consumption.

Van Nieuwenhuijzen et al. (2001) showed that both moisture loss and solids gain increased with decreasing sample size. This is explained by the fact that smaller particle size allows for a larger surface area to volume ratio than with larger samples, meaning that sugar can enter the sample more easily and water can leave the sample more easily. Similarly, Ramaswamy and van Nieuwenhuijzen (2002) found that the moisture diffusion coefficient generally decreased with smaller particle size. Therefore, in the case of cut foods, sample size can be altered in order to suit the end goals of the process (i.e. a specific moisture content, solids uptake, or quality parameter).

2.5 Effects of Osmotic Dehydration on Food Characteristics

Like any other food processing operation, osmotic dehydration alters characteristics of the product. However, because of moderate conditions, effects are often advantageous when compared to other drying methods. The extent of changes to the cells varies widely according to the tissue structure as well as the process parameters such as osmotic agent, concentration and temperature (Chiralt & Talens, 2005). While mass fluxes into and out of the cell alter physical properties of the food, cell destruction or deformation can also occur due to the dehydration and gas-liquid exchanges that are taking place across the cell membrane (Chiralt & Talens, 2005). These cellular changes can vary widely even within a sample as cells in direct contact with the osmotic solution may be in perfect equilibrium with the solution while cells further within the sample may be untouched and in their native state. Cell damage will not only affect organoleptic properties such as color or texture, but may also make the product more susceptible to further damage such as changes to volatile compounds, exposure of substrates to enzymes, or development of off-flavor chemicals associated with changes in respiratory pathways (Chiralt & Talens, 2005). In terms of nutritional content, osmotic drying has been shown to increase nutrient retention during subsequent drying steps such as hot air drying (Krokida et al., 2000).

2.5.1 Color and Flavor

Osmotic dehydration stimulates the movement of pigments and flavors out of the food material to such a degree that it may be feasible to further market the syrup as a natural additive to other food or cosmetic products after several use cycles (Osorio et al., 2007). Even though pigments are lost to the osmotic syrup during osmotic drying, several studies have shown that the OD process improves quality (in terms of color, texture, and rehydration capacity) after finish-drying when compared to samples that were only air-, freeze- or vacuum- dried (Lerici et al., 1985; Nsonzi & Ramaswamy, 1998b; Azarpazhooh & Ramaswamy, 2011b). Additionally, osmotic drying largely excludes oxygen and allows for the elimination of sulphur dioxide application to the fruits, which is typically applied to maintain color during dehydration (Torreggiani, 1993; Grabowski et al., 1994; Raoult-Wack, 1994; Lazarides et al., 1995; Lenart, 1996; Krokida et al., 2000). In one case, non-sulphited grapes dried by osmo-convection were slightly browner than those sulphited prior to convective drying, however the samples were free of the unacceptable residual sulphite smell (Grabowski et al., 1994).

Although the sugar infused into the sample has been shown to provide a protective effect on pigments (Raoult-Wack, 1994), Chiralt and Talens (2005) demonstrated that the color and transparency of fruits may change considerably during osmotic dehydration due to both physical and chemical changes they summarized as:

1- Degradation or loss of pigments and development of browning.
2- Increased effective concentration of pigments due to water loss, which in turn enhances selective light absorption, refractive index and surface reflection; an effect that will vary by product.
3- Exchange of gas for liquid near the sample surface, which leads to increased homogeneity of refractive indexes, higher light absorption and a resultant increase in sample transparency

Of these, the alteration of fruit pigments and browning represent the most important factors for product acceptance because they result in changes in product hue (Chiralt & Talens, 2005). As described by Krokida et al. (2000), maintaining color during drying is marked by relatively constant L^* (lightness), a^* (red - green) and b^* (yellow - blue) values. This study found that when subjected to an osmotic pre-treatment, fruit browning during subsequent drying was suppressed

and L^* decreased slightly while a^* and b^* increased slightly. Samples not treated osmotically underwent extensive enzymatic browning, marked by a large decrease of L^* value and significant increase in a^* and b^* values**.** As such, it was found that osmotic dehydration exhibited a protective effect on color by infusing sugar that stabilizes pigments and excludes oxygen to limit enzymatic browning, while at the same time reducing water activity thereby limiting non-enzymatic browning (Krokida et al., 2000). Nsonzi and Ramaswamy (1998b) found that in general drying blueberries tended to increase *L*-values regardless of method, mostly due to degradation of color compounds. In this study, none of the osmo-convective dried samples had total color difference (ΔE) values that were significantly different than those of air dried samples, and only a few of them showed significant differences from freeze-dried samples, showing that osmo-convective drying was a good way to minimize total color change of dried blueberries (Nsonzi & Ramaswamy, 1998b). Moreover, apples dried via a microwave-osmotic treatment with subsequent air drying indicated that the process was able to produce samples with color approaching that of a freeze dried sample (Azarpazhooh & Ramaswamy, 2011b).

2.5.2 Texture

Textural properties are often measured using puncture force and shear tests (Lin et al., 1998). The puncture force required to pierce the sample gives an indication of the extent of case hardening that has taken place during drying while shear tests provide information on the toughness of the product. Osmotic dehydration alters product texture attributes by modifying cell structure both physically and chemically (Lewicki & Porzecka-Pawlak, 2005; Chiralt & Talens, 2005). Mechanical properties of dried products are closely related to the physical state and structure developed as a result of typical deformations such as cell shrinking or swelling, changes in intercellular spaces (volume) and rupturing of cell bonds (Contreras et al., 2006). These changes influence mechanical behavior in several fashions; first, air and liquid volumes within the sample change as solute is taken into the food, and the size of the product can be altered as well (Fito, 1994). Secondly, detachment of the middle lamella of plant cells results in the loss of cell turgor, which in turn affects cell wall and puncture strength (Alzamora et al., 2000; Chiralt et al., 2001; Chiralt & Talens, 2005). Finally, compositional changes and concentration profiles of both water and solute particles created within the sample also affect texture, where sugar infused during osmotic dehydration appears to reinforce the cellular matrix and tissue structure (Salvatori et al.,

1998; Raoult-Wack, 1994). Overall, properties of the cell wall and the middle lamella and their effect on cell turgor pressure represent the most significant factors that affect texture of food products (Chiralt et al., 2001). Contreras et al. (2007) also report that soluble pectin levels increase during drying, resulting in a firmer and more rigid structure in the product.

While most foods exhibit viscoelastic behavior, sugar uptake during osmotic dehydration will decrease elasticity in food products and increase viscosity (Telis et al., 2005). Additionally, changes in viscoelastic behavior after rehydration is due to damage done to the product during the drying process (Krokida et al., 1999). As a result, understanding these changes and minimizing their impact could have a positive effect on maintaining the viscoelastic properties of the fresh product. Monsalve-Gonzalez et al. (1993) found that osmotically dried apple pieces became significantly softer and more plastic (less elastic) when compared to their fresh counterparts. This effect was especially pronounced on the outer edges of the sample, and while adding calcium chloride minimized the softening, the typical crispness of fresh apple could not be maintained. The inverse appears to be true when an osmo-dehydrated product is freeze dried as the elasticity increases (Telis et al., 2005). Prothon et al. (2001) determined that osmotically dehydrated products typically have a softer product tissue because of calcium leaching, and Nsonzi and Ramaswamy (1998b) found that for the most part osmo-convective dried blueberries were softer than those dried by conventional hot air drying. However, samples treated at some conditions such as high sugar contents resulted in a harder texture than those dried by hot air, an effect that is most likely due to the increased sugar level causing case-hardening during finish-drying (Nsonzi & Ramaswamy, 1998b). Similarly, grapes dried via a fluidized bed osmo-convective setup proved to be more pliable than those dried solely by hot air convection (Grabowski et al., 1994). Moreover, samples dried via a microwave-osmotic/air drying operation were found to be softer than those prepared using hot air drying alone (Azarpazhooh & Ramaswamy, 2011b).

2.5.3 Rehydration Capacity

In many cases, such as when incorporated into a breakfast cereal, dried products are rehydrated prior to consumption. Rehydration comprises three simultaneous steps: absorption of the water into the dry material, swelling of the rehydrated product, and loss of soluble components (Lee et al., 2006; Maldonado et al., 2010). There are three general approaches to predict rehydration capacity: (i) water absorption capacity (WAC), which gives the ability of a matrix to

absorb water that was lost during drying; (ii) dry mass retention capacity (DHC), which measures the ability of a material to retain soluble solids after rehydration and (iii) rehydration ability/capacity, (RA or RHC, respectively), which measures the ability of a dehydrated product to re-hydrate, thereby giving an indication of damage caused to tissues during drying (Maldonado et al., 2010). Rehydration is also considered to be positively affected by temperature, where higher temperatures increase rehydration rates as well as the equilibrium moisture content the sample will obtain (Krokida & Marinos-Kouris, 2003).

Rehydration capacity is typically tested using water or other aqueous solutions such as juices, milk, or glucose solutions, among others, depending on how the product would likely be used (Lee et al., 2006). The aim for rehydration is to restore the water that was present in the original fresh samples in other to re-obtain the original product characteristics. However, the degree to which a product can be rehydrated is inversely proportional to the amount of cellular and structural disruption in the sample caused by dehydration, a certain degree of which is unavoidable (Lee et al., 2006; Krokida & Marinos-Kouris, 2003). As a result, the degree of rehydration can be used as a quality index for dehydrated products. It has been found that osmotic dehydration increases the rehydration capacity of apple slices (Taiwo et al., 2001). Similar results were found with microwave-osmotic treated apple cylinders, which provided excellent rehydration characteristics approaching that of the freeze dried sample (Azarpazhooh & Ramaswamy, 2011b). Conversely, it was found that osmotically dried blueberries provided a lower rehydration capacity than either freeze or convective air dried samples, and therefore may be better suited to direct consumption without rehydration (Nsonzi & Ramaswamy, 1998b). The conflicting nature of these reports indicates that the effects of osmotic dehydration on rehydration capacity will depend on the properties of the sample itself as well as parameters used during the process.

2.5.4 Cell Structure

As previously discussed, cell structure will have a significant bearing on the properties of the final product in terms of texture and rehydration capacity. Therefore, it is important to monitor the destruction or collapse of the cells that takes place during the dehydration process. Fernandes et al. (2008) observed that differences in cell structure during conventional osmotic dehydration can be observed only after 30 min, where cell walls become distorted and smaller throughout the sample, causing a corresponding increase in intercellular space. In other areas of the tissue,

however, the intercellular spaces were reduced as the cells became swollen. As the process continued the cells generally increased in size, further eliminating intercellular space, before beginning to break down after 1 h of processing. After 2 h, virtually all the cell walls had lysed and those which were still intact were severely distorted. The cell lysis is generally attributed to diminished cell strength due to solubilisation of pectin as well as the high osmotic pressure and flow of sugar into the fruit (Fernandes et al., 2008). Lewicki and Porzecka-Pawlak (2005) observed the cellular structure of apple tissue before and after osmotic dehydration and found that there was a substantial difference of the effects of osmotic dehydration on cell structure depending on whether or not the cell was surrounding by other cells or was exposed to intercellular spaces. In general, cells surrounded by other cells became more circular at the beginning stages of OD and gradually became more elliptical with folded and wrinkled cell walls over the course of the process. Cells that were in contact with intercellular spaces, however, were distorted and elongated from the very beginning of the process, where the cell wall tended to concave towards the center of the cell and the intercellular spaces themselves became elongated and displayed irregular shapes (Lewicki & Porzecka-Pawlak, 2005). This main difference between this study and that of Fernandes et al (2008), was that Lewicki and Porzecka-Pawlak (2005) found that at no time during the OD process were there broken or damaged cell walls. There is no explanation proposed but the difference may be due to the cell structure itself, the higher concentration of the osmotic solution (70°B for the melon dehydration versus 61.5°B for the apple) as well as the fact that watermelon has much higher moisture content than apple (92% versus 84% for the apple), resulting in more cell deformation as the mass of water is removed, eventually resulting in more severe structural changes and eventually lysis.

Fernandes et al. (2008) also applied an ultrasound pre-treatment to a separate set of melon samples before subjecting them to OD. The structure changes induced by ultrasound were found to be different than those caused by osmotic dehydration; there was no lysis of cells after ultrasound but it did cause dislodging of cells and cell compression, changes that resulted in the formation of microchannels. Cell disruption and lysis are the goals of various methods employed to improve mass transfer during osmotic dehydration, a range of which are presented in the following section.

2.6 Improving Osmotic Dehydration

Because conventional osmotic dehydration is such a slow process, there have been various studies on improvements that aim to enhance moisture transfer while improving product quality, including treating the skin of waxy fruits (Grabowski et al., 2007), determining optimal solution temperature (Li & Ramaswamy, 2006a) and applying technologies such as pulsed vacuum (Ito et al., 2007; Chafer et al., 2003), ultrasound (Rodrigues & Fernandes, 2007; Fernandes et al., 2008), pulsed electric field (Andrés et al., 2007), high pressure (Rastogi & Niranjan, 1998), as well as microwave energy (Li & Ramaswamy, 2006c; Azarpazhooh & Ramaswamy, 2012; Azarpazhooh & Ramaswamy, 2011b; Azarpazhooh & Ramaswamy, 2011a; Azarpazhooh & Ramaswamy, 2010a; Azarpazhooh & Ramaswamy, 2010c; Azarpazhooh & Ramaswamy, 2010b).

2.6.1 Skin Treatments

Small berries and similar fruits have a waxy outer skin (cuticle) designed to keep the berry from drying out during growth as well as provide protection from weather, insects, and parasites (Grabowski et al., 2002; Grabowski et al., 2007). The cuticle layer is made of a variety of waxes and cutin, which if left intact will have little permeability to moisture and will therefore diminish the effectiveness of dehydration operations (Grabowski et al., 2002). Fruits that possess this attribute generally require a skin pre-treatment in order to avoid the need for much longer osmotic drying times which would lead to high energy consumption and low product quality (Saravacos & Charm, 1962; Grabowski et al., 2002). Pre-treatment steps generally require that the agent used to disrupt the skin should be cheap, non-toxic, water soluble (or easily dispersible) and possess a relatively low molecular weight (Grabowski et al., 2002).

Treatments to disrupt the cuticle layer can be classified as chemical, thermal, mechanical or combination in nature (Lewicki, 1998; Grabowski et al., 2007). Grabowski et al. (2007) used cranberries to compare various techniques from each category for their effect on taste acceptability as well as effect on moisture loss in later processing. Overall, the treatment deemed to be most effective was mechanical halving of the cranberries as this technique allowed for the osmotic solution to come into full contact with the inner flesh of the fruit, resulting in a 100-fold increase in the mass diffusion through the open area and an additional moisture content decrease of 4.25% (dry basis) over the length of drying when compared to untreated berries. Other benefits of slicing the berries include the exclusion of chemicals (such as ethyl oleate or NaOH) or heat (steam or

boiling water at 100°C), which could alter sensory attributes or bioactive molecules within the fruit flesh. The same authors found that steamed samples allowed the berries to be left intact and provided the next-best moisture loss improvement when compared to the halved cranberries, but they also found that steamed berries ranked relatively low in terms of taste acceptability as determined by an informal taste panel. Other studies have found that blanching the berries in boiling water for 120s had no positive effect on moisture removal, but rather lowered the dry basis moisture content by increasing sugar uptake (Rennie et al., 2007; Chafer et al., 2003).

2.6.2 Vacuum in Osmotic Dehydration

Vacuum can be used in osmotic dehydration to enhancing mass transfer of both moisture and solids across the cell wall, where vacuum has a larger effect on moisture loss than on solids gain (Fito, 1994; Ito et al., 2007). Pulsed vacuum is most often used for biological materials because extended time under high vacuum during osmotic dehydration can cause irreversible deformation of the food tissue and decrease the free volume available for impregnation of solute (Ito et al., 2007). As described by Fito and Pastor (1994), reasons for enhanced mass transfer kinetics under VOD conditions are twofold: first HDM contribute to total mass transport in a much more important fashion when compared to atmospheric conditions, and secondly other mechanisms (diffusional and osmotic) have a larger interphase surface due to larger occupation of intercellular spaces, which allows for higher mass transport.

Chafer et al. (2003) applied pulsed vacuum osmotic dehydration (PVOD) at 50mbar for initial 5 min to pear samples in order to promote vacuum impregnation of the solute. It was determined that PVOD favored solids gain in unblanched samples, whereas for blanched samples PVOD appeared to promote water loss over solids gain. It was also found that in terms of texture there was no negative impact of PVOD beyond those already exhibited by OD, as both samples became softer. They reported that PVOD did preserve fruit color, most likely due to two mechanisms: (1) VOD limits browning by excluding oxygen from contact with the internal part of the tissue in the intercellular spaces and (2) the leaching/removal of the components of the broken cells on the surface of the piece of sample where endogenous enzymes and substrates would normally be in contact, producing enzymatic browning. The authors also noted that lightness (L^*) of the PVOD sample decreased, most likely due to an increase in transparency induced by degasification of the outer layer of cells in the sample (Talens et al., 2002; Chafer et al., 2003).

However it has also been found that PVOD improves *L**-value in apple samples (Deng & Zhao 2008a). Further studies confirm that the application of vacuum during osmotic dehydration allows higher water diffusional rates at lower solution temperatures for mangoes, apricot, pineapple and strawberry (Ito et al., 2007; Shi et al., 1995). In general, fruits with a higher porosity are more conducive to VOD treatment (Shi et al., 1995). Additionally, Deng and Zhao (2008a) found that application of pulsed vacuum resulted in higher solids gain and lowest loss of firmness of Fuji apple samples. These results stem from PVOD samples having only moderate cell deformation and collapse when examined using scanning electron microscopy.

2.6.3 Ultrasound in Osmotic Dehydration

Ultrasound has been investigated in recent years for its potential to increase mass transfer during osmotic dehydration (Rodrigues & Fernandes, 2007). Ultrasonic technology has good potential because of its ability to increase mass transfer at ambient temperatures, thereby enhancing drying rates as well as reduced oxidative damage and heat-induced degradation reactions (Mason et al., 1996; Rodrigues & Fernandes, 2007; Fernandes & Rodrigues, 2007). It was also found that both ultrasound as well as PV-OD depressed a_w, making the fruit less susceptible to degradation processes (Deng & Zhao, 2008a).

Rodrigues and Fernandes (2007) subjected melon cubes to ultrasound in a water bath prior to OD and determined that this method removes sugar and alters tissue structure making it more easily traversed by water molecules during subsequent drying operations, enabling faster finish-drying as well as the ability to create lower-sugar dried fruit products. A similar study subjected Fuji apple samples to ultrasound during OD and showed that although water loss was enhanced, there was also the significant damage to cell structure and cell collapse which resulted in lower product firmness (Deng & Zhao 2008a). However, this effect can vary according to target tissue and intensity, as when applied to melon there was no cell collapse observed, there was only the creation of micro channels between the cells (Fernandes et al., 2008). When ultrasound is applied during OD, it has been shown that the apple samples show a 117% increase in effective water diffusivity and 137% increase in dry matter diffusivity when compared to a static OD process, which would allow for an overall shorter process time (Cárcel et al., 2007). Overall, the enhanced water diffusivity is most likely due to the creation of micro channels within the tissue that allow water to move more readily and there is more research necessary to determine the full extent of

damage this does to the cell tissue and to determine the ideal ultrasonic frequency to be used in this process (Cárcel et al., 2007; Rodrigues & Fernandes, 2007; Fernandes et al., 2008).

2.6.4 Pulsed Electric Field in Osmotic Dehydration

Pulsed electric field is another emerging technology that has been studied for application during osmotic dehydration. In this technique, short bursts of electric field are applied to the sample, creating small holes in the cell wall which increase permeability and water diffusivity while minimally altering the food matrix (Ade-Omoware et al., 2002). Exposure to high intensity electric field pulses (HELP) enhanced moisture removal while limiting solids gain in apple, which was attributed to the good structural integrity after HELP treatment as determined by conductivity testing (Taiwo et al., 2003). This work also concluded that samples that underwent HELP pre-treatment prior to osmotic dehydration were brighter in color, better retained ascorbic acid, and provided a firmer texture when compared to samples that underwent traditional pre-treatments such as blanching or freezing.

A similar study was performed by Rastogi et al. (1999) in which carrot slices were subjected to HELP prior to osmotic dehydration. For both solids and water, the effective diffusion coefficient increased exponentially as a function of increasing electrical field strength up until 1.09kV/cm, beyond which increased field strength had little effect. Overall, the application of HELP to the carrot slices increased the mass transfer rates during the subsequent osmotic drying procedure. However, much like high pressure treatments HELP contributes to cellular disintegration and loss of texture (compressive strength). Much like the diffusion coefficients, the compressive strength did not change much with applied fields of over 1.09kV/cm, leading to a correlation between cell damage and these parameters (Rastogi et al., 1999). It has also been shown that membrane breakdown is not the main factor determining solute uptake, indicating that this pre-treatment has good potential for promoting moisture loss over solids gain (Taiwo et al., 2003).

2.6.5 High Pressure in Osmotic Dehydration

Exposing pineapple pieces to high hydrostatic pressure for 5 min enhanced moisture loss and solids gain during subsequent osmotic treatment when pressure levels up to 400MPa were used, where higher pressures had little effect on the moisture diffusivity (Rastogi & Niranjan, 1998). Furthermore, microscopic analysis confirmed that there was extensive cell rupturing, where the severity of the damage was directly correlated to the pressure of the HP treatment. As a result

this study concluded that the cell rupturing allowed for more complete moisture removal because the cell membranes could no longer retain water. Textural analysis also showed that the pressure treatment decreased puncture force in samples exposed to pressures up to 300MPa, beyond which the additional pressure had little effect. Overall the cell collapse contributed negatively to sample texture and also limited rehydration capacity (Rastogi & Niranjan, 1998). A similar study demonstrated that not only did pressure increase moisture loss during osmotic treatment but it made even more of an impact on solids (sugar) uptake, making it suitable for products that require sugar uptake as part of processing (Taiwo et al., 2001). This by extension indicates that high pressures effectively destroy the cellular structure, allowing relatively free movement of moisture and solute in the plant tissue.

2.6.6 Microwave Energy in Osmotic Dehydration

Microwave based drying techniques are more typically employed during finish-drying because of the ability of electromagnetic energy to penetrate into the sample and enhance moisture removal. This effect is particularly evident during the falling rate period, as the inner residual water is selectively heated thereby forcing the moisture outwards (Orsat et al., 2007). Microwave energy was more recently applied during osmotic dehydration, in either immersion (Li & Ramaswamy, 2006c) or spray based configurations (Azarpazhooh & Ramaswamy, 2010a; Azarpazhooh & Ramaswamy, 2011a; Azarpazhooh & Ramaswamy, 2011b; Azarpazhooh & Ramaswamy, 2012; Azarpazhooh & Ramaswamy, 2010b; Azarpazhooh & Ramaswamy, 2010c; Wray & Ramaswamy, 2013). Initially (Li & Ramaswamy, 2006c) it was found that apple cylinders that were exposed to microwave energy while submerged in a continuous flow of osmotic syrup had improved moisture transfer rates when compared to conventional osmotic dehydration (COD), while solids gain was reduced compared to prior studies using both traditional static batch (Li & Ramaswamy, 2006a) and continuous flow (Li & Ramaswamy, 2006b) conditions in the same experimental setup. The enhanced moisture transfer persisted even when the osmotic solution temperature was lower, thereby preventing heat-induced loss of labile nutrients or flavor volatiles. In the immersion technique (Li & Ramaswamy, 2006a; Li & Ramaswamy, 2006b; Li & Ramaswamy, 2006c), samples were submerged in a relatively large volume of osmotic solution. Therefore, the incident microwave energy would be predominantly absorbed by the osmotic solution itself and as a result wouldn't have as large an effect on the samples themselves. To that end, improvements to this

method were made by modifying the apparatus to a spray setup (Azarpazhooh & Ramaswamy, 2010c). In this case, microwave-assisted osmotic dehydration (MWOD) of apple pieces were performed under continuous spray (MWODS) conditions and compared to the earlier developed immersion (MWODI) conditions. By continuously coating the samples with a thin layer of temperature controlled osmotic solution in the MWODS setup, even higher moisture loss and lower solids gain was attainable, as compared to the MWODI technique (Azarpazhooh & Ramaswamy, 2010c). This was attributed to more microwave power being incident on the samples themselves instead of being absorbed by the osmotic solution, which would in turn promote the driving of moisture out of the samples.

As an additional benefit, by spraying the osmotic solution, the classical issue of food pieces floating in the osmotic solution was avoided, which has been described in the past as an issue with the process (Raoult-Wack, 1994). When combined with hot air drying to produce a shelf stable product, the MWODS-air dried samples were shown to be softer and chewier than either the freeze dried or air dried (without osmotic treatment) samples, which were brittle and hard, respectively (Azarpazhooh & Ramaswamy, 2011b). Moreover, the color of the MWODS-AD samples either approached or exceeded that of the freeze dried samples. Overall, the MWODS process was shown to provide higher moisture loss and weight reduction in combination with the lower solids gain and shortest process time when compared to earlier iterations of microwave-osmotic or conventional osmotic treatments.(Azarpazhooh & Ramaswamy, 2010a) As a result, MWODS provides a good basis as a primary drying step in the development of new drying techniques.

2.7 Principles of Microwave Heating

With this application in mind, and before examining the range of finish-drying techniques, it is first important to understand the principles and heating mechanisms of electromagnetic radiation, and specifically microwave energy. Microwaves are members of the electromagnetic spectrum in the frequency range of 300MHz to 300GHz. Frequencies reserved for microwave heating applications include the 915MHz, 2450MHz, and 5800MHz bands, where 2450MHz is most commonly used for food production, and exclusively so in consumer based microwave ovens (Ramaswamy & van de Voort, 1990; Orsat et al., 2007; Venkatesh & Raghavan, 2004). Microwaves heat foods differently than conventional heating methods, where in conventional thermal processes, energy is transferred to the material through convection, conduction, and

radiative heat transfers (Venkatesh & Raghavan, 2004). Conversely, microwaves cause the material to heat internally according to the dielectric properties of the target material, causing an effect known as volumetric heating (Nijhuis et al., 1998; Orsat et al., 2007; Beaudry et al., 2004). More specifically, heat production within the food product is the result of the following two mechanisms: first by molecular friction due to the rapid movement of molecules with permanent dipole moments in response to the changing direction of microwaves, which takes place 2.45 billion times per second in the case of the 2450MHz band. Secondly, the charge drift of ionic species under the action of the microwaves leads to collisions between ions and increasingly disordered kinetic energy throughout the sample and subsequent heat generation (Nijhuis et al., 1998; Orsat et al., 2007). Non-polar molecules that are asymmetrically charged may behave as dipoles in an electric field, but their responses to microwave energy are typically an order of magnitude less than that of water (Venkatesh & Raghavan, 2004). This, together with the fact that foods are typically made up largely of water (i.e. a molecule with a permanent dipole), the molecular friction mechanism is mainly responsible for heating of foods by microwaves (Nijhuis et al., 1998).

When a material is subjected to electromagnetic (EM) radiation such as microwaves, part of the energy is reflected and part of it is transmitted through the surface, where a fraction of this latter portion is actually absorbed (Venkatesh & Raghavan, 2004). The proportions of energy that fall into these three categories are defined by the dielectric properties of the material, which govern how it will behave when EM radiation is applied (Sosa-Morales et al., 2010; Venkatesh & Raghavan, 2004). More specifically, the dielectric constant (ε') refers to the EM-field distribution in the sample material and indicates the ability of a material to couple with microwave energy, while the loss factor (ε") expresses the loss interactions or the materials ability to dissipate electromagnetic energy as heat (Orsat et al., 2007). These parameters vary with frequency of the applied field, temperature, moisture content, composition and particle density of the sample material (Orsat et al., 2007). Overall, the complex relative permittivity (ε *) expresses the ability of a material to couple with and dissipate EM energy and is described as (Venkatesh & Raghavan, 2004):

$$\varepsilon^* = \varepsilon' - j\varepsilon'' \qquad (2.7)$$

where $j = \sqrt{-1}$, indicating the phase shift between the real (ε') and imaginary (ε") portions of the dielectric constant.

Furthermore, the energy absorbed by the sample is given by the following equation (Orsat et al., 2007):

$$P = 2\pi f \varepsilon_0 \varepsilon'' |E|^2 \qquad (2.8)$$

where P (in W/m^3) is the energy developed per unit volume, f is the frequency of the EM wave in Hertz (Hz), ε_0 is the absolute permittivity of vacuum (8.854188x10^{-12} F/m), ε'' is the loss factor, and $|E|$ is the strength of the electric field (in V/m).

Penetration depth is also topical when considering the application of EM energy to food products, where most fresh foods have a penetration depth of approximately 0.6-1cm at 2450MHz (Venkatesh & Raghavan, 2004). The penetration depth (d_p) is defined as the distance into a sample at which the power has dropped to 1/e (or 36.8%) of its incident power. This can be expressed in terms of the dielectric properties of the material and is given as (Sosa-Morales et al., 2010):

$$d_p = \frac{\lambda o \sqrt{\varepsilon'}}{2\pi\varepsilon''} \qquad (2.9)$$

where λ_O is the wavelength of the microwave in free space, which for 2450MHz = 12.2cm.

The various factors that affect dielectric properties are summed up well by Sosa-Morales et al. (2010) and include: (i) sample composition; (ii) sample density, as the amount of mass per unit volume will determine how much material is present to interact with the electromagnetic field; (iii) temperature, where at low frequencies the loss factor (ε'') will increase with temperature and vice versa at high frequencies; (iv) the frequency of the applied EM field, as molecules tend to react more or less vigorously to different wavelengths depending on their dipole moment and finally (v) storage time, as compositional changes that take place when a food product is in storage may affect its dielectric properties (Sosa-Morales et al., 2010).

One of the most easily controlled factors is the applied frequency of the EM field, where the lower the frequency the higher the penetration depth. When barley was dried at various frequencies, it was found that the final temperature is higher at 2450MHz than at 915MHz or 27MHz (L. P. Wang et al., 2014). This fact likely contributed to the poorer color of the 2450MHz dried product. At 2450MHz, the dominant factor influencing dielectric properties in food products is water content, as this molecule accounts for the majority of absorbance of microwave energy in foods (Venkatesh & Raghavan, 2004; Sosa-Morales et al., 2010). As a result, as the moisture content of a food increases, so too does the dielectric constant and loss factor, resulting in better microwave heating properties for that product (Komarov et al., 2005). It has also been proposed

that the dielectric properties of pure distilled water are always greater than those of food products (Mudgett, 1982). However this assumption may not always be true because microwave absorption is affected by sample mass, geometry, dielectric properties in addition to its physical position within the microwave oven cavity (Yongsawatdigul & Gunasekaran, 1996a).

One of the main issues associated with microwave based drying techniques is temperature uniformity. Because microwaves penetrate the sample and heat is generated within the material itself, the sample is heated more quickly (Alibas, 2007). Moreover, the standing wave pattern within the microwave cavity can produce hot spots within the microwave cavity where the sample will rapidly heat to unacceptable temperatures where damage such as charring will occur. Both the overall temperature and temperature uniformity of the sample can be controlled in several ways. First, suitable power density, or watts of microwave power applied per gram of sample in a given volume of cavity, is critical to minimize the possibility of thermal runaway. Decreasing magnetron output, increasing sample size, as well as increasing cavity size will all have the effect of reducing power density. Further, the modification of duty cycle (magnetron on/off periods) during the process can allow heat to dissipate and temperature to equilibrate throughout the sample between magnetron power-on times. This also allows some time for the moisture to be removed into the surroundings so that the surface of the food product remains free of condensation, thus allowing for further moisture removal from the interior of the product during the next power-on time. The evaporative cooling that takes place as moisture is removed therefore also plays a critical role in reducing product temperature (Gunasekaran, 1990). The use of duty cycle as a means to modify power density can be considered a suboptimal method to control product temperature, in that the off periods represent time where moisture is not being removed maximally and therefore process efficiency can degrade accordingly. To that end, other parameters are often employed to maintain product temperature at acceptable levels. For one, the role of air flow is an important factor in maintaining product temperature, where depending on the temperature sensitivity of the product, the process can make use of heated, ambient or cool air flowing through the chamber. Perhaps most importantly, proper mixing of the sample will move the product in and out of cavity hot spots and therefore spread the applied microwave power more evenly across the bulk of product, increasing temperature uniformity across the sample mass. Similarly, the dispersion of the standing wave pattern within the microwave cavity can ensure the heating is more uniform in relatively thicker materials, thus avoiding thermal gradients typical of conventional heating (Venkatesh &

Raghavan, 2004). Together these principles, along with proper microwave design which ensures microwave energy uniformity, are critical in order to ensure even drying and high quality end products.

2.8 Secondary (Finish) Drying

As a partial drying method, osmotic dehydration needs to be coupled with a secondary (finish) drying step in order to remove moisture to a point where the water activity of the product is sufficiently low to ensure shelf stability. Drying has traditionally been performed using convective hot air drying, but more recently alternative strategies have been employed, such as drying under vacuum or with the addition of microwaves. This section will outline the traditional (hot air) techniques as well as several modern microwave based approaches to finish-drying.

Typically, quality attributes of dried products are monitored using techniques such as color (typically monitored by a colorimeter), texture (Texture Analyzer or Instron device), or sensory quality (taste panel). More and more, chemical markers that are identified as heat labile health positive components in the product such as phenolics and vitamins are being used to more accurately determine damage during drying and thus the suitability of the process for that product. The quality attributes of the product dried via the novel technique is then compared to pre-established benchmarks such as products dried via convective air drying, vacuum drying, or freeze drying. Generally speaking novel methods are relied on to improve product quality in order to justify what would be a substantial investment on an industrial scale and so when possible these comparisons with other drying methods are highlighted as part of the study.

2.8.1 Hot air drying

Finish-drying has traditionally been performed using hot air drying, where samples are held in ovens with or without moving air, for 10-12 hours at temperatures of about 60°C. In one example, convective air drying of cranberries to a moisture content of 15% (wet basis) took 12.6h at 62°C with air circulated at 1.0 m/s (Beaudry et al., 2004). Oven drying is usually used as a reference method for moisture content determination and AOAC methods typically require that fruit samples be dried for periods of 16-20h at temperatures at or above 100°C. However, these time and temperature combinations can still lead to incomplete moisture removal depending on how tightly bound the water is or if it is impeded by low moisture diffusivity or case hardening (Bouraoui et al., 1993). Drying time can be decreased when forced air dryers are used to better remove moisture

from the samples (Yongsawatdigul & Gunasekaran, 1996a). However the main concerns for hot air drying include its notoriously high power consumption, low drying efficiency and the use of high temperatures which degrade important flavor, nutritional and color compounds (Yongsawatdigul & Gunasekaran, 1996a; Yongsawatdigul & Gunasekaran, 1996b; Drouzas & Schubert, 1996; Alibas, 2007). Hot air drying also causes a phenomenon known as case hardening, which is caused by water evaporating faster from the sample surface than its core. The surface dries quickly and acts as a water barrier, trapping moisture in the interior of the sample (Yongsawatdigul & Gunasekaran, 1996a). Overall, the non-uniformity within the dried sample, the slow drying rates and low quality of resulting product can generally be improved by using other drying methods (Beaudry et al., 2004).

In fact, many of the quality loss attributes associated with drying are associated with changes that take place during hot air drying. Drying alters the characteristics of food products, where in general dried fruit suffers from several faults including loss of juiciness and lignified tissue, both of which result in a harder or chewier product (Lenart, 1996). Additionally, changes can be noted in terms of loss of flavors and aroma volatiles, deterioration of color and texture, and an overall decrease in nutritional value, effects that are largely attributed to products' exposure to high temperatures for long periods of time in the presence of air (Nijhuis et al., 1998; Lenart, 1996; Alibas, 2007). These effects are therefore exacerbated by convective air drying, which despite being the oldest dehydration technique, is still the most widely used in the food industry. While air drying has proliferated because of its simple operation, relatively low construction costs, ability to burn biomaterials to provide the necessary thermal energy, and well characterized operating principles, it has also been shown to be hugely energy inefficient and destructive to product quality (Grabowski et al., 2002).

There is an ongoing push from increasingly health aware consumers for higher quality dried products that maintain more characteristics of the fresh product. With that in mind, the key to improving the quality of dried products is to limit changes to the aforementioned quality characteristics during processing. In addition to quality concerns, the main interest from the industrial perspective should be from the perspective of reducing energy consumption and associated long term savings. Microwave based drying techniques have tremendous potential to address both sides of the equation, and examples of recent developments in microwave based techniques for dehydrating food products will be reviewed in the following sections.

2.8.2 Microwave Convective Drying

Microwave energy is rarely used alone in drying processes and is typically combined with a flow of hot air. In a static chamber, moisture can remain on the surface of the product as the cavity infuses with moisture, whereas the flowing air of a microwave-convective setup allows for continual removal of moisture, thereby increasing drying rates and decreasing product temperature through evaporative cooling.

Microwave (MW) energy can be applied in conjunction with convective air drying in three different methods, which were summed up well by Andrés et al. (2004). The first is the application of MW energy at the beginning of the drying process, where the interior of the product is quickly heated to the evaporation temperature causing a large flux of vapor from the inner core of the sample towards the outer surface of the product, to be removed by the surrounding air. In this case, the improved drying rate throughout the process is largely attributed to the puffing of the sample which creates a porous structure that facilitates moisture to flow to the surface (Zhang et al., 2006). Secondly, microwave energy can be applied when the drying rate begins to fall. In this case the moisture near the surface of the product has been removed, while the inner core of the food particle remains moist. The application of MW energy thus heats this trapped moisture to evaporation temperature and promotes its movement to the outer layers of the sample. Finally, microwave energy can also be applied in the final stages of drying in order to remove bound water and to overcome the effects of product shrinkage, which can cause distinct drops in drying rate over time (Zhang et al., 2006; Andrés et al., 2004). Microwave energy is well suited for use in finish-drying because of the volumetric heating effect and its affinity to excite water molecules. As microwaves penetrate into the sample and interact with water molecules, the moist inner core of the sample is selectively heated, thereby creating an internal pressure that pushes water out of the core of the sample (Beaudry et al., 2003; Sosa-Morales et al., 2010). This effect complements air drying which typically takes much longer to dry out the inner portion of a food product and as a result, drying that would take several hours in a conventional oven can be obtained in a matter of minutes in a MW-based setup (Bouraoui et al., 1993).

Over the past several years, microwave energy has been successfully applied during convective air drying of a vast array of food products, including but not limited to apple (Marzec et al., 2010; Prothon et al., 2001), banana (Maskan, 2000), carrot (Prabhanjan et al., 1995), cranberries (Sunjka et al., 2004), strawberry (Contreras et al., 2006; Contreras et al., 2008), grapes

(Tulasidas et al., 1995; Tulasidas, 1995), kiwifruit (Maskan, 2001), potato (Lu et al., 1999), hawthorn (Amiri Chayjan et al., 2014), parsley (Soysal et al., 2006), red peppers (Soysal et al., 2009), spinach (Karaaslan & Tunçer, 2008), soybeans (Gowen et al., 2008; Hemis & Raghavan, 2014), okra (Dadalı et al., 2007), various herbs (Śledź et al., 2013), pistachios (Kouchakzadeh & Shafeei, 2010), tea leaves (Hatibaruah et al., 2013), mushrooms (H. Wang et al., 2014; Bhattacharya et al., 2013), thyme (Sarimeseli et al., 2014) and tilapia (Duan et al., 2011). In most of these studies, the primary goal in applying microwave energy during drying is to reduce drying times, while often quality attributes are recorded and compared to other drying techniques. In both cases, effects will vary by product and experimental setup, in which duty cycle, air flow, power density, sample size, etc, can all have a significant effect on the drying kinetics and final product quality. For instance, a study on microwave-convective drying of soybeans found that drying rate varied with the properties of the incoming air, where drying rate increased with higher relative humidity and lower air temperature (Hemis & Raghavan, 2014).

The applicability and benefit to the application of microwave energy during drying will vary according to product. In the case of carrot slices, drying time was reduced by 25-90% and product quality was enhanced as compared to slices produced by conventional air drying (Prabhanjan et al., 1995). For kiwifruit, drying times were reduced by 40-89% and produced samples with less shrinkage and better rehydration characteristics when subjected to microwave-convective drying as opposed to convective alone (Maskan, 2001). For bananas, the inclusion of microwave energy reduced drying time by 64.3% and produced a lighter colored banana sample with the highest rehydration value (Maskan, 2000). More recently microwave-convective drying was compared with electrohydrodynamic (EHD) drying for banana slices, where the MW based technique reduced drying times but the EHD process induced the least color change (Esehaghbeygi et al., 2014). For cranberries it was found that drying times for microwave drying ranged from 2.2-5h whereas hot air drying in the same setup took 12.6h (Beaudry et al., 2003). Microwave convective drying of garlic reduced drying times by up to 80% as compared to hot air alone, and produced a higher quality product (Sharma & Prasad, 2006). Collard greens dried via microwave dehydration were found to provide optimal drying time, color and ascorbic acid content when compared to vacuum and air drying (Alibas, 2009). Similar results were later found for grape leaves (Alibas, 2014). In the case of sage leaves, the amount of essential oil in sage leaves decreased during microwave-convective drying, whereas the loss was minimal during air drying

alone (Esturk, 2010). For oyster mushrooms, the application of microwave during convective drying reduced dehydration times by 75% and the authors noted the technology also enables other benefits such as uniform energy distribution, high thermal conductivity to the inside of the product, reduced footprint, precise process control, fast start-up and shut-down times, and potential for energy savings (Bhattacharya et al., 2013). In the case of shiitake mushrooms, while the microwave-convective process dried the samples in the shortest period of time, both the radio frequency and mid-infrared based techniques produced higher quality end products (H. Wang et al., 2014). For pumpkin slices, microwave-convective drying was found to be the most suitable method as compared to microwave alone and traditional air drying when compared in terms of drying times, energy consumption, and color characteristics (Alibas, 2007). Another study found that osmotically pre-treated strawberries that were finish dried using a combination of hot air and microwaves resulted in final product quality that was comparable to freeze drying but had a significantly shorter drying time (Venkatachalapathy & Raghavan, 1999).

While the studies listed above show the potential for the application of microwaves during drying there are also various drawbacks to using microwaves in dehydration, of which the most typical are poor accuracy and repeatability (Bouraoui et al., 1993). Moreover, studies are necessary to determine the optimal input parameters in order to avoid uneven heating and optimize product quality. Microwave input parameters (and where applicable, dryer setups) must therefore be properly tested and designed to not only maintain product quality but also to ensure the proper functioning of the drying apparatus and to limit potential damage from microwaves reflecting back into the magnetrons which will cause damage. From a product perspective, uneven or excessive microwave energy application will lead to rapid localized temperature increases and subsequent destruction of volatiles and charring along with under-dried samples in other locations (Bouraoui et al., 1993; Drouzas & Schubert, 1996). The use of microwave can also promote caramelization reactions due to the high sugar content of some fruits, particularly those that have been osmotically pre-treated. Additionally, high moisture content of food samples in combination with a relatively intact cellular structure can lead to localized pressure build-up and higher internal temperatures unless the structure allows for larges fluxes of vapor (Bouraoui et al., 1993). These issues are mostly due to sample heterogeneity, uneven power density and geometric effects like partial reflection at interfaces and are usually avoided by applying a lower power density (i.e. by increasing sample size or reducing microwave power), which allows for more even heat

distribution and reduced charring (Bouraoui et al., 1994). One recent study outlined that a process with high initial applied power which was then continued at the lowest power setting still shortened the process time and gave the best quality of beetroot and carrot slices and alleviated the color change and loss of carotenoids seen with higher power processes (Musielak & Kieca, 2014). Many studies on microwave-based drying of foods have focused on alleviating these issues by integrating other techniques or principles such as application of vacuum or incorporation of flowing air in the form of a spouted or fluidized bed. The following sections will provide a review of these methods designed to overcome these typical drawbacks of microwave based drying.

2.8.3 Microwave-Freeze Drying

Freeze drying operates below the triple point of water and therefore allows for removal of water by sublimation, wherein water transforms directly from its solid form (ice crystals) to a gas, bypassing the liquid state. This process therefore allows for low drying temperatures and high product quality, where freeze dried products are often regarded as a 'best case' scenario in terms of quality and are therefore often used as a reference for other drying procedures (Lenart, 1996; Nijhuis et al., 1998; Azarpazhooh & Ramaswamy, 2010c). Freeze dried products generally possess very good structural rigidity which prevents structural collapse and maintains the porosity of the food matrix, enabling the excellent rehydration capacity that is typical of these products (Beaudry et al., 2004). However, this technique is also very expensive, where at an industrial scale the cost of freeze drying has been estimated to be 5-10 times more than hot air drying, limiting its use to high value products (Duan et al., 2007). Along with installation costs, the expensive nature of freeze drying can be mainly attributed to energy, which is very high due to the high level of vacuum that must be maintained throughout in order to allow sublimation as well as the fact that the product must first be frozen. As the process can take several days to achieve the desired moisture content, enhancing the rate of moisture removal during freeze drying would reduce the amount of time required, increase throughput, and as a result likely reduce its energy consumption.

One way this has been addressed is through the development of microwave freeze drying (MFD). However, MFD is not a recent breakthrough—the technique was first studied decades ago and proven to be effective in reducing the drying time associated with traditional freeze drying (FD) (Copson, 1958). Since then, however, various technical problems have restricted the use of MFD to laboratory settings. Corona discharge and arcing can be an issue at the high vacuum levels

required for freeze drying and can result in localized thawing of the sample. Another major issue is the non-uniform distribution of the microwave field in the chamber, which in turn leads to uneven heating of the product, which can in some cases lead to overheating and quality deterioration (Duan et al., 2007). These issues have largely been addressed by cyclically modulating the pressure in the chamber in synchronization with magnetron power-on times to address both the overheating of the sample as well as the corona discharge (Lombraña et al., 2001). Various studies (Ma & Peltre, 1975; Wang & Shi, 1998; Tao et al., 2005) have developed partial models for the process, however while these models can predict the MFD process to a certain degree, a model incorporating the electromagnetic field distribution in the chamber needs to be developed in order to fully predict the process and expand its use (Duan et al., 2007).

Regardless of these issues, various studies have looked at the applicability of the MFD process to various food products. The potential for this process is substantial, as some results indicate that the switch from FD to MFD can enable energy savings of up to 35.7%, with 40% shorter drying times in the case of banana slices (Jiang et al., 2013). In this case, all but the highest applied power density (2W/g) produced banana chips that were acceptable to consumers (Jiang et al., 2013). Further, bananas of various maturity levels could be used, where those of medium maturity level providing the best sensory scores (Jiang et al., 2010). Cabbage was subjected to MFD where it was found that the process reduces drying time by 50% when compared to freeze drying alone, and has additional benefit of being able to perform a sterilization operation as part of an integrated process (Duan et al., 2007). Moreover, the drying rate increased with increasing microwave power and decreased pressure and material thickness (Duan et al., 2007). MFD was also applied to onion slices, where it was found that the dried onion slices were comparable with regular freeze drying while drying times were reduced by up to 96% with associated savings in terms of energy and capital investment (Abbasi & Azari, 2009). In the case of sea cucumbers, the MFD process was found to be highly useful to dehydrate a product that is inherently difficult to process and preserve (Duan et al., 2010). In this case, the pressure applied was between 50-100 Pa in order to avoid issues associated with corona discharge. The sea cucumbers could also be pre-treated with a nanoscale of silver in order to reduce the microbial load and alter their dielectric properties, with no apparent change in drying time or sensory attributes (Duan et al., 2008a). For potato, it was also concluded that below 1.6W/g, the application of microwave yielded no significant differences from conventional freeze dried samples in terms of rehydration rate or

texture (Wang et al., 2010b). Moreover, compared to conventional freeze drying of potato slices, MFD reduced drying times by 37% and yielded no significant loss of Vitamin C, sugar, and starch (Wang et al., 2010c). A study on the application of MFD to beef found that the process was particularly beneficial to large beef pieces, where drying times were most significantly reduced from traditional freeze drying (Wang & Shi, 1999). Recommendations from this study outline that the electric field strength should be lower than 150 V/cm at a pressure of about 10 Pa in order to avoid corona discharge (Wang & Shi, 1999).

In terms of formulated food products, MFD has also been applied in the production of instant vegetable soup mixes (Wang et al., 2009; Wang et al., 2010a). Initially, it was found that drying time and product quality decreased with increasing microwave power, while too low a power led to excessively long drying times (Wang et al., 2009). In this case, a power density of 1.0-1.5W/g, material thickness of 15-20mm, and material temperature of 50-60°C produced an acceptable dried sample in a relatively short period (Wang et al., 2009). Later work studied the effect of individual ingredients, where addition of NaCl and sucrose decreased drying times, while sodium glutamate had no effect (Wang et al., 2010a). This study highlights the importance of tailoring a product for MFD processing, where more lossy materials play an important role in terms of dictating heat transfer and subsequent drying time. To that end, an interesting derivative of MFD has been explored by studies in which a dielectric material with a large loss factor is frozen within the product (Wang et al., 2005; Wang & Chen, 2003). Since the dielectric material has a much higher loss factor than either the ice or solid, microwave energy will be preferably absorbed by the dielectric material and heat conducted to the sublimation front (Wang et al., 2005). In these cases, the MFD drying times with the dielectric material were reduced significantly from when no microwave energy was applied or if the dielectric material was omitted.

2.8.4 Microwave Fluidized/Spouted Bed

As previously mentioned, one of the main issues with microwave based drying techniques is local heat building and thermal runaway. Therefore, an emerging field of research is the application of microwave energy during spouted or fluidized bed drying in order to ensure the proper mixing of the sample and more even distribution of the applied energy throughout the sample load. As a result, these techniques typically enhance both the rate of moisture removal and product quality. Microwave assisted fluidized-bed (MFB) has been studied with many products

including carrot (Wang et al., 2002; Stanisławski, 2005), garlic (Abbasi Souraki & Mowla, 2008), macaroni beans (Goksu et al., 2005), peppercorns (Kaensup & Wongwises, 2004), soybeans (Zare & Ranjbaran, 2012), and shelled corn (Momenzadeh et al., 2011), among others. For carrots, MFB drying times were found to be 2-5 times faster than fluidized bed (FB) alone (Stanisławski, 2005). For macaroni beans, this drying time reduction was approximately 50% (Goksu et al., 2005). In the case of peppercorns, drying times were reduced by as much as 80-90% when dried via MFB at the same inlet temperatures and airflow speeds and the process allowed for the creation of a new bright yellow color of peppercorn, as opposed to the black product from the traditional process (Kaensup & Wongwises, 2004). For shelled corn, the time reduction was about 50% at a given inlet temperature, and results were able to be accurately modelled using artificial neural network based approach (Momenzadeh et al., 2011). For soybeans, drying times decreased by 83.39-98.07% and energy consumption by 82.07-95.22% when using MFB in place of FB (Zare & Ranjbaran, 2012).

Similarly, microwave-spouted bed (MSB) technique has been applied to various sample types, including sweet potato (Liu et al., 2015; Liu et al., 2014), lettuce cubes (Feng et al., 2012), bulgur and wheat (Kahyaoglu et al., 2010), wheat (Kahyaoglu et al., 2012; Jumah & Raghavan, 2001), potato (Lu,Zhang,Liu,et al., 2014; Yan et al., 2010b), carrot (Yan et al., 2010a), and blueberries (Feng et al., 1999). As compared to tray drying, MSB reduced the drying time by 95% and 96% for osmotically pre-treated and non-treated blueberries, respectively (Feng et al., 1999). MSB dried lettuce cubes dried in much less time than freeze drying and produced quality much higher than any other tested method, as monitored via rehydration ratio, chlorophyll content, color, and sensory evaluation (Feng et al., 2012). Parboiled wheat dried via MSB exhibited a more porous structure as compared to air dried samples, while MSB treated bulgur showed lower water absorption capacity as compared SB produced samples (Kahyaoglu et al., 2010). Potato cubes dried via MSB exhibited brighter color and higher rehydration capacity than those prepared via air drying, and results were able to be modelled accurately (Lu,Zhang,Liu,et al., 2014). The method was also employed with potato cubes in order to create a product similar to deep-fried potato chips as a healthier snack alternative, where the resulting product had acceptable breaking force, expansion ratio, and rehydration ratio (Yan et al., 2010b). When various drying techniques were compared for carrot pieces, the microwave-spouted bed process had the highest drying rate and uniform product color (Yan et al., 2010a). Results for purple fleshed sweet potato were mixed in

that the process did not lead to a porous microstructure, and therefore the final hardness of the product was high and rehydration capacity was low, even while color and anthocyanin content was encouraging, particularly when combined with steam blanching (Liu et al., 2014). This follows a related study where it was determined that microwave blanching rapidly reduced peroxidase activity and best maintained anthocyanin content of purple fleshed sweet potato after MSB drying (Liu et al., 2015). A variation of the process, known as microwave-assisted pulsed spouted bed dehydration, produced burdock root cubes with desirable color, flavor, and textural attributes, while the process also encouraged the maintenance of natural flavor compounds (Lu,Zhang,Sun,et al., 2014).

Microwave-spouted bed techniques can be further refined by performing the drying under vacuum conditions. In the case of shiitake mushrooms it was found that microwave-vacuum spouted bed process enabled the highest quality product in terms of texture, color, sugar content, sensory evaluation, and rehydration capacity (Qi et al., 2014). A further derivatization of this process is microwave assisted pulse-spouted vacuum drying (MPSVD), where as compared to microwave spouted bed drying, microwave vacuum drying, and vacuum drying, it was found that the MPSVD apple cubes had the best color and highest sensory score (Mothibe et al., 2014). The MPSVD technique was applied to lettuce leaves and it was found that the microwave-vacuum spouted bed drying time was about 50% of the conventional microwave dried samples (Y. Wang,Zhang,Mujumdar,et al., 2013). Beyond its application for fruits and vegetables, a similar process was used in order to provide crispy fish granules of optimal quality and consumer acceptance (Chen et al., 2014).

A further derivatization has been the development of pulse-spouted bed microwave freeze drying (PSMFD). In the case of lettuce slices, PSMFD was found to reduce color changes, shrinkage, and final moisture content as compared to static MFD, while also reducing the drying time by 20% (Wang et al., 2012). Additionally, once rehydrated the samples were harder and more elastic than those dried via either static MFD or traditional FD (Wang et al., 2012). In the case of banana cubes, it was found the PSMFD was able to uniformly dry the sample than static MFD and maintain ascorbic acid values at those found in traditional FD while reducing drying time by 50% (Jiang et al., 2014). PSMFD was also shown to produce desalted duck egg white powders with better color, lower apparent density, and shorter drying times as compared to conventional FD (Y. Wang,Zhang,Adhikari,et al., 2013).

2.8.5 Microwave-Vacuum Drying

The application of vacuum during microwave drying has been considered for many years to be a good solution for alleviating physical damage caused during microwave drying such as scorching, off-color production and uneven heat distribution (Gunasekaran, 1990). Because of the presence of a vacuum, during microwave-vacuum (MWV) dehydration the continuous application of microwave energy can cause massive fluxes of vapor towards the surface early in the process, and cause damaging temperature spikes later in the process. Moreover it has been shown, at least on a bench-top scale, that continuous application of microwave energy does not accelerate the rate of water removal once a critical moisture content has been reached and it has been shown that there is no energy or quality advantage of continuous over pulsed application of microwave energy (Gunasekaran, 1990; Yongsawatdigul & Gunasekaran, 1996a; Beaudry et al., 2003). As a result, the magnetron duty cycle is typically altered in order to limit power application to the samples and their resulting temperature.

Typically, vacuum is applied to reduce absolute pressure to at least 7kPa, where the boiling point of water is reduced to 39°C (Beaudry et al., 2004). This property allows water to vaporize at lower temperatures than under atmospheric conditions and therefore the product can be maintained at much lower temperatures which in turn limits quality degradation (Yongsawatdigul & Gunasekaran, 1996a). Moreover, because air is excluded during drying, oxidation reactions are minimized (Gunasekaran, 1990). These characteristics all contribute towards a dried product with better color, texture and flavor, making it advantageous to use this process despite high installation and operating costs (Yongsawatdigul & Gunasekaran, 1996a). MWV drying has been shown to reduce volatile loss, accelerate moisture removal and slow heat transfer to the solid phase due to absence of convection (Drouzas & Schubert, 1996). The process has been studied with an array of products such as apple (Erle & Schubert, 2001), banana (Mousa & Farid, 2002), cranberry (Yongsawatdigul & Gunasekaran, 1996a; Yongsawatdigul & Gunasekaran, 1996b; Sunjka et al., 2004; Leusink et al., 2010), sour cherry (Wojdyło et al., 2013), carrot (Sutar & Prasad, 2007; Cui et al., 2004), pomegranate arils (Dak & Pareek, 2014), mushroom (Argyropoulos et al., 2011; Giri & Prasad, 2007a), whole and sliced garlic (Figiel, 2009), garlic powder (Li et al., 2007), honey (Cui,Sun,et al., 2008), grape (Clary et al., 2007), mint leaves (Therdthai & Zhou, 2009), pineapple (Corrêa et al., 2011), potato (Bondaruk et al., 2007), durian (Bai-Ngew et al., 2011), beetroot (Figiel, 2010), strawberry (Changrue et al., 2008; Bohm, 2006), raspberry (Bórquez et al., 2010),

thai green tea (Hirun et al., 2014) and pineapple (Corrêa et al., 2011), among others.

As with most novel drying techniques, the main target of MWV dehydration is the reduction of drying times. Further, in terms of quality retention, various studies have found the process to be comparable to freeze drying rather than convective microwave or air drying based techniques. In the case of honey, a product that is almost entirely made up of carbohydrates and thus would be prone to caramelization, it was found the a MWV drying process could dry honey to a moisture content of about 2.5% in 10 min at temperatures of 30-50°C and an end product with minimal color change and small volatile losses (Cui,Sun,et al., 2008). However, MWV dried lychee fruits were found to decrease in quality with increasing product temperature in every stage of the drying profile; however the process was able to generate dried lychees with better color, less shrinkage and better taste in less time and consuming less energy than convective air drying (Duan et al., 2014). In terms of predicting drying kinetics, sour cherries were used to demonstrate that artificial neural networks (ANN), can be used to model the MWV dehydration of sour cherries, proving to be a reliable alternative to the more commonly applied thin layer drying models (Motavali et al., 2013).

Various quality parameters have been selected as the basis for comparing the MWV process to other methods. For banana slices, MWV dried samples rivaled freeze dried products in terms of color, flavor, aroma and sample shrinkage (Drouzas & Schubert, 1996). The same authors also found that in terms of rehydration capacity the microwave-vacuum dried banana slices absorbed twice the moisture that conventionally dried slices did, making the method appropriate for use in various food products such as cereals or bakery products (Drouzas & Schubert, 1996). For potato cubes, it was found that microwave drying at a partial vacuum of 24kPa enabled the fastest drying time and best overall quality index, indicating its applicability to this product (Bondaruk et al., 2007). Similar results were found for potato slices, where higher microwave and vacuum levels were found to promote moisture loss, where microwave wattage was shown to be the most significant variable (Song et al., 2009). For mint leaves, rehydration capacity was higher and drying times were reduced by up to 85-90% by MWV as compared to air drying (Therdthai & Zhou, 2009). Similarly, when compared to microwave freeze drying and air drying, the MWV process was fastest method to dry wild cabbage chips, while the best quality chips were produced by microwave freeze drying (Zhang et al., 2011). For mushrooms, while freeze dried samples exhibited the best color, softest texture when rehydrated, lowest apparent density, and highest

rehydration capacity, it was found that these products were spongy and fragile (Argyropoulos et al., 2011). In this case, employing microwave vacuum drying resulted in a superior quality product when compared to hot air dried sample, and also produced puffed structures with crispy texture that was preferable to the freeze dried product. It was suggested that this type of product could be mixed with other dried vegetables and spices and developed as a fat free snack (Argyropoulos et al., 2011). Button mushrooms dried via MWV were found to have better rehydration characteristics and 70-90% shorter drying times as compared to those that were air dried (Giri & Prasad, 2007a). Further work with button mushrooms indicated that the system pressure strongly affected color, hardness, rehydration ratio, and sensory attributes of the dried mushrooms, where lower pressure resulted in higher quality end products (Giri & Prasad, 2007b). Microwave-vacuum drying has also been applied in the case of restructured (surimi) fish cubes, where the process was used to produce fish cubes with uniform shape and texture along with good color and flavor (L. Wang et al., 2013).

Owing to the lower temperatures and reduced level of oxygen, microwave vacuum processes are particularly well suited to maintain heat labile compounds and those subject to oxidation. When compared to sun-dried grapes (raisins), MWV drying better preserved heat sensitive nutrients, particularly Vitamin A, Vitamin C, thiamine, and riboflavin (Clary et al., 2007). For garlic slices, it was found that the highest microwave power tested resulted in the highest retention of volatile oils, and drying times obtained with the microwave-vacuum method were an order of magnitude lower than those found for convective drying (Figiel, 2009). In the case of Thai green tea, it was found that total polyphenol content and color parameters were not significantly affected by the MWV process, while amount of catechins and scavenging ability were; regardless, an optimal process was found to take only 30 min to dry the tea (Hirun et al., 2014). Bioactive compounds were retained well in the case of sour cherry, where a microwave vacuum drying process produced samples that were comparable to freeze dried samples in terms of phenolics, antioxidant activity, and color, which was in turn consistent with anthocyanin content (Wojdyło et al., 2013). Similarly, when compared with freeze drying and air drying, it was found that MWV drying of frozen-thawed whole cranberries was able to achieve the desired water activity (≤ 0.43) after only 30-35 min, as compared to 5-10 days for freeze drying and 60-65h for air drying (Leusink et al., 2010). In this case, samples dried via microwave-vacuum and freeze drying exhibited similar retention of anthocyanins and antioxidant activity, and in both cases were higher

than samples produced via hot air drying (Leusink et al., 2010).

It is worth noting, however, that microwave based techniques do not always prevail when compared to air drying, particularly with fragile products such as strawberries. In one study it was found that there was a significant loss of ascorbic acid, antioxidant capacity, and total phenolics in either convective air or microwave-vacuum based finish-drying (Bohm, 2006). In this case, while soluble phenolics and anthocyanins were primarily lost into the osmotic solution, temperature peaks imposed by the application of microwaves during finish-drying were found to be most responsible for the loss of ascorbic acid and total phenolics and thus considerable effort must go into optimizing drying processes for retention of nutritive compounds (Bohm, 2006). In some cases it has also been shown that further enhancements could be made to the process, whether through the incorporation of spouted/fluidized beds (discussed in a later section), or the application of other electromagnetic energy to further boost drying rates. In the case of red chilies, it was found that by incorporating far-infrared (FIR) energy into the process, drying times could be reduced while quality markers (color, texture, rehydration capacity, and shrinkage) of the FIR-MWV process exceeded that of the standalone MWV (Saengrayap et al., 2014). Similar results have also been noted in the case of shiitake mushrooms (Kantrong et al., 2012).

In other cases, combining MWV with convective air drying provided notable benefits. Figiel (2010) studied the application of MWV in combination with a convective air drying step and it was found that increasing the applied microwave power and reducing the amount of time spent in convective air drying improved the quality of beetroots. In this case, the combination method provided beetroot with antioxidant capacity approaching that of a freeze dried sample, and that the earlier the MWV process was applied in the process the closer the final product came to the overall quality produced by freeze drying (Figiel, 2010). A similar combination technique was studied in the case of pomegranate arils and rind, where it was found that both the MWV and combined AD-MWV process were a good option to reduce time and energy consumption, but still the standalone MWV process required less energy (Calín-Sanchez et al., 2013). Regardless, these applications show the potential benefit of a combination process where if air drying facilities already exist, a lower capacity MWV setup could be installed as a pre- or post-AD treatment in order to augment capacity and increase product quality.

Another common combination technique of particular interest to this work is the application of microwave-vacuum dehydration after an osmotic pre-treatment, the use of which

will be explored in the following section.

2.9 Microwave-Based Finish-drying of Osmotically Pre-Treated Foods

There have been various combinations of osmotic and microwave based dehydration techniques. Most commonly, conventional osmotic treatments are performed on the sample after which the products are then finish dried using a microwave-convective or microwave-vacuum treatment. These methods have, at least in the literature, made substantial headway in terms of replacing hot air drying as the de facto standard for post-osmotic finish-drying. Finish-drying is required in order to reduce the water activity to a shelf stable level, as post-osmotic treatment food products are typically classified as intermediate moisture food products with moisture contents of at least 50% (wet basis) and are still perishable as a result. In these combination techniques, the osmotic treatment removes the initial bulk of moisture, thereby reducing the amount that must be removed by the more intensive and destructive finish-drying processes.

Microwave-convective finish-drying has been employed successfully on cranberries, where it was found that product color and texture was shown to diminish as power density increased and as the magnetron power-off times were shortened, an effect largely attributed to the fruits beginning to burn at higher power densities (Beaudry et al., 2003). A later study tested the effects of four drying methods (hot air, freeze, microwave-convective and vacuum drying) and found that microwave-dried samples provided toughness and overall acceptability values similar to those of commercial dried cranberry samples in much less time than conventional methods (Beaudry et al., 2004). In this study, rehydration capacity was identified as one area in which microwave dried samples could improve, where a lower internal product temperature is desirable and future work on the application of vacuum during microwave drying was recommended (Beaudry et al., 2004). Osmotically treated apple cubes were finish dried with a microwave-convective method which took approximately 5h and temperature was monitored with fiber optic probes, where the authors suggest that future work should focus on optimizing the finish-drying process (Prothon et al., 2001). For osmotically treated strawberry, drying times were reduced from 41 to 11h when employing microwave-convective drying instead of air drying alone (Contreras et al., 2006). In this case, the microwave-convective dried berries were firmer, more rigid, and showed higher glass transition temperatures, all of which was attributed to an increase of water soluble pectins as a consequence of losses of both protopectin and oxalate soluble pectic fractions

(Contreras et al., 2006). Furthermore, the samples were softer when rehydrated, illustrating the damage to the cellular structure imparted by the microwave treatment (Contreras et al., 2006).

Particularly relevant to microwave finish-drying, osmotic treatments can have an effect not only on the moisture content but also on the dielectric properties of the product. For example, the incorporation of solutes (sucrose or salt) were found to increase the dielectric properties of potato puree at low temperatures, and therefore increase the drying rate during microwave-freeze drying (Wang et al., 2011). Salt content was found to have the larger effect, where drying times reduced by 17-54% as salt content increased from 1-7%, while there was an 11.1-33.3% decrease in drying time with sucrose contents from 3 to 15% (Wang et al., 2011). Similar results have been described with mushrooms, where the incorporation of salt through an osmotic pre-treatment was found to modify dielectric properties and result in more homogenous heating along with reduced drying time, shrinkage, and improved final porosity and rehydration characteristics (Torringa et al., 2001). Moreover, an osmotic pre-treatment was found to be beneficial in that it further reduced the MFD drying time by 2h (Duan et al., 2008b). Similar results were found when applied to potato chips, as an osmotic pre-treatment was able to improve the drying rate versus samples with no pre-treatment (Wang et al., 2010b).

Microwave-vacuum finish-drying has also been found to be a suitable finish-drying technique for osmotically pre-treated samples. Pineapple was subjected to MWV finish-drying where it was found that the process leads to intensification of the yellow coloring typical of pineapple (Corrêa et al., 2011). For MWV finish-drying of osmotically pre-treated strawberries, it was determined that pulsed microwave input was able to decrease product temperature, save energy, and produce a suitable product in terms of overall appearance (Changrue et al., 2008). For osmotically pre-treated raspberries a high quality (in terms of color, taste, and structure) was obtained in 40 min of MWV finish-drying (Bórquez et al., 2010). Furthermore, it was concluded that instead of continuous application of microwave energy, temperature control was critical and that manipulating the power level was able to maintain the product at the reference level. Yongsawatdigul and Gunasekaran (1996a, 1996b) studied the effect of MWV drying of osmotically pre-treated cranberry halves and compared them to convective air dried samples in terms of energy efficiency and quality characteristics. Absolute pressure levels of 5.33 and 10.67kPa were used and microwave power (at either 250 or 500W) was applied both continuously as well as pulsed with various on (30 and 60s) and off (60, 90 and 150s) times. Results showed

that both continuous and pulsed MWV drying modes provided more favorable drying times, energy input, drying efficiency and drying rates when compared to conventional air drying. Furthermore, when higher vacuum is applied, microwave-off times can be increased, leading to increased efficiency, lower sample temperatures and better product quality. Microwave-vacuum dried samples were redder and had a softer texture than hot air dried samples, while storage stability at room temperature was similar between all the methods. Overall optimal drying conditions were found to be a cycled magnetron process (30s on/150s off) at an absolute pressure of 5.33kPa (Yongsawatdigul & Gunasekaran, 1996a; Yongsawatdigul & Gunasekaran, 1996b). Moreover in a later study it was found that MWV dried samples showed softer texture and were less tough than convective dried berries, where additional benefits were noted in terms of energy efficiency (Sunjka et al., 2004).

2.10 Energy Use in Drying Processes

Energy use is a major consideration in drying processes, particularly when looking to scale up a process or setup a new process in industry. In fact, dehydration can account for up to 15% of all food industry energy usage (Fernandes et al., 2006). This is of particular concern with microwave base techniques as the need for electricity as an energy source represents a substantial increase in the cost of energy when compared to fossil fuel sources typically used to heat air for conventional convective air drying. Furthermore, in much of the world even when electricity is required by a process it is typically generated by burning fossil fuels, where a typical energy conversion rate is below 50% (Durance & Wang, 2002). While this doesn't hold true in Quebec due to the prevalence of hydroelectricity, thermal energy can be at least partially recovered using multistage drying setups, while the cost of electrical energy needed to power the magnetrons, vacuum pumps, and related equipment such as condensers is expensive. As a result, comparisons in this regard are delicate as industrially speaking the decision would largely be influenced by geographical concerns such as the availability of cheap/sustainable power generation, among other considerations.

Regardless, various studies have attempted to quantify energy consumption in microwave and hot air based drying setups For instance, mean power consumption for microwave vacuum drying of cranberry halves was 2.66MJ/kg H_2O, which is an improvement of 40-60% over hot air drying and 46% over the continuous-microwave vacuum drying method from the same study,

although this figure does not account for power consumption by the vacuum pump (Yongsawatdigul & Gunasekaran, 1996a; Yongsawatdigul & Gunasekaran, 1996b; Beaudry et al., 2003). Sunjka et al. (2004) found that over a range of power densities, longer power off times (with constant power-on times) tended to decrease the drying performance, defined in kg_{water}/MJ, implying an increased energy consumption per unit mass water removed as power-off times increased. At atmospheric pressure, Beaudry et al. (2003) observed that optimal energy consumption for a pulsed-microwave cranberry drying procedure was 8.7MJ/kg H_2O at a power density of 1.00W/g and a power cycle of 30s on/60s off, significantly more than required when vacuum is applied. Similar values were found in vacuum microwave dehydrated tomatoes, where average values showed energy consumption of 29.9MJ/kg H_2O for an entirely air dried sample as opposed to 8.6MJ/kg H_2O for an entirely microwave vacuum (6.65kPa abs) dried sample (Durance & Wang, 2002). Of particular interest in this study is the change in the overall power consumption when the percentage of water removed gradually shifts from 100% AD to 100% VM. In one of the intermediate steps (where 70% of the water was removed by air drying and the remaining 30% was removed by vacuum microwave drying), the power consumption of water dropped from the aforementioned 29.9MJ to 17.3MJ/kg H_2O, whereas it only increased to 8.9MJ from 8.6MJ/kg H_2O for the vacuum drying portion. This demonstrates the efficiency of microwave-vacuum drying in removing the more bound water that is typical of the falling rate period of drying (Zhang et al., 2006).

While the aforementioned study on Roma tomatoes included the energy consumption of the vacuum pump, typically this value is ignored when calculating energy consumption on a benchtop scale. The form of equation typically employed is based on the equation described by Yongsawatdigul and Gunasekaran (1996a), which is given by:

$$\mathrm{EC} = \frac{t_{on}\ P_{MW} \cdot (1 - m_f) \cdot 10^{-6}}{M_i \cdot (m_i - m_f)} \qquad (2.10)$$

Where EC is energy consumption (MJ/kg moisture removed); t_{on} is the total magnetron power-on time (s) calculated as total drying time multiplied by the duty cycle; P_{MW} is the microwave power absorbed by a 20g sample (W); M_i is the initial sample mass (kg); and m_i and m_f is the initial and final moisture fractions, respectively.

Note that the original equation was for Drying Efficiency, or DE, but was more accurately described as Energy Consumption (EC) several years later by Beaudry et al. (2003). The main

issue with including the vacuum pump is that generally speaking the pumps employed on a bench-top setup far exceed the capacity required for the relatively small system and sample size, and are only used because they are available for use. On the other hand, the pilot scale setup described for Roma tomatoes (Durance & Wang, 2002) was a pilot scale setup that was presumably engineered with a properly rated pump. As a result, there is an ongoing need to be able to estimate the energy consumption of MWV drying on a bench-top scale, at least for comparison of different treatments in the same experimental setup.

2.11 Kinetic Models for Finish-drying

Modeling of finish-drying is needed in order to get a full understanding of the overall influence of parameters which affect the drying behavior and quality of the final product, where the concern is primarily on moisture transfer as affected by drying conditions (Ramaswamy & van Nieuwenhuijzen, 2002). There are various approaches to modeling thin layer drying kinetics of biological materials, which are grouped into theoretical, semi-theoretical, and empirical models (Erbay & Icier, 2010). As summarized by Erbay and Icier (2010), theoretical models take into account only internal resistance to moisture transfer and can be used to fully explain the drying behaviors of the product in all process conditions, but do include many assumptions that can contribute to significant error levels. These models are most often derived from Fick's second law of diffusion. On the other hand, both semi-theoretical and empirical models include fewer assumptions due to their use of experimental data, but are largely restricted to the experimental setup used and within the range of process conditions applied and therefore provide limited information about the drying behavior of the product in question (Erbay & Icier, 2010).

While in theory there are many variations of models employed for drying kinetics, most often drying processes have been described by fitting experimental data to semi-experimental models such as the Exponential model (equation 2.11) or Page's empirical model (equation 2.12), which are given by:

$$MR = \exp(-Kt) \qquad (2.11)$$

$$MR = \exp(-kt^n) \qquad (2.12)$$

where MR (moisture ratio) is defined as $(M - M_e)/(M_o - M_e)$ and M = moisture content at time t; M_e = equilibrium moisture content; M_o = initial moisture content at time = 0; K = the drying rate

constant (min^{-1}); k and n are the parameters of Page's model; and t = drying time in min. All moisture contents are expressed in dry basis (kg moisture/kg dry matter). For vacuum based drying processes, the equilibrium moisture content is considered to be zero (Kiranoudis et al., 1997). Moreover, various studies of microwave-vacuum and microwave-convective dehydration of biomaterials have found these models, and particularly Page's model, able to fit experimental data well (Giri & Prasad, 2007a; Sutar & Prasad, 2007; Prabhanjan et al., 1995). More recently, other modeling approaches, such as those employing artificial neural networks, have also been employed for microwave vacuum drying (Motavali et al., 2013; Poonnoy et al., 2007).

2.12 Conclusion

Overall, then, microwave-based dehydration techniques can be described as methods employed to various food products in order to rapidly produce high quality dried goods. Generally speaking, the various derivatives of microwave based drying methods were developed to incorporate some means to level heat distribution in the product, usually through product mixing or incorporation of vacuum. The incorporation of an osmotic spray setup into a microwave setting could be looked at the same way, where the osmotic solution removes heat produced by the incident microwaves. Moreover, osmotic treatments have found to be an effective means to remove the initial bulk of moisture from a fresh product while incorporating some solids into the product to increase palatability and yield. Microwave-osmotic treatments, despite being well developed for cut fruit samples, are lacking thorough investigation into whole fruits such as berries, for which there is no data available. There is significant promise shown by combining multiple microwave based drying techniques to obtain the benefits of each technique, a concept that provides the basis for the research described in the following chapters.

CONNECTIVE STATEMENT TO CHAPTER 3

From the overview presented in Chapter 2, it's clear that there are many different pathways to take to obtain a dried product, each with a range of benefits and drawbacks. Past publications have proven the efficiency of both the immersion and spray based microwave-osmotic processes (MWODS and MWODI, respectively) with cut fruit particles (apple cylinders). However, no work had yet been completed on whole uncut fruits, where skin pre-treatments prior to osmotic dehydration of cranberries and other small berries has been described as necessary, where the intact skin limits the impact of the process. Additionally, drying procedures are detrimental to product quality, particularly to aspects that are affected by exposure to temperature and air (oxygen). Cranberries are laden with anthocyanins, which are widely recognized as heat labile and water soluble molecules and are thus ideal candidates for a novel process that promotes quality retention. The focus of this chapter was to determine the applicability of the MWODS process to whole cranberries, the effects of process parameters on the resulting intermediate moisture product, and establish if skin pre-treatments are necessary.

Parts of Chapter 3 have been adapted for presentations and publications as follows

Wray, D and Ramaswamy, H.S., 2011. Microwave-Osmotic Dehydration of Cranberries under Continuous Flow Medium Spray (MWODS) Conditions. Northeast Agricultural and Biological Engineering Conference (NABEC) 2011. July 24-27, 2011, South Burlington, Vermont.

Wray, D and Ramaswamy, H.S., 2013. Microwave-Osmotic Dehydration of Cranberries under Continuous Flow Medium Spray Conditions. *International Journal of Microwave Science and Technology*, 11 pages, Volume 2013. DOI:10.1155/2013/207308

CHAPTER 3

MICROWAVE-OSMOTIC DEHYDRATION OF CRANBERRIES UNDER CONTINUOUS FLOW MEDIUM SPRAY (MWODS) CONDITIONS

Abstract

Microwave osmotic dehydration of cranberries was evaluated under continuous flow medium spray conditions (MWODS) after some pre-treatments. A central composite rotatable design was used in conjunction with a response surface methodology with three input variables at five levels (temperature, 33°C-67°C; sucrose concentration, 33°B-67°B; and contact time, 5-55 min). Responses were moisture loss (ML), solids gain (SG), weight reduction (WR) as well as color and texture parameters. The responses were related to process variables using RSM and statistical analysis, with each of the models tested for lack of fit to assure it is not significant ($p>0.05$), and each of the process variables tested for their statistical significance ($p<0.05$ or $p<0.0001$). Temperature was found to have the most prominent effect as it was significant with all drying parameters (ML, SG, WR) as well as quality parameters (hardness and chewiness) while contact time was found to be significant with ML and WR. Concentration was not found to be significant for any of the responses. Additionally, all skin pre-treatments that damaged the fruit skin increased solids gain during the process; the only exception chemical (NaOH) peeling, which made no difference. Moisture loss remained relatively constant between all treatments except for the chemically peeled product which had a slightly higher ML when compared to the other skin treatments. Overall, MWODS as a process provided the ability to osmotically dehydrate a food product in a much faster period of time than conventional osmotic dehydration (COD) while specifically targeting moisture loss and limiting solids uptake of the product.

3.1 Introduction

Dehydration is one of the oldest methods of food preservation and is still prevalent in the food industry. The main objective of the dehydration process is to remove moisture to a point where the product is microbiologically and enzymatically stable and limits product deterioration during storage (van Nieuwenhuijzen et al., 2001). There is also interest in producing dried ingredients which can then be incorporated into other products like breakfast cereals or baked goods. Drying often results in degradation of flavor volatiles, deterioration of color and texture, and an overall decrease in nutritional value, largely due to exposure to high temperatures for long periods of time in the presence of air (Alibas, 2007). Therefore, the key to improving the quality of dried products is to limit changes to the aforementioned quality characteristics during processing.

Osmotic dehydration (OD) represents a mild processing step in which texture is only moderately affected, nutritional value is well maintained and the product quality, especially the color, can often be enhanced throughout the process (Lerici et al., 1985). In osmotic dehydration, the driving force is the osmotic pressure across a semi-permeable membrane, which in food products is the cell wall. In addition to water exiting the plant tissue there is also a counter-current flow of solutes from the osmotic solution into the product. Furthermore, since the plant cell wall does not represent a perfect membrane, there is usually also a small leakage of low molecular weight substances such as vitamins, minerals, or organic acids which diffuse out of the cell along with the water (Torreggiani, 1993). This last diffusion tends to be insignificant in terms of mass balance but can be important in terms of quality aspects; it has been noted that anthocyanin content in cranberries post-OD was 10% less than in fresh berries (Grabowski et al., 2002).

OD can easily be adapted to industrial applications and represents an energy efficient means to obtain an intermediate moisture food product. The energy efficiency is attributed to both the use of moderate temperatures and to the fact that there is no need to provide the latent heat of vaporization because water is removed by physical diffusion instead of as a vapor (Azarpazhooh and Ramaswamy, 2012). One drawback of conventional osmotic dehydration is the relatively slow process and therefore there has been a push to develop techniques that can be applied in conjunction with osmotic dehydration in order to speed up the process without negatively affecting the product quality (Rastogi et al., 2002). The methods that are applied either before or during osmotic dehydration and examples include application of vacuum (Deng & Zhao, 2008a, 2008b; Fito, 1994), ultrasound (Deng & Zhao, 2008a, 2008b) as well as pulsed electric field and high

hydrostatic pressure (Taiwo et al., 2001).

In general, microwaves have been more commonly been applied in conjunction with air drying in various other studies (Orsat et al., 2007). Microwave energy has proven to be effective in drying for several reasons. First, microwaves generate heat by exciting dipolar molecules (mainly water) and polarizing ionic salts, both of which try to orient themselves to the microwave field, causing rapid heating from within the sample itself, an effect known as volumetric heating (Orsat et al., 2007). During microwave-assisted dehydration there is a rapid and differential heat generated within the food product as a result of the microwave absorption, largely because the main component in the food product is water. This results in a pressure buildup within the food which in turn promotes moisture loss by forcing moisture out of the product (Sosa-Morales et al., 2010). In the case of osmotic dehydration, the increased rate of moisture loss under microwave conditions tends to reduce the inward flow of solids gain. This effect was demonstrated by Li & Ramaswamy (2006a, 2006b, 2006c) and Azarpazhooh & Ramaswamy, (2010a, 2010b, 2012). In these studies, apple cylinders were treated by combined osmotic and microwave drying with a continuous flow of the osmotic medium either in an immersion (MWODI) or spray mode (MWODS). As compared to conventional osmotic dehydration, these techniques were demonstrated to provide high moisture loss, weight reduction and ML/SG ratio along with the low solids gain and short dehydration times.

Cranberries (*Vaccinium macrocarpon*) represent an important cash crop in North America. The United States and Canada are first and second in world production and together represent about 98% of worldwide yield (Grabowski et al., 2002). The vast majority of that crop is juiced, frozen, or dried prior to use, most often with sugar incorporated because naturally cranberries are generally considered too sour and tart for direct consumption. As such, cranberries represent ideal candidates for osmotic drying because the incorporation of sucrose during the process sweetens the product as it is being dehydrated. Cranberries are also garnering interest for their health benefits which could include decreased risk of coronary heart disease (Knekt et al., 1996), stroke (Keli et al., 1996), and lung cancer (Knekt et al., 1997). Moderate drying techniques are ideal in this case as high temperatures could destroy the heat labile flavonoid compounds responsible for these activities including various anthocyanins and catechins (Zheng & Wang, 2003).

The objective of this study was to evaluate the potential for the MWODS process to be applied to a new product as each of the prior projects had been completed using apple cylinders.

Further, as an extension to previous studies the focus was to quantify the effects of skin pre-treatment and more specifically, MWODS process variables (temperature, contact time, sucrose concentration) on moisture loss, solids gain, weight reduction, as well as texture and color changes in cranberry samples using a central composite rotatable design (CCRD) for the experiments and response surface methodology (RSM) for analysis of results.

3.2 Materials and Methods

3.2.1 Raw Materials

Frozen whole cranberries (Ocean Spray Canada) were obtained from a local food service supply company and kept frozen (-21 to -27°C) until use. Prior to use the cranberries were thawed for one hour in room temperature water (approximately 20°C), following similar parameters to those already described for cranberries destined for OD (Yongsawatdigul and Gunasekaran, 1996a). Commercial grade sucrose (Lantic Sugar Ltd., Montreal, Quebec) was used in conjunction with tap water for the osmotic solution and the concentration was determined using a handheld refractometer (Model N2-E, ATAGO Company, Tokyo, Japan).

3.2.2 MWODS Setup

The experimental setup used was the same as previously described by Azarpazhooh and Ramaswamy (2010a, 2010b, 2010c), and is illustrated in Figure 3.1. It consisted of a custom made microwave transparent glass sample holder (12.5cm diameter) inside a domestic microwave oven (Danby DMW1153 BL 0.031m^3, Guelph, Ontario, Canada) with a nominal power output of 1100W at 2450MHz. The sample itself was contained in a nylon mesh and placed inside the glass sample holder on top of a porous acrylic sample "stage" which allowed the osmotic solution to drip down and be recycled through the system while keeping the sample itself in the direct path of the microwaves. Placed on top of the glass sample container was a commercial spray head (Model CF-151-S, 12cm diameter, Waterpik Technology Inc, Markham, ON) which continuously and evenly distributed the osmotic solution over the sample. The gap from the spray head to the sample represents the only gap in the system in what was otherwise a closed system. The solution was pumped at the required flow rate using a peristaltic pump (Model 75211-30 Digital Gear Pump, Barnant Company, IN) through the spray head, collected under the sample, and then pumped through a series of coils inside a steam jacketed water bath (Model TDB/4, Groen Division, Dover Corp, IL). The effect of the coils was that of a heat exchanger which allowed for control of the

temperature of the osmotic solution inside the system. The coils were also the main reservoir of osmotic solution in the system, and were made of a sufficient length to allow for a solution-to-sample ratio of 30:1. The large amount of solution together with the near-completely closed system allowed for the sucrose concentration to remain constant throughout the experiments, as measured by a handheld refractometer. The water bath was set to the required inlet temperature of the osmotic solution and the solution was allowed to circulate to allow the temperature to equilibrate before the sample was placed in the system. The temperature of the osmotic solution was monitored throughout the experiments using a pair of in-line Type-T thermocouples placed immediately before and after the microwave oven cavity using a digital thermometer (Omega DP-462, Omega Technologies, Laval, QC). Regardless of the inlet temperature, the increase in temperature of solution after its residence time in the sample container was in the range of 3-5°C, which represented about 70% of the total applied microwave power.

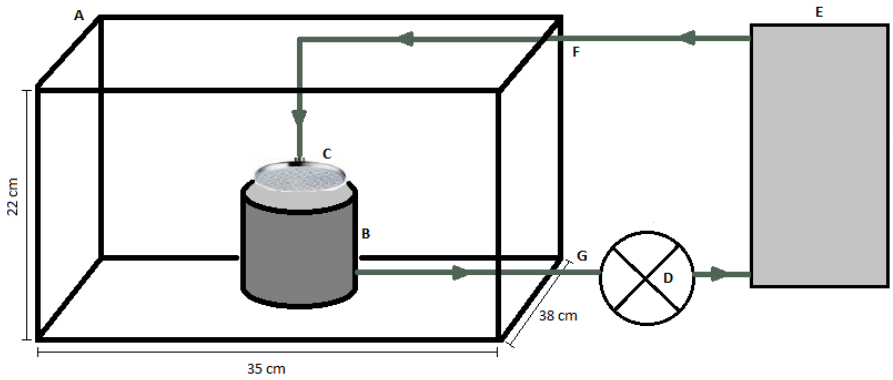

Figure 3.1: Schematic of MWODS Setup

A: Microwave Oven Cavity, B: Microwave Transparent Sample Chamber, C: Spray Head, D: Peristaltic Pump, E: Water Bath (containing heat exchanging coils, not pictured), and F & G are Thermocouple Measuring Points immediately before and after the solution enters and leaves the microwave cavity, respectively.

3.3 Methodology

3.3.1 Sample Determination

In this study some initial tests were performed in order to select a sample type because previous authors (Grabowski et al., 2007) made reference to the difficulty in working with cranberries for an osmotic dehydration process because of the resistance against water and solids

transfer provided by the waxy skin that encases the fruit. For this series of tests, frozen berries were thawed in room temperature water as previously described. Pre-treatments were applied when the berries were completely thawed and immediately before the samples were placed in the MWODS setup. Each of these tests were done at the same conditions (50°C, 50°B and 30 min), to demonstrate the effects of the skin pre-treatments only. The treatments were performed as outlined here. The 7-hole treatment consisted of poking through the skin 7 times with a fine tipped needle. There were 5 holes places around the equator of the berry and one at each end. For scored berries the tip of a knife was moved around the long end of the berry (starting and ending at the stem) to create either a single U-shaped cut around the fruit for the 'scored' type, or two intersecting U-shaped cuts for the double scored type pre-treatment. Halved berries were cut in half along the equator by hand just prior to treatment. Finally, for chemical peeling the berries were placed in 0.5% NaOH for 3 min at 25°C, quickly rinsed in tap water, blotted dry and then placed in the MWODS setup as outlined by Grabowski et al. (2007). Each sample was prepared in triplicate, and the results averaged for Figure 3.2.

3.3.2 MWODS Experiments

Individual samples of approximately 20g (17-18 berries) were weighed and placed in a Nylon mesh bag to contain the sample. The system was set up and solution pre-heated according to the prescribed temperature of the run type. The sample was then placed on the acrylic stage in the sample chamber in a single layer, the pump was turned on and the solution allowed to flow, and then the microwave was turned on. After the allotted time the pump was stopped and the sample removed. The berries were then rinsed twice in a container of room temperature tap water to remove excess sugar solution from the surface of the product. The cranberries were blotted with a moist paper towel to remove surface moisture, weighed again and were then either examined for quality parameters or dried to constant weight in an oven set at 105°C for approximately 24 hours (AOAC, 1975). The moisture content of the frozen-thawed (untreated) berries was determined to be 89.1 ± 1.02% (wb) on average.

3.3.3 Experimental Design

The experimental design employed differed from traditional studies of osmotic dehydration. Because conventional osmotic dehydration is a relatively slow process, studies tend to fix variables such as temperature, concentration and flow rate and measure samples at a given interval until a

targeted equilibrium is reached (Azarpazhooh & Ramaswamy, 2010c). Because of the requirement to test the statistical significance of each of the process variables, Design Expert v6.1 (Stat-Ease Inc, Minneapolis, Minnesota, USA) was used to create a central composite rotatable design (CCRD) with three factors (temperature, sucrose concentration, and contact time) at five coded levels each (-1.68, -1, 0, 1, 1.68). The complete experimental design with both real and coded values can be seen in Table 3.1. By design, the program does not require duplicates of each individual run, as there are six repeated run types (center points) which determine the variability of the process and the lack of fit of the model. However, due to the intrinsic variability of microwaves in drying, each run type was performed in triplicate and the mean value entered into Design Expert for analysis; mean values with standard deviation are shown in Table 3.2.

3.3.3 Quality Analysis

For each run type, partial samples were taken for quality analysis while the rest of the samples were dried until completion for the determination of solids gain and moisture loss. Color values of the MWODS treated samples were determined in the L^*, a^*, b^* system using a tristimulus Minolta Chroma Meter (Minolta Corp., Ramsey, NJ, USA). The Chroma Meter was warmed up 20 min prior to use and calibrated against a white standard. Eight measurements were taken with each sample and the values averaged in order to obtain the L^* (lightness), a^* (green (-) to red (+)) and b^* (blue (-) to yellow (+)) values of the individual trials. The ΔE (total color change), C^* (chroma) and H° (hue angle) were also determined according to the following equations (Maftoonazad & Ramaswamy, 2008):

$$\Delta E = \sqrt{(L_0 - L)^2 + (a_0 - a)^2 + (b_0 - b)^2} \qquad (3.1)$$

$$\text{Chroma (C*)} = \sqrt{a^2 + b^2} \qquad (3.2)$$

$$\text{Hue Angle (H°)} = \tan^{-1}\frac{b}{a} \qquad (3.3)$$

where L_0, a_0, b_0 and L, a, and b represent the values of the fresh and processed samples, respectively.

Texture profile analysis (TPA) of both the MWODS treated samples and fresh berries were performed using a TA.XT*Plus* Texture Analyser (Stable Microsystems, Surrey, UK). TPA allows for the determination of a wide range of responses such as adhesiveness, chewiness, cohesiveness, fracturability, gumminess, hardness and springiness (Bourne, 1982). In this study hardness and chewiness were selected as parameters of interest as they represent quality indicators one would experience during mastication of a raisin-type semi-dried product. Hardness was taken as the peak

of the first curve (in Newtons), while chewiness (mJ) is calculated as the gumminess multiplied by springiness, as defined by Bourne (1982). The analysis was performed with eight replicates and the average values (with standard deviation) are presented in Table 2. Analysis was performed by means of TPA using a flat bottom probe (25mm diameter) with pre-test speed of 1mm/sec, test speed of 5mm/sec and post-test speed of 5mm/sec. The target was a distance of 10mm, which represents the 50% of the average diameter of the cranberries tested. These settings were used with guidance from previous authors who had employed TPA on a similar product, dried dates (Rahman & Al-Farsi, 2005).

3.3.4 Dehydration Responses and Data Analysis

To analyze the mass exchange that took place during osmotic dehydration, the parameters of moisture loss (ML), solids gain (SG) and weight reduction (WR) were calculated according to the following equations:

$$\mathrm{ML}\ (\%) = 100\,\frac{\mathrm{M}_0 x_0 - \mathrm{M}_t \mathrm{x}_t}{\mathrm{M}_0} \qquad (3.4)$$

$$\mathrm{SG}\ (\%) = 100\,\frac{\mathrm{M}_0 s_0 - \mathrm{M}_t s_t}{\mathrm{M}_0} \qquad (3.5)$$

$$\mathrm{WR}\ (\%) = 100\,\frac{\mathrm{M}_0 - \mathrm{M}_t}{\mathrm{M}_0} \qquad (3.6)$$

where M_0 and M_t are the total sample mass as time 0 and time t, respectively; x_0 and x_t are the moisture fractions (kg/kg wet basis) at time 0 and time t, respectively; and s_0 and s_t are the solid fractions (kg/kg wet basis) at time 0 and time t, respectively. These equations assume a one way mass transfer of sucrose into the product (that is, there is no significant leaching of solids from the sample into the solution). These parameters were collected by weighing the samples before MWODS treatment (M_0), after treatment (M_t). The initial solids fraction (s_0) was calculated by difference from the moisture content of fresh cranberries, and the post-treatment solids content (s_t), was defined as the mass gained after drying to constant weight. Each run was completed in triplicate with average values used for data analysis.

Table 3.1: CCRD Experimental Design for MWODS in Real and (Coded) Values

Run #	Temperature (°C)	Concentration (°B)	Contact Time (min)
1	50 (0)	50 (0)	30 (0)
2	50 (0)	67 (+1.68)	30 (0)
3	50 (0)	50 (0)	30 (0)
4	40 (-1)	60 (+1)	15 (-1)
5	50 (0)	50 (0)	30 (0)
6	40 (-1)	60 (+1)	45 (+1)
7	60 (+1)	60 (+1)	15 (-1)
8	40 (-1)	40 (-1)	15 (-1)
9	40 (-1)	40 (-1)	45 (+1)
10	50 (0)	33 (-1.68)	30 (0)
11	60 (+1)	60 (+1)	45 (+1)
12	67 (+1.68)	50 (0)	30 (0)
13	60 (+1)	40 (-1)	15 (-1)
14	33(-1.68)	50 (0)	30 (0)
15	50 (0)	50 (0)	30 (0)
16	50 (0)	50 (0)	5 (-1.68)
17	50 (0)	50 (0)	30 (0)
18	60 (+1)	40 (-1)	45 (+1)
19	50 (0)	50 (0)	30 (0)
20	50 (0)	50 (0)	55 (+1.68)

3.4 Results and Discussion

3.4.1 Skin Pre-Treatment

For most of the treatment types the moisture loss for the various skin treatments remained near constant and certainly within the error of the samples (Figure 3.2). The only exception is the chemically (NaOH) peeled sample, which did have a slightly higher moisture loss when compared to the rest. Interestingly, the halved berries provided nearly the same amount of moisture loss when compared to the whole berry. This is in contrast to Grawbowski et al. (2007), who found that cutting the berries in half increased the moisture diffusion by about 100-fold when compared to the mass transfer through the cranberry skin and overall about a 4.5% increase in moisture loss over the length of the process. There are a few possible explanations for this change, including a smaller solution-sample contact area in a spray setup when compared to a traditional immersion setup. This is particularly important when you consider the positioning of the cranberry halves under the spray head. While each sample was placed facing "up" to sit like a bowl on the sample stage, if a stream of spray didn't exactly enter and fill that piece, it wouldn't have had the same nearly the same effect as if the sample was completely submerged in the solution. It's also possible the lack of difference between the whole and halved berries in terms of moisture loss was due to the substantial effect of the incident microwaves, as contrary to convention osmotic dehydration the moisture loss is not only due to osmotic differential but also the excitation of water molecules by MW energy, which pushes them out of the sample, a phenomenon described by Sosa-Morales et al. (2010).

The solids gain for the most part increased with the level of destruction to the skin. The lone exception is that halved berries accounted for less solids gain, on average, than the double scored samples, although the variation is within the error. Also of interest is the fact that the chemically peeled samples showed no increased absorption of sucrose when compared to untreated samples. This suggests that while removing the waxy layer allows water to more easily traverse the skin, the skin tissue that remains may still be a physical barrier that prevents solids uptake.

In the end it was decided to use the untreated whole berries for two key reasons. First, the unaltered skin on the whole sample provided an interesting property in that it would limit the uptake of solute. This is of particular interest in osmotic dehydration where it is optimal to provide a high ML/SG ratio, i.e. provide the highest possible moisture loss while limiting solids gain

(Azarpazhooh & Ramaswamy, 2010c). Secondly, while the NaOH treatment increased the moisture loss and potential ML/SG over the untreated berries, it was concluded that the effect was not enough to justify the use of chemical peeling in the process. These results agree with another conclusion from a similar study where it was determined that chemical pre-treatment provided no significant influence on water transfer during osmotic dehydration of cranberries (Sunjka & Raghavan, 2004). However, throughout the study it was observed that there were random breaks in the skin likely due to the freeze-thaw process. This possibly contributed to the variation of the results and would have therefore reduced the accuracy of the predicting mode and therefore likely the continued use of skin pre-treatments would have minimized these effects.

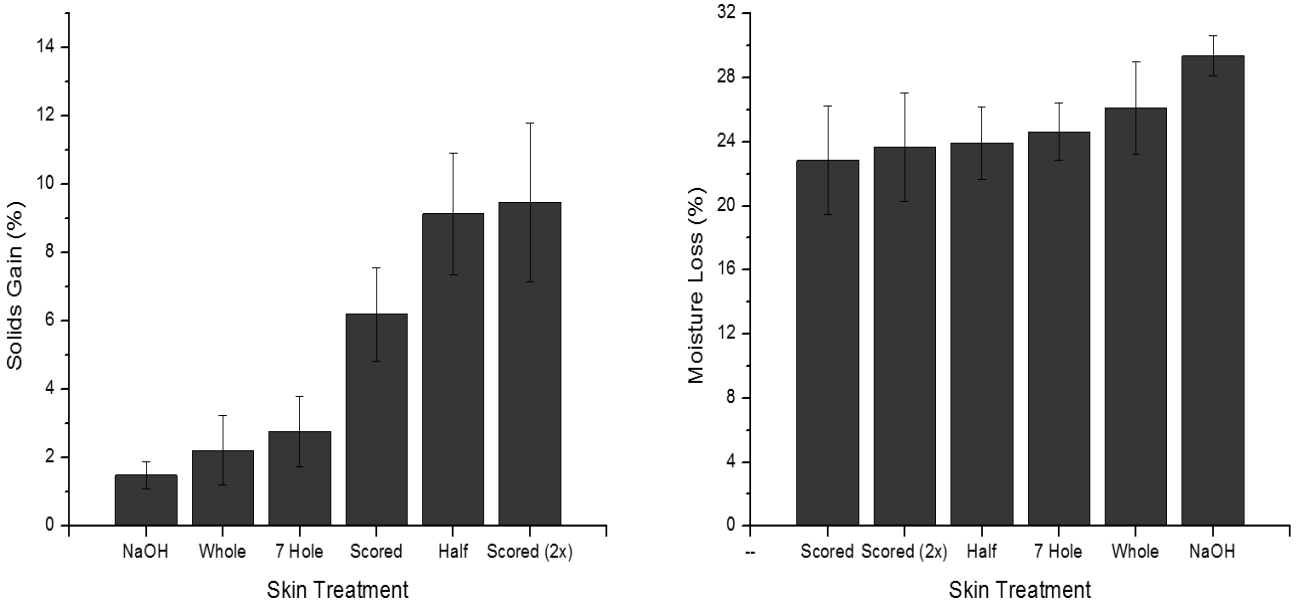

Figure 3.2: Moisture Loss and Solids Gain for Various Cranberry Skin Pre-Treatments

Average values with standard deviation shown

3.4.2 Response Surface Methodology

In working with a CCRD design, one of the most important steps is to determine the statistical significance of the model and each of the parameters using analysis of variance (ANOVA). The models selected for each of the responses in this study were selected according to their statistical significance and lack of fit values (Table 3.3). For moisture loss and weight reduction, this represented the linear model (both $p<0.0001$), while solids gain and hardness used a quadratic model (both $p<0.05$) and finally chewiness was best represented by an interaction (2FI)

model (p<0.05). For each models it is critical to ensure the lack of fit is not significant (p>0.05); this value for each model is shown along with correlation coefficients in Table 3.3. Lack of fit is determined by testing the repeated center points, and an insignificant lack of fit tells us that the model is able to adequately predict the response variables. Using the predicting equations determined by Design Expert (Table 3.3), we can predict the outcome for responses such as moisture loss, solids gain, weight reduction, hardness or chewiness as a function of input process variables.

Table 3.2: CCRD Run Numbers with Results for Post-MWODS Drying and Quality Parameters

Run #	ML (%)	SG (%)	WR (%)	Hardness (N)	Chewiness (mJ)
1	22.2 (3.10)	2.73 (0.53)	22.4 (2.68)	162 (41.4)	89.9 (41.3)
2	21.7 (1.16)	2.74 (0.16)	21.9 (1.10)	92.2 (25.8)	24.4 (14.5)
3	23.8 (0.60)	2.75 (0.51)	24.0 (0.31)	154 (14.8)	64.8 (18.4)
4	14.3 (1.29)	1.92 (0.22)	15.3 (1.30)	206 (61.5)	79.4 (28.4)
5	22.3 (2.35)	2.28 (0.27)	22.9 (2.32)	157 (22.2)	62.6 (33.1)
6	17.6 (1.77)	2.31 (0.21)	18.2 (1.94)	205 (27.9)	94.2 (22.5)
7	22.5 (2.20)	1.99 (0.66)	23.5 (1.43)	162 (24.9)	66.6 (14.0)
8	19.8 (1.26)	2.65 (0.86)	14.3 (2.75)	155 (24.5)	67.4 (13.9)
9	22.0 (3.55)	1.79 (0.32)	23.2 (3.71)	257 (33.6)	184 (31.0)
10	19.8 (1.26)	2.75 (0.31)	20.0 (1.56)	178 (38.0)	73.0 (30.0)
11	29.7 (1.89)	3.27 (1.03)	29.4 (2.83)	125 (14.1)	36.0 (6.26)
12	21.3 (3.09)	5.91 (1.30)	18.4 (2.86)	156 (66.8)	66.5 (48.0)
13	23.7 (1.18)	2.20 (0.13)	24.5 (1.05)	180 (39.4)	66.3 (32.1)
14	17.0 (3.65)	2.36 (2.34)	17.6 (3.62)	239 (36.4)	143 (23.6)
15	22.1 (2.37)	2.34 (0.98)	22.6 (3.32)	156 (27.1)	49.9 (19.3)
16	17.3 (2.11)	2.10 (0.58)	18.3 (2.50)	208 (20.4)	76.5 (12.5)
17	21.7 (1.08)	2.49 (0.40)	22.1 (0.72)	183 (24.8)	105 (28.0)
18	30.8 (2.87)	5.41 (2.62)	28.3 (1.49)	108 (17.6)	34.8 (10.6)
19	25.1 (2.07)	1.93 (0.42)	26.1 (1.68)	194 (33.3)	77.0 (32.0)
20	24.0 (1.14)	2.34 (0.52)	24.6 (0.78)	154 (17.2)	78.9 (35.2)
Fresh				293 (71.9)	121 (69.7)

Average values with (standard deviation) shown

3.4.3 Moisture Loss

Beginning with moisture loss, it was found that only the linear terms of temperature ($p<0.0001$) and contact time ($p<0.05$) had a significant effect on ML. No interactions or quadratic terms were found to have any significant effect. Based on the sum of squares produced by ANOVA, it can be stated that temperature had a larger effect than contact time in terms of determining moisture loss during MWODS. Since the coefficients for both of these terms were positive, it can be further stated that an increase in either of the variables would result in higher moisture loss. This makes sense in the context of previous studies as osmotic dehydration has been previously described as a temperature dependent process (Li & Ramaswamy, 2006a). Response surface plots showing the effect on moisture loss of increasing temperature (Figure 3.3A) and concentration (Figure 3.3D) as a function of a time show that while increasing temperature has a large effect on the ML of whole cranberries over the length of the process, concentration has little to no effect. In this case, moisture loss remains relatively stable as concentration increases and changes mainly with longer contact times.

Many studies have formed the general conclusion that increasing temperature or contact time increased moisture loss whether it be in an immersion or spray setup and with or without microwaves being applied (Azarpazhooh & Ramaswamy, 2010c; Azarpazhooh & Ramaswamy, 2010a; Li & Ramaswamy, 2006a; Li & Ramaswamy, 2006b; Li & Ramaswamy, 2006c; van Nieuwenhuijzen et al., 2001; Sereno et al., 2001; Nsonzi & Ramaswamy, 1998a). The effects of temperature on moisture loss can be largely attributed to three key points.

First, higher temperatures reduce the solution viscosity, allowing better contact between the sample and the osmotic solution, higher mobility of water molecules, and overall higher extraction ability of the solution. This effect is particularly important at high sucrose concentrations where viscosity can cause issues in a spray based system (Azarpazhooh & Ramaswamy, 2010c). Second, higher temperatures cause the individual cells in the sample to swell, thereby increasing the permeability of the cell wall, which usually moderates moisture movement. Finally, thermal energy promotes moisture diffusion within the sample itself, which means the water molecules can more easily reach the sample surface and be removed into the osmotic solution. These three causes were determined by several studies (Azarpazhooh & Ramaswamy, 2010c; Li & Ramaswamy, 2006a; Sereno et al., 2001).

While contact time was found to provide a significant effect on the moisture loss of the

sample, it was lower than that of temperature. This is in contrast to some previous studies on both conventional (Li & Ramaswamy, 2006a; van Nieuwenhuijzen et al., 2001) and microwave assisted (Azarpazhooh & Ramaswamy, 2010c) osmotic dehydration, all of which concluded that contact time had the largest influence on moisture loss. Similarly, past studies concluded that concentration does provide a significant impact on moisture loss, just not as large as that of temperature (Nsonzi & Ramaswamy, 1998a). These incongruities with past results were perhaps caused by the effect of the cranberry skin, which is naturally intended to keep water inside the fruit as well as foreign substances out. If on the skin, which is at the junction of the fruit flesh and the osmotic solution, there was a layer of sucrose that formed near the beginning of the run, it's possible that this would provide enough resistance to moisture removal that longer run times or increased concentration had no appreciable effect on the overall moisture loss.

3.4.4 Solids Gain

In terms of solids (sucrose) gain by the cranberry samples only the temperature had a significant effect, where it was found to be significant ($p<0.05$) at both the linear and the quadratic level. The interaction effect between temperature and contact time was also found to be significant ($p<0.05$). Like moisture loss, all of the significant terms for solids gain had positive coefficients, signifying that increasing temperature or contact time would results in higher solids gain. This effect can be visualized in Figure 3.3B, where the interaction effect between contact time and temperature show an increase in either of these variables results in increasing solids gain. These results agree with the general conclusions of several studies where increased temperature also increases the solids gain of the product (Azarpazhooh & Ramaswamy, 2010c; Li & Ramaswamy, 2006a; van Nieuwenhuijzen et al., 2001; Lazarides et al., 1995). The concentration of sucrose in the osmotic solution was found to be insignificant and actually slightly decreased the solids gain. This trend can be seen in Figure 3.3E, where higher concentrations actually result in lower solids gain throughout the range, an effect that partially disagrees with the majority of published reports. It has been seen in past studies that solids gain increases with solute concentration until extremely high concentrations at which point solids gain is often lower than at more moderate concentrations. This effect is likely caused by the formation of a dense superficial layer of solute at the surface of the sample, which then blocks further uptake of the solute (Nsonzi & Ramaswamy, 1998a, Li & Ramaswamy, 2006a). While normally only evident at higher concentrations in the case of whole

cranberries it's likely that the skin provides an additional barrier which blocks solids uptake in the fruit and facilitates the formation of the dense surface layer of solute, thereby slowing the uptake of solids over a broader range of concentrations instead of only at high concentrations. In considering the reducing effect on solids gain and the minimal effect on moisture loss, the process appears to favor lower concentration osmotic solutions, particularly when looking ahead to industrial settings where solute cost becomes a factor.

3.4.5 Weight Reduction

Since weight reduction is determined by the moisture loss mediated by the solids gain and the moisture loss is typically larger than the solids gain by an order of magnitude, it is expected that the responses of weight reduction and moisture loss will follow a similar trend (Azarpazhooh & Ramaswamy, 2010c). Therefore, it is not surprising to see that for weight reduction, like moisture loss, only the linear terms of temperature ($p<0.0001$) and contact time ($p<0.05$) were significant, while all of the quadratic and interaction effects proved to be insignificant. For the linear terms, the positive coefficients confirm that increasing either the temperature or contact time would increase the level of weight reduction, much like moisture loss. In general, increasing temperature will increase the weight reduction over the length of the MWODS process (Figure 3.3C), which shows that higher temperature tends to favor moisture loss over solids gain, thereby promoting moisture loss. It can also be concluded that concentration had little to no effect on weight reduction (Figure 3.3F), where the increase was due to increased contact time alone. This is nearly identical to the response of the same interaction for moisture loss (Figure 3.3D).

3.4.6 Color

In this study, none of the parameters (or models) had any significant effect on change in color measurements of the MWODS samples (in terms of $L^* a^* b^*$, Chroma (C*), Hue Angle (H°), or total color change (ΔE) values). As such, none of these values are presented here. For these responses, statistical analysis dictated that the mean change in the value better represented the predicted outcome than any linear (or higher) model. There are two possible conclusions from this outcome; first there is the possibility that there was no significant change in the color throughout the MWODS process. This is quite possible as typically these quality tests have only been performed on finished products (after secondary drying). The second possible conclusion is that even the least severe MWODS treatment made some change to the color properties, and this

change did not increase with increased treatment severity. 3.4.7 Texture

Like color measurements, mechanical properties are typically only tested after the Talens, 2005), and this in turn affects the cell wall and puncture strength (Chiralt et al., 2001; Chiral Talens, 2005). In examining the relationship between cell structure and texture, it would be a logical conclusion that higher temperatures and concentrations would exacerbate cell damage and therefore further affect the mechanical properties, which concur with the trends seen here. The effects of concentration of textural responses were more

Table 3.3: Selected Model, Predicting Equation, and Model Evaluation for Each Response

Response	Model	Prob > F	Equation in Terms of Actual Factors	Lack of Fit	R^2
ML	Linear	<0.0001	ML (%) = 0.649 + 0.336T + 0.180t - 0.0232C	0.0527 (NS)	0.7304
SG	Quadratic	0.0018	SG (%) = 9.550 - 0.367T - 0.128t + 0.0936C + $5.456x10^{-3}T^2$ - $5.531x10^{-4}t^2$ + $6.838x10^{-4}C^2$ + $3.300x10^{-03}$Tt – $3.918x10^{-03}$TC + $2.617x10^{-4}$tC	0.0556 (NS)	0.8749
WR	Linear	<0.0001	WR (%) = 0.0272 + 0.355T + 0.158t – $4.56x10^{-3}$C	0.2856 (NS)	0.8230
Hardness	Quadratic	0.0233	Hardness (N) = 56.705 - 0.602T + 9.662t + 11.433C + $0.109T^2$ + $0.024t^2$ - $0.108C^2$ -0.174Tt + $3.71x10^{-04}$TC - 0.056tC	0.0839 (NS)	0.7765
Chewiness	Interaction (2FI)	0.0006	Chewiness (mJ) = 155.644 - 3.194T + 12.625t - 3.598C - 0.161Tt + 0.099TC - 0.084tC	0.5006 (NS)	0.8003

Where T is Temperature (°C), t is Contact Time (min) and C is Concentration (°B); $\alpha = 0.05$

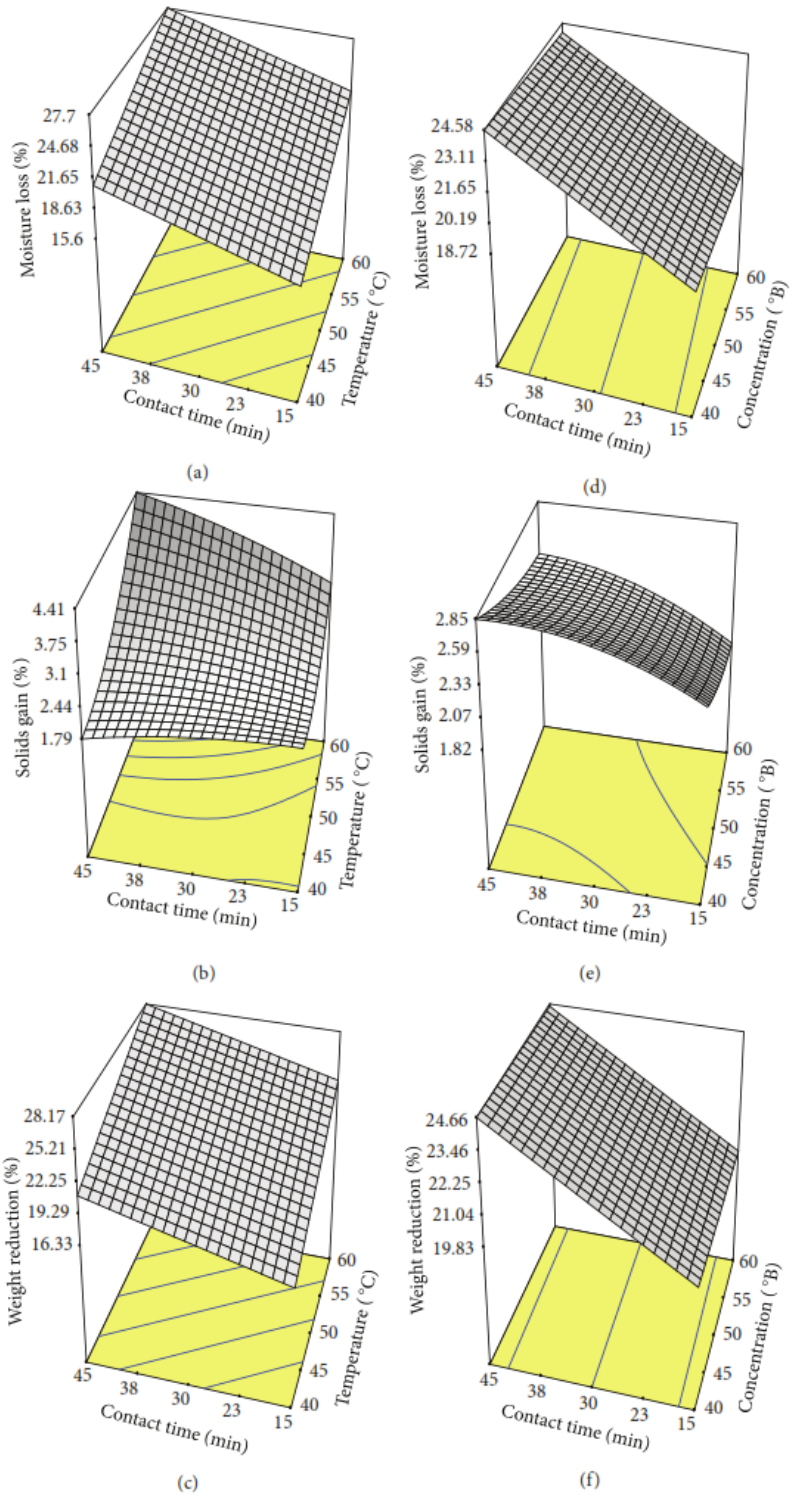

Figure 3.3: Response surface plots for dehydration parameters (ML, SG and WR).

For variable temperature plots (A-C), concentration was kept constant at its center point (50°B), while for variable concentration plots (D-F), temperature was kept at its center point (50°C)

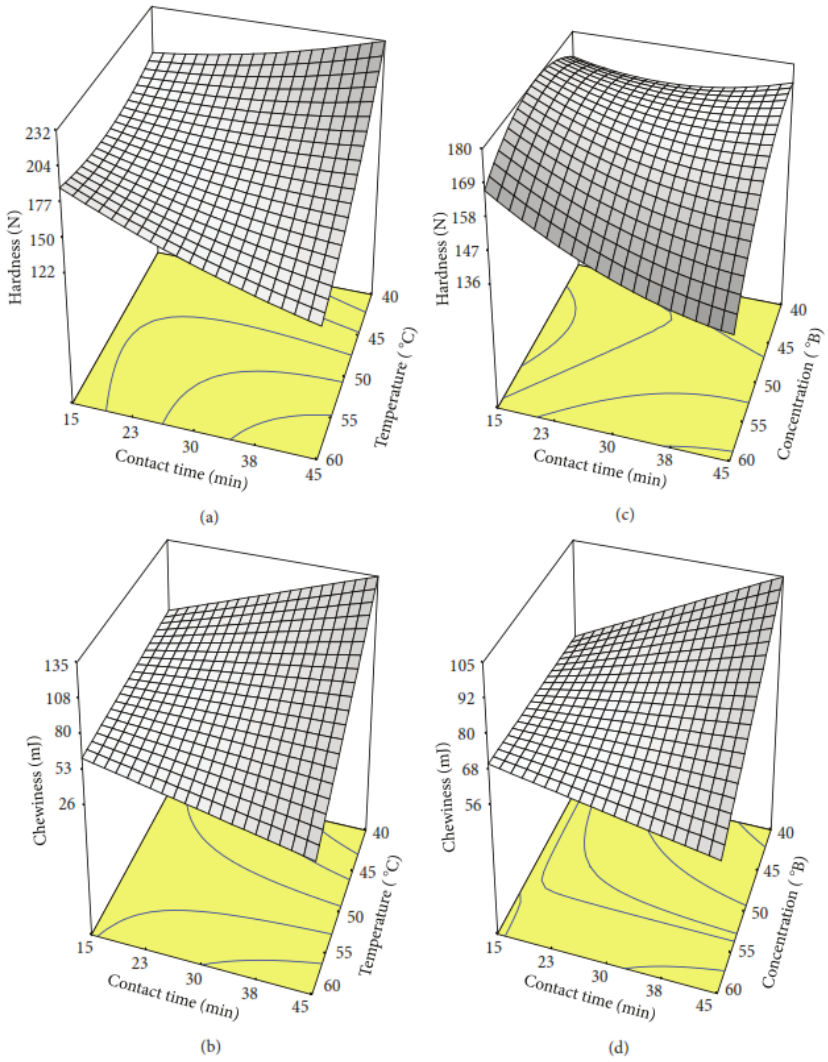

Figure 3.4: Response Surface Plots for Quality Parameters (Hardness and Chewiness). For variable temperature plots (A, B), concentration was kept constant at its center point (50°B), while for variable concentration plots (C, D), temperature was kept at its center point (50°C)

3.5 Conclusions

Overall the level of destruction of cranberry skin increased moisture and solids diffusion, however not to a significant extent. Therefore, the decision to leave the cranberries whole with no skin pre-treatment was done in part to omit chemical peeling techniques and ease of processing but also to observe the ability of the MWODS system to overcome the effect of a natural moisture barrier that is prevalent in small berries such as cranberries. A CCRD model combined with RSM analysis was used to determine the effect of individual process parameters (temperature, sucrose concentration, and contact time) on a series of responses (ML, SG, WR, hardness, and chewiness). The CCRD model was used to reduce the number of experiments required while still testing each variable independently. Overall, it was found that temperature was a significant factor for every response, where higher temperatures produced higher moisture loss, solids gain, and weight reduction along with reduced hardness and chewiness. Additionally, contact time was found to be a significant positive independent variable for ML, SG and WR, implying increasing process time would in turn enhance these responses, while longer process times tended to decrease textural characteristics. Concentration effects tended to be minimal for each of the responses, which can be largely attributed to the unique properties of the cranberry skin. No model was found to be significant for any color change response, and therefore the color destruction during MWODS was insignificant.

CONNECTIVE STATEMENT TO CHAPTER 4

After establishing the application of the MWODS process to frozen-thawed whole cranberries and determining that the berry could be used with no skin pre-treatment, the next step was to develop the second stage (finish) drying. Finish-drying is a necessary step to remove enough moisture from the product such that the water activity decreases to a point where microbial growth is limited ($a_w < 0.7$). Traditionally, finish-drying is achieved using convective hot air drying, an energy intensive process that is destructive to product quality because of the need to expose the product to high temperatures for long periods of time. The application of electromagnetic radiation during finish-drying has been suggested as a means to enhance rates of moisture loss and promote quality retention. Therefore, the focus of this chapter was to assemble and test a bench-top scale microwave-vacuum (MWV) drying apparatus. Moreover, drying kinetics and energy consumption of the various MWV treatments applied to both fresh and MWODS pre-treated berries were determined in order to provide some indication of the behavior of the process.

Parts of Chapter 4 have been adapted for presentations and publications as follows

Wray, D and Ramaswamy, H.S., 2014. Development of Microwave-Vacuum Finish-drying for Whole Cranberries Pretreated by Microwave-Osmotic Dehydration under Continuous Flow Spray (MWODS) Conditions. Northeast Agricultural and Biological Engineering Conference (NABEC) 2014. July 27-30th, 2014, Kemptville, Ontario.

Wray, D and Ramaswamy, H.S., 2015. Development of a Microwave-Vacuum Based Dehydration Technique for Fresh and Microwave-Osmotic (MWODS) Pre-Treated Whole Cranberries *(Vaccinium macrocarpon)*. *Drying Technology.* DOI: 10.1080/07373937.2014.982758

CHAPTER 4

DEVELOPMENT OF A MICROWAVE-VACUUM BASED DEHYDRATION TECHNIQUE FOR FRESH AND MICROWAVE-OSMOTIC (MWODS) PRE-TREATED WHOLE CRANBERRIES (*VACCINIUM MACROCARPON*): ENERGY CONSUMPTION AND DRYING KINETICS

Abstract

A bench top scale microwave-vacuum (MWV) dryer was developed using a modified consumer grade microwave oven. MWV dehydration was first tested as a standalone method on whole frozen-thawed berries. Subsequently a new combination drying technique was developed employing microwave osmotic dehydration under continuous flow medium spray (MWODS) conditions together with MWV as a secondary drying operation. Fresh (frozen-thawed) and MWODS pre-treated berries were dried under a range of MWV treatments employing continuous and decreasing microwave power settings (duty cycles). Initial microwave power density for all treatments was approximately 10.2 W/g while magnetron power-on and power-off times varied from 3 to 15 and 27 to 15 seconds, respectively. Drying times to 20% (dry basis) were recorded and energy consumption was calculated according to the total magnetron power-on time where overall it was found that drying times and energy consumption decreased with increasing MWV process intensity, where drying times for all MWV treatments were significantly shorter than those of conventional air drying. Drying kinetics were fit using two models (Exponential and Page's Empirical Model), where Page's model better fit the experimental data. The quality of the berries was monitored visually through evidence of scorching in order to screen treatments and establish upper limits of treatment intensity for further studies.

4.1 Introduction

Dehydration is one of the most widespread preservation methods employed within the food industry. It is typically used in order to transform a crop into a shelf stable commodity, reduce packaging, lower storage and transportation costs by reducing weight and eliminating the need for refrigerated storage, and to offer the possibility of adding value to processed foods (Orsat et al., 2007). However, drying is also energy and cost intensive due to its simultaneous mass and heat transfer process accompanied by a phase change as water evaporates (Fernandes & Rodrigues, 2007). This is a particular concern with conventional air drying, a method which results in shrunken products with tough texture, severe browning, and low nutritive value (Deng & Zhao, 2008b). The quality loss typical of dehydration comes in the form of degradation of both color and flavor as well as loss of nutritional profile, effects which are largely attributed to exposure to high temperatures for long periods of time (Alibas, 2007). Therefore, there is considerable interest in developing novel dehydration techniques in order to more efficiently dry food products. This is of particular concern with cranberries as these berries possess a wide range of phytochemicals that are thermolabile and subject to degradation during processing (Pappas & Schaich, 2009). These phytochemicals (primarily flavonols, flavan-3-ols, anthocyanins, tannins, and phenolic acid derivatives) have been implicated in a wide range of health positive functions in the body including prevention of cardiovascular diseases, various cancers, urinary tract infections, and pylori-induced stomach ulcers, as well as promoting dental health (Côté et al., 2010b). Because of the wide range of health positive functions, there is particular interest in modernizing processes to promote their retention during dehydration.

The application of microwave energy has great applications in drying because of the ability of applied microwaves to directly couple with the sample material, producing heat within the product itself. This alleviates the reliance on the much slower convective heat transfer that is relied on in traditional convective air drying as is particularly useful during the falling rate period of drying processes, which characterizes the majority of the length of microwave drying of foods (Orsat et al., 2007; Soysal et al., 2006). The ability of microwave energy to heat a product is dictated by the products dielectric properties, which is positively correlated to its water activity (Erle & Schubert, 2001; Orsat et al., 2007). This can in effect impose a self-regulatory aspect to microwave based dehydration techniques as the portions of the sample containing more moisture tend to absorb more power, dry more quickly, and thus absorb less power later on (Erle & Schubert,

2001). However, if the applied power density is too high overheating and burning of dry areas will occur, an effect commonly referred to as thermal runaway (Buffler, 1993). In fact, thermal runaway and sample charring represent the main trouble spots in applying microwave base drying techniques to food products. The application of vacuum has been suggested as one strategy for alleviating physical damage typically caused during microwave drying such as scorching, off-color production and uneven heat distribution (Gunasekaran, 1990). Moreover, the combination of microwave energy with vacuum conditions during drying is useful to overcome the usual problem of poor heat transfer during standalone vacuum drying (Erle & Schubert, 2001). Application of vacuum allows water to vaporize at lower temperatures and therefore the drying operation can be maintained at much lower temperatures, offering higher product quality (Raghavan & Orsat, 2007). It's worth noting, however, that particularly in the final stages of microwave vacuum (MWV) drying, the temperature can increase substantially but thermal damage is still relatively low because heat sensitivity decreases with decreasing water content (Erle & Schubert, 2001). Moreover, because air is excluded during drying, oxidation reactions are minimized (Gunasekaran, 1990). This is particularly important with a product such as cranberry where biologically active antioxidants are easily oxidized and degraded. Overall, the microwave vacuum process then allows a dried product with better color, texture and flavor, making it advantageous to use this process despite high installation and operating costs (Yongsawatdigul & Gunasekaran, 1996a). MWV has been successfully applied to various food products in order to reduce volatile loss, accelerate moisture removal and slow heat transfer to the solid phase due to absence of convection (Drouzas & Schubert, 1996). Products tested include apple, banana, carrot, cranberry, strawberries, mushroom, and cabbage, among others (Giri & Prasad, 2007b; Cui et al., 2003; Cui,Li,et al., 2008; Mousa & Farid, 2002; Yanyang et al., 2004; Yongsawatdigul & Gunasekaran, 1996a). Microwave-vacuum dehydration has been suggested as a particularly advantageous technique to dry cranberries as the antioxidant activity retained through MWV dehydration approaches that of freeze dried samples (Leusink et al., 2010).

Beyond the application of vacuum, other approaches to moderate product temperature are to control magnetron duty cycle (power on/power off times) as well as control power density, or applied watts/g sample material (Orsat et al., 2007). It has been found that continuous application of microwave energy does not accelerate the rate of water removal once a critical moisture content has been reached and furthermore pulsed application of microwave provides energy benefits over

continuous heating (Yongsawatdigul & Gunasekaran, 1996a). Power cycling also allows better redistribution of the temperature and moisture profile within the product during power off times (Sunjka et al., 2004).

Whereas MWV is suitable for finish-drying, cranberries are typically osmotically pre-treated in order to incorporate some sugar into the product to make them palatable for direct eating as a snack food. However, even with a tart product like cranberries there is interest in reducing solids gain to a degree that both makes it easier to reuse syrup, as well as produces a product with fewer added sugars. Microwave osmotic dehydration under continuous flow medium spray (MWODS) conditions has been described as a method to accelerate moisture loss from fruit while limiting solids gain (Azarpazhooh & Ramaswamy, 2010c). This technique has also been applied to whole cranberries where it was found that the process was able to overcome the moisture barrier property of the cranberry skin with no skin pre-treatment (Wray & Ramaswamy, 2013). This is despite previous work on osmotic dehydration of cranberries which suggested it is necessary to disrupt the skin prior to osmotic treatment where chemical, thermal, mechanical or combined techniques have been tested (Grabowski et al., 2007).

The objective of this study was to develop a bench top MWV drying setup and determine suitable treatments for MWV finish-drying of cranberries by subjecting the berries to a wide range of treatments by monitoring the berries visually for quality degradation and taking into consideration energy consumption and drying kinetics. Also, to determine the applicability of combining a microwave-osmotic treatment (MWODS) with MWV finish-drying.

4.2 Materials and Methods

4.2.1 Cranberries

Previous work indicated that frozen-thawed whole cranberries were suitable for drying with no skin pre-treatment necessary (Wray & Ramaswamy, 2013). Therefore, individually quick frozen (IQF) whole cranberries (Atoka Cranberries Inc., Manseau, QC, Canada) were kept frozen (-21 to -27°C) until use, at which point the berries were thawed by floating ≈200g batches of berries in approximately 2L of room temperature tap water for 1h as previously described (Wray & Ramaswamy, 2013). During this time the berries were sorted, where only whole, undamaged, and ripe cranberries of medium size (approximately 10-15mm diameter) were selected and under-ripe (white), broken, crushed or otherwise damaged berries were discarded. Samples were then

blotted to remove surface moisture before being weighed and transferred either directly to the MWV setup or first to the MWODS pre-treatment. The average moisture content of the fresh berries (89.1 ± 1.02% wet basis) was determined immediately after thawing by drying to a constant weight at 105°C (AOAC, 1975).

4.2.2 MWODS Pre-Treatment

The experimental setup employed for the MWODS pre-treatment was the same as previously used in Chapter 3. The only variation to the setup was the use of a new spray head (Model RPB-173C, Waterpik Technology Inc., Markham, ON, Canada) instead of the now-discontinued model that was used previously. The RPB-173C was chosen because its diameter matches that of the sample container (12.5cm) and because of its even spray distribution over the entire area of the sample stage. The MWODS process used in this study employed a sucrose based osmotic solution and parameters (50°C, 50°B, and 30 min) that represented the midpoint of the previously established central composite rotatable design (CCRD) for this process (Chapter 2). In this process, the sample is held inside the microwave cavity under a spray head which continually showers the product with osmotic solution that is circulated and maintained at a fixed input temperature (50°C in this case). This setup allows for the product to be coated in a thin layer of osmotic solution which allows for temperature maintenance and moisture removal while still allowing the majority of the microwave energy to be absorbed by the product itself. Overall MWODS has been found to enhance moisture loss and product quality while limiting solids gain and decreasing process time when compared to both conventional and immersion based microwave-osmotic dehydration (Azarpazhooh & Ramaswamy, 2010c). The system features a solution-to-sample ratio of approximately 30:1 as estimated in previous work (Azarpazhooh & Ramaswamy, 2010c). As the midpoint of the CCRD design, this represents a medium intensity treatment meant to be representative of MWODS on the whole for purposes of selecting suitable MWV treatment to follow a wider range of microwave osmotic treatments in subsequent studies.

The method employed for MWODS was similar to the previously published work with slight modifications. Briefly, the method entailed placing accurately weighed (≈50g) portions of cranberries into the MWODS setup, starting the circulation of osmotic solution which was maintained at 50°C with use of an external water bath heat exchanger, and applying the microwave at full power for 30 min. After the allotted time the samples were removed, shaken to remove

excess sugar solution, and allowed to cool at room temperature for 10 min. In order to accurately determine the moisture content of the samples set to undergo microwave-vacuum finish-drying, half the post-MWODS berries were taken to determine the moisture content by oven drying to constant weight (approximately 24h) at 105°C (AOAC, 1975). The other half of the sample was sealed and held at 4-6°C until the next day when their moisture content could be estimated from the first half of the sample that had been dried overnight. This method was able to accurately predict (R^2 = 0.96) the moisture content of the second half of the berries. Overall, the post-MWODS moisture content of the cranberries varied from 77-82% (wet basis).

4.2.3 Convective Air Drying

MWODS pre-treated cranberries were air dried using a domestic drying oven (Equi-Flow Food Dehydrator, Marysville, WA) which was modified with a digital thermostat to maintain conditions of 60 ± 1°C, 0.64 ± 0.02m/s and a RH of approximately 15%. Berries were arranged in a single layer on a metal mesh and suspended from a balance in the middle of the drying chamber, where they were subjected to constant horizontal airflow. While the inclusion of the balance allows for constant weighing without the need for interrupting the process, at four times during the process the door was quickly opened and the sample container rotated 90° so as to rotate the side of the sample exposed to the oncoming hot air. Air drying was used to produce the baseline comparison as air drying is the method typically used to finish dry cranberries in industrial settings.

4.2.4 Microwave-Vacuum Finish-drying

A bench-top scale microwave vacuum dryer (Figure 1) was assembled and consisted of (A) a consumer grade microwave (Samsung Model AMW8113ST, 1kW nominal magnetron output, cavity dimensions 33x32x21cm) in which (B) a custom made cylindrical glass vacuum chamber (12cm ID x 14cm tall) was suspended from (C) an analytical balance (Model TSK4D, Ohaus Corporation, Parsippany, NJ). The vacuum chamber was connected to a cold water condenser/water trap (D) and (E) a vacuum pump (Model M100EX, Emerson Motors, Markham, ON, Canada) on one side and (F) a standard analog vacuum gauge (Wika Instruments LP, Edmonton, AB) on the other. All tubing used was small gauge Masterflex Norprene A-60-F food grade tubing (McMaster-Carr, Cleveland, OH). The chamber was sealed with a custom food grade O-ring fashioned from consumer grade silicone baking sheets (Wilton Industries, Etobicoke, ON) and was capable of maintaining approximately 93% vacuum (approximately 6 kPa abs), which was the condition employed in all experiments.

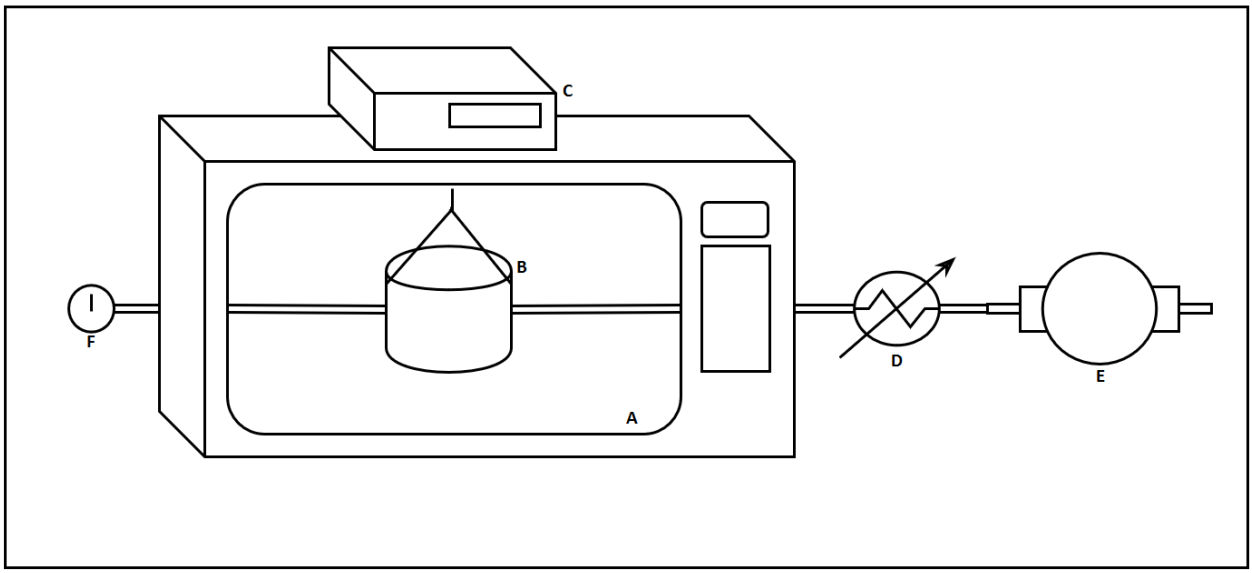

Figure 4.1: Schematic of Microwave-Vacuum Drying Setup

For the MWV process, first the empty vacuum chamber was depressurized and the balance zeroed. Accurately weighed fresh or MWODS pre-treated cranberries samples (20 +/- 0.5g) were placed in 10cm diameter Pyrex petri dishes lined with food grade silicone to prevent sticking to the glass. The sample holders were dried beforehand and kept in a desiccator prior to use. Samples were spread into a single layer and spaced so there was no contact between individual berries. Once the petri dishes were placed inside the chamber it was depressurized to the operating pressure (about one minute), the mass recorded, and the microwave set at the prescribed power level. In the case of combination run types the initial power setting (e.g. the 50% in a 50/10% process) was applied for the first ten minutes of the process and then the setting was changed to the secondary level in order to reduce the magnetron power-on time as the sample mass decreased and power density increased accordingly. Intervals between recording of the mass of the sample varied from once every 2-10 min depending on the length of the process, and was continuously monitored once the sample approached the target mass to achieve a moisture content of 20% (dry basis). The mass of the sample was recorded without stopping the system or breaking the vacuum by observing the balance on top of the microwave from which the sample chamber was suspended and subtracting the mass of the petri dish. Once the sample reached the target mass, the microwave was stopped and the vacuum was partially relieved to a level of ≈13 kPa abs for 5 min in order to allow the sample to cool slightly. The pump was then disengaged from the system in order to fully restore

atmospheric pressure, at which point the sample was removed, weighed, and sealed in a plastic bag for further analysis. All treatment types were performed in duplicate.

4.2.5 Microwave Characterization

While the magnetron of the microwave was rated at a nominal magnetron power output of 1kW, the amount of energy actually absorbed by the sample will depend on not only the real output of the magnetron, but also sample mass, geometry, dielectric properties, and location within the cavity itself (Yongsawatdigul & Gunasekaran, 1996a). In this case, the combined effects of a small sample size, modifications to the microwave cavity (to allow for the integration of the balance and the vacuum lines), and the lack of programming available in a consumer grade microwave necessitated several experiments to fully characterize the microwave setup.

Magnetron power-on times were timed manually to determine the power cycle while magnetron power output was measured calorimetrically. Two sizes of water samples (20.0g and 250.0g) were exposed to microwave energy for one magnetron power-on cycle and then quickly removed, stirred, and temperature measured using a calibrated thermocouple (Omega Technologies DP462, Laval, QC). Power determination was repeated 5 times with each sample size, and power calculated according to the following equation:

$$\text{Microwave Power} = \frac{m_w c_p (T_i - T_0)}{t} \qquad (4.1)$$

Where microwave power is the microwave energy absorbed by the sample (Watts); m_w is the mass of water, in grams; c_p is the specific heat capacity of water (4.1855 J/g·°C); T_o and T_i represent the temperature of the water initially (20°C ±1) and after irradiation, respectively; and t is time, (seconds).

4.2.6 Energy Consumption

Energy consumption was compared in terms of energy input required to remove a unit mass of moisture by building on the equation for drying efficiency (Equation 4.2) set forth by Yongsawatidigul and Gunasekaran (1996a), which was more accurately described as an energy consumption rate in a more recent study (Beaudry et al., 2003):

$$\text{EC} = \frac{t_{on}\ P_{MW} \cdot (1 - m_f) \cdot 10^{-6}}{M_i \cdot (m_i - m_f)} \qquad (4.2)$$

Where EC is energy consumption (MJ/kg moisture removed); t_{on} is the total magnetron power-on

time (s) calculated as total drying time multiplied by the duty cycle; P_{MW} is the microwave power absorbed by a 20g sample (W); M_i is the initial sample mass (kg); and m_i and m_f is the initial and final moisture fractions, respectively.

It is important to note that this original equation only takes into account the energy consumption of the microwave and not the energy required to maintain the vacuum in the system (Sunjka et al., 2004). Therefore in this study an effort was made to calculate a value closer to the true energy required in this system by including the energy required by the vacuum pump, that is to say:

$$\mathrm{EC_T} = \frac{(E_{MW} + E_{VP}) \cdot (1 - m_f) \cdot 10^{-6}}{M_i \cdot (m_i - m_f)} \qquad (4.3)$$

Where EC_T represents the total energy consumption per unit moisture removed (MJ/kg) and E_{MW} and EC_{VP} represent the energy input (in J) by the microwave and vacuum pump, respectively.
The energy consumption for microwave (E_{MW}) and vacuum pump (EC_{VP}) were calculated as shown in equations 4.4 and 4.5 below:

$$\mathrm{E_{MW}} = t_{on}\ x\ P_{MW} \qquad (4.4)$$

$$\mathrm{E_{VP}} = \frac{P_{VP} \cdot \mathrm{M_i}(\mathrm{m_i} - \mathrm{m_f}) \cdot \rho_s}{\dot{V}_{VP}} \qquad (4.5)$$

Where t_{on} is the total magnetron power-on time (s) calculated as total drying time multiplied by the duty cycle; P_{MW} is the microwave power absorbed by a 20g sample (W); M_i is the initial sample mass (kg); m_i and m_f are the initial and final moisture fractions, respectively, ρ_{steam} is the density of steam under vacuum (23.733 kg/m^3), $\dot{V}_{VP}$ is the volumetric flow rate of the pump (8.3x10^{-4} m^3/s), and P_{VP} is the power draw of the pump (approximately 125 J/s) as determined with a consumer grade wattmeter. For this calculation the contribution of leaks in the system were omitted as it was determined that with the pump turn off and the system sealed it took approximately 45 min to return to atmospheric pressure, representing a flux of several orders of magnitude lower than either the flow rate of the pump or the volume of steam produced.

4.2.7 Data Analysis and Drying Kinetics

Mean values for parameters such as drying time and energy consumption were analyzed using the ANOVA function of Minitab v16.1 (Minitab Inc, State College, PA, USA) using the Tukey method for determining statistically different groups on 95% confidence interval.

Drying kinetics have been described by fitting experimental data to the exponential model (Equation 4.6) and Page's empirical model (Equation 4.7), which are given by:

$$MR = \exp(-Kt) \quad (4.6)$$

$$MR = \exp(-kt^n) \quad (4.7)$$

Where MR (moisture ratio) is defined as $(M - M_e)/(M_o - M_e)$ and M = moisture content at time t; M_e = equilibrium moisture content; M_o = initial moisture content at time = 0; K = the drying rate constant (min^{-1}); k and n are the parameters of Page's model; and t = drying time in min. All moisture contents are expressed in dry basis (kg moisture/kg dry matter).

For the purposes of determining the moisture ratio, the equilibrium moisture content is considered to be zero, due to the vacuum conditions in the process (Kiranoudis et al., 1997). The initial surface moisture content of the berries was also assumed to be 0 as the berries were blotted free of excess moisture. The nonlinear regression function of Minitab was used to fit the curve and determine the parameters K, k, and n. The degree to which the model fits the experimental data was compared using the standard error of the regression (S) in order to compare the fit between models. The S value provides the average distance that the observed values fall from the regression line, and therefore the smaller the standard error of the regression, the better the fit of the model to the data. More to the point, the more widely used R^2 value was omitted because this value is not applicable to nonlinear regression analysis and may lead to incorrect conclusions regarding the validity of the regression (Spiess & Neumeyer, 2010).

4.3 Results and Discussion

4.3.1 Microwave Characterization

The magnetron power output was determined calorimetrically in two ways. By using the manufacturer suggested amount of 250.0g of water the full output of the magnetron was measured. Separately, a smaller sample size of approximately 20.0g of water was placed in a similar geometry and location to the berries in order to mimic the initial size and placement of the cranberry sample. This latter test was done to approximate the "true" power to the sample size being used in this study in order to more precisely estimate the power density. While more accurate in terms of sample size, this still makes the assumption that the 20g of cranberries will absorb the same amount of microwave energy as 20g of water, which is unlikely to be true particularly as drying progresses. This is because water is the major absorber of microwave energy in foods, and therefore changes

in moisture content will alter the dielectric properties of the samples (Sosa-Morales et al., 2010). Even with the larger of the two water loads, microwave power was found to be significantly less than the nominal magnetron power output (Table 4.1). This discrepancy can be accounted for in two ways. First, there is a normal loss of power due to lack of efficiency as the magnetron converts electrical to microwave energy. More importantly, the modifications made to the microwave in order to allow for the incorporation of the balance as well as the vacuum tubing entailed drilling through the microwave cavity walls and would explain the lower amount of energy resonating in the cavity. Overall, however, because the incident for the full power microwave would have been excessive for this sample size, the reduced amount of microwave energy absorbed by the product could actually be considered beneficial for this application. Still, this study employed higher power densities (Table 4.1) and shorter power-on times (Table 4.2) than those typically used for microwave-based dehydration processes, where past studies employed power densities ranging from 0.5-5 W/g and magnetron power-on and power off times between 30-60s (Sunjka et al., 2004; Beaudry et al., 2003; Yongsawatdigul & Gunasekaran, 1996a). This study is therefore indicative of the potential of using duty cycle as a product temperature mediation strategy.

Table 4.1: Calorimetrically Determined Magnetron Output Levels

Sample Size (g)	Power (W)	Power Density (W/g)
20	204.7 +/- 9.6	10.2
250	561.7 +/- 12.7	2.25

Table 4.2: Magnetron Power-on and Power-off Times (Duty Cycle)

Power Setting	Power On Time (s)	Power Off Time (s)	Duty Cycle (%)
10%	3	27	10
20%	6	24	20
30%	10	20	33
40%	12	18	40
50%	15	15	50

4.3.2 Drying Time

Individual treatment types (power level combinations) were selected with several things in mind. Initially, the range of useful power levels were determined by monitoring the berries for scorching over the course of dehydration, starting with 10% but working up to 60%, where the 60% power setting (results not shown) scorched the samples after only a few minutes and therefore the next lowest setting (50%) was used as the upper end cut-off. While the 50% and even the 40% setting still produced notable scorching when used until completion, data was still collected for these settings both as a comparison and also to test the benefits of using these higher power levels as an initial step before reducing to lower power levels later during drying. The full range of prescribed power levels, along with their corresponding drying times, can be seen in Table 4.3.

Typical drying curves can be seen in Figure 4.2, where curves were recorded both for untreated and MWODS pre-treated samples dried at constant microwave power settings. Total drying times to 20% moisture content (Table 4.3) indicate that as magnetron duty cycle increases the total drying time decreases. This is typical of an intensifying process as longer magnetron power-on times allows for more energy to raise product temperature and evaporate moisture in a given period of time. Elevated temperatures maintained by the longer power-on times were empirically noticeable both in the berries themselves through increased evidence of charring as well as excessive heating of the microwave cavity and vacuum chamber itself, particularly for samples that were dried at consistently high power levels. Interestingly, there was no effect of different initial moisture contents in the case of the MWODS pre-treated samples as drying times were comparable and in some cases longer for samples with lower moisture contents. This is likely due to the fact that differences in moisture content at high levels are most likely in the outer layers of the product easily accessed by the osmotic treatment, whereas the overall drying time is largely dictated by the rate at which moisture is removed from the inner core of the sample as this is typically the most difficult portion of sample to dehydrate. The range of drying times found in this study encompasses a wide range, but generally agree with times found in previous studies for which published values include 32.8-44 min (Yongsawatdigul & Gunasekaran, 1996a), 18.3-61.1 min (Sunjka et al., 2004), to as much as 2.2-5h (Beaudry et al., 2003). The wide range of published values can be attributed to differences in experimental setups, applied power density, and duty cycle. While it is difficult to make a direct comparison because of the different power densities and cycle times, the drying times found in this study were found to be within the previously

established ranges for microwave-vacuum finish-drying of osmotically pre-treated cranberries. Furthermore, employing the MWV process decreased drying times by at least an order of magnitude as compared to convective air drying, which agrees with common conclusions of previous reports comparing the techniques.

Table 4.3: Microwave-Vacuum Drying Times for Fresh and MWODS Pre-Treated Cranberries

Treatment Type	Drying time (minutes)							
	MW-V (Fresh)				MW-V (MWODS)			
10%	182	±	2.1	a	95	±	4.1	c
20%	43	±	2.5	e	38	±	1.2	f,g
30%	28	±	2.2	h,i	20	±	0.5	j,k,l,m,n
40%	20	±	1.0	i,j,k,l,m,n	15	±	0.5	l,m,n
50%	12	±	0.5	n	12	±	1.0	n
20/10%	119	±	1.0	b	91	±	0.5	c
30/10%	71	±	1.0	d	33	±	2.5	g,h
30/20%	30	±	1.6	h	24	±	1.5	h,i,j,k,l
40/10%	61	±	0.5	e	29	±	1.0	h,i
40/20%	28	±	2.1	h,i,j	25	±	0.5	h,i,j,k
40/30%	16	±	0.5	k,l,m,n	19	±	0.5	k,l,m,n
50/10%	19	±	3.3	k,l,m,n	17	±	2.1	k,l,m,n
50/20%	21	±	1.0	i,j,k,l,m	14	±	1.0	m,n
50/30%	14	±	0.5	m,n	15	±	0.0	l,m,n
Air Dry					1345	±	15.0	

Mean values with standard deviation and Tukey groupings (95% confidence interval) shown: means that do not share a letter (a,b,c) are significantly different

4.3.3 Drying Kinetics

In comparing the standard error of the regression (S), the empirical Page model was a better fit for the experimental data when compared to the exponential model (Table 4.4). The suitable fit of the Page model agrees with various prior studies of microwave-vacuum and microwave-convective dehydration of biomaterials, where this model was most able to model experimental data (Giri & Prasad, 2007a; Sutar & Prasad, 2007; Prabhanjan et al., 1995). The standard error tended to be higher in treatments where there was a large drop in power setting (e.g. the 30/10,

40/10, and 50/10% processes), where increasing the finishing power to 20% (e.g. 30/20, 40/20, or 50/20%) tended to decrease the standard error dramatically regardless of model or sample type, an example of which can be seen in Figure 4.3C. This is attributed to the fact that the models tend to overestimate the moisture loss once the power level drops and the rate of moisture removal decreases to fall more in line with the lower intensity power setting. The trend dictates that the higher the finishing power setting, the smaller to temperature decrease once the setting changed and therefore, the smaller the decrease seen in rate of moisture loss.

Overall, the parameters *k* (Page model) and *K* (Exponential model) tended to increase with increasing process intensity (Table 4.4), where in the continuous power setting treatments the *k* value increased from 0.0003 min^{-1} (10% treatment) to 0.157 min^{-1} (50%) and 0.002 min^{-1} (10%) to 0.051 min^{-1} (50%) for frozen-thawed and MWODS pre-treated berries, respectively. A similar trend can be seen in the case of split power level treatments where the change can be seen with increasing finishing power levels. A similar trend exists in both cases for the drying constant (*K)* values of the exponential model. The increasing *K* and *k* values are indicative of the higher intensity processes ability to increase moisture loss over the course of the process, which of course agrees with the decreased drying times (Table 4.3). Similar results have been found in the case of mushrooms dried under microwave-vacuum conditions, where increases in these parameters were attributed to lower pressure, smaller sample size or higher incident microwave power (either of which would increase power density) (Giri & Prasad, 2007a). Overall, the values for the parameters *K*, *k*, and *n* vary from previously published reports, and are generally lower (Sosa-Morales et al., 2010; Giri & Prasad, 2007a; Sutar & Prasad, 2007). This is attributed to the different treatment (relying on higher incident power and shorter duty cycles) as well as the effect of the cranberry skin, which is an effective moisture barrier and would therefore slow moisture removal when compared to other samples which in many cases are sliced or don't feature a waxy skin. In this case, the increase is attributed to the increasing magnetron power-on times which allow for more constant moisture removal as the temperature of the product would remain higher throughout the process. The Page model parameter *n* tended to decrease with increasing power level (and increasing *k*), indicating a general flattening of the kinetic curve with increasing process intensity, which is indicative of a more constant drying rate as the more intense processes would allow for much shorter falling rate periods.

Table 4.4: Effect of Microwave Treatment Intensity and MWODS Pre-Treatment on the Parameters for the Exponential and Page's Model

Treatment Type	Fresh (Frozen Thawed)					MWODS Pre-Treated				
	Page Model			Exp. Model		Page Model			Exp. Model	
	k (min^{-1})	n	S	K (min^{-1})	S	k (min^{-1})	n	S	K (min^{-1})	S
10	0.0003	1.794	0.013	0.012	0.100	0.002	1.263	0.017	0.031	0.041
20	0.002	2.443	0.009	0.049	0.092	0.004	1.898	0.012	0.056	0.106
30	0.049	1.733	0.013	0.083	0.148	0.012	2.277	0.009	0.067	0.136
40	0.093	1.363	0.012	0.181	0.052	0.042	1.602	0.009	0.140	0.082
50	0.157	1.169	0.011	0.210	0.028	0.051	1.839	0.014	0.195	0.108
20/10	0.014	1.143	0.014	0.024	0.026	0.008	1.296	0.016	0.025	0.047
30/10	0.069	1.171	0.023	0.065	0.021	0.037	1.266	0.032	0.077	0.039
30/20	0.078	0.942	0.019	0.105	0.032	0.053	1.297	0.017	0.106	0.047
40/10	0.064	1.517	0.017	0.119	0.028	0.031	1.512	0.040	0.136	0.039
40/20	0.125	0.997	0.001	0.124	0.001	0.042	1.720	0.018	0.148	0.095
40/30	0.270	0.682	0.011	0.169	0.070	0.134	1.642	0.007	0.148	0.085
50/10	0.011	2.240	0.034	0.135	0.102	0.009	1.752	0.036	0.118	0.083
50/20	0.068	1.522	0.015	0.179	0.034	0.033	2.170	0.030	0.149	0.121
50/30	0.119	1.218	0.020	0.178	0.070	0.035	1.954	0.011	0.178	0.117
Air Drying	0.003	0.832	0.034	0.001	0.044	0.0004	1.164	0.018	0.001	0.031

In comparing the fresh-frozen and MWODS pre-treated berries, for equivalent MWV treatments the parameters k and K tend to be lower for the pre-treated samples, which is likely an effect of the lower starting moisture content of the berries. There was no clear trend for the n-value, where in some cases the value is higher for fresh berries and in others for the MWODS pre-treated berries. Both k and K values are higher (often by several orders of magnitude) for MWV finish-drying as compared to air dried samples, regardless of sample type. The exception of the k-value of the Page model for the Fresh 10% and 20% is somewhat mediated by the exponential n parameter, as this difference disappears when comparing the K-values of the exponential model (Table 4.4).

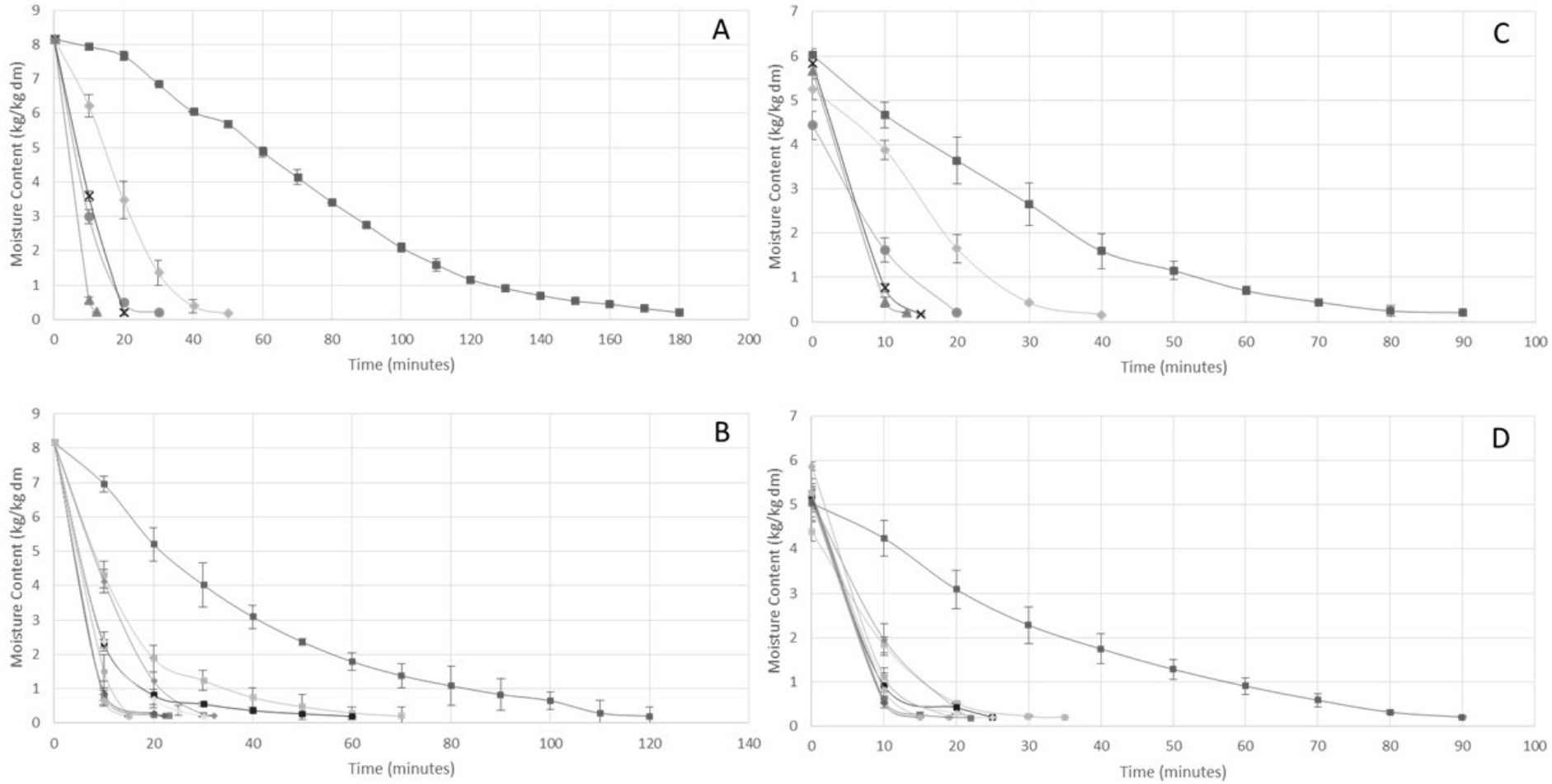

Figure 4.2: Selected MWV Finish-drying Curves

Where A and B represent Fresh samples under continuous and combination and C and D are for MWODS pre-treated cranberries under continuous and combination power levels, respectively. For both sample types the follow legend applies:

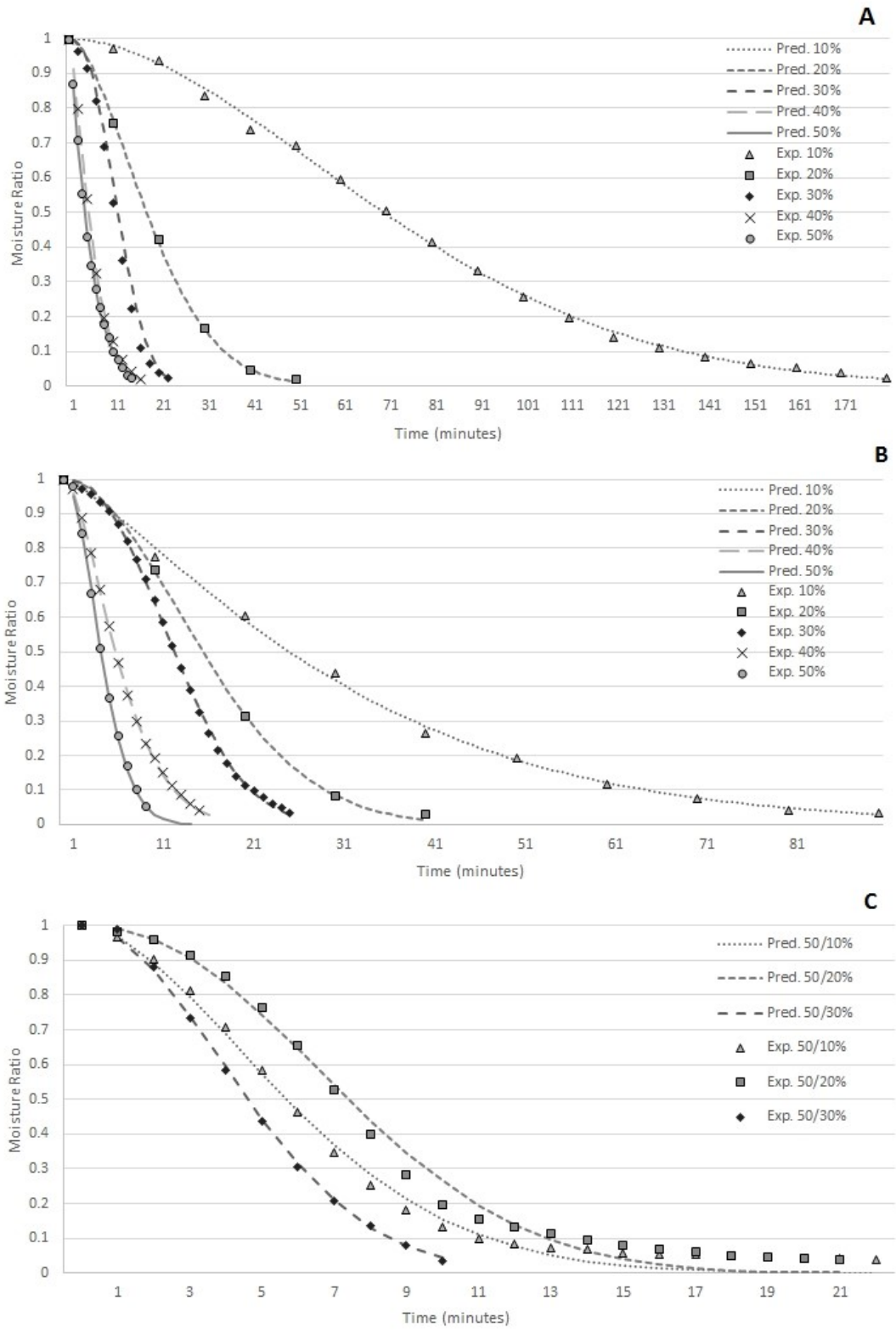

Figure 4.3: Experimental vs Predicted (Page model) Drying Kinetic Curves

Where Fresh (A) and MWODS Pre-treated (B) Samples as well as MWODS Pre-treated Berries Under Select Combination Power Setting Treatments (C) are shown

4.3.4 Energy Consumption

The effect of duty cycle on energy consumption (Table 4.5) indicates higher power settings (corresponding to longer magnetron power-on times) required less energy per unit of moisture removed from the product over the length of the process. This is particularly visible when increasing the power setting in the constant-power treatments, where increasing the power setting from 10% to 50% decreased the energy required per unit mass of water by approximately 70% in the case of fresh berries and 60% in the case of MWODS pre-treated berries. The same trend could be seen in the split power setting treatments (e.g. 30/10% to 30/20%, 40/10% through 40/30%), however the reduction grew less evident at higher power levels for both sample types. To that end, both sample types eventually reached a point where increasing power settings provided no further benefit in terms of reducing energy consumption. This is likely due to the fact that so much water is removed early on in the process (Figure 4.4) that any subsequent power treatment is so short that it is of virtually no consequence in terms of reducing the total time and energy consumption. More specifically, for the MWODS samples, the energy consumption minima was reached at 30/10% and 30/20%, where evidence of quality degradation (charring) beyond this level was also noticeable. A similar conclusion could be drawn for fresh berries, where in this case there it a higher power setting (40/30%) was required to reach a minimum power consumption, however charring was also a concern and thus quality of the product would also be the limiting factor in this case. Overall, the trend of increasing efficiency (lower energy consumption) with increasing power-on times runs opposite to trends identified by previous authors, where processes with shorter power on times were found to more efficiently utilize energy input to remove water (Yongsawatdigul & Gunasekaran, 1996a). This effect was attributed to the influence of shorter power on times to gradually increase product temperature and allow water to relocate within the cranberries (Yongsawatdigul & Gunasekaran, 1996a). However, results in this study indicate higher energy consumption with decreasing power settings which indicates that the shorter power-on times were not capable of maintaining the product temperature at a level suitable to promote evaporation. In this case, the product will cool during the power-off times and therefore energy applied at the next power-on cycle would need to physically heat the water as opposed to solely providing the latent heat of vaporization. A similar trend was reported by Sunjka et al. (2004), where over a range of power densities longer power off times (with constant power-on times)

tended to decrease the drying performance, defined in kg_{water}/MJ, implying an increased energy consumption per unit mass of water removed as power-off times increased. With this in mind it appears as though that in terms of minimizing energy consumption a process with either shorter power-off times or longer power-on times may be beneficial, although this would necessitate lower power densities to avoid product degradation.

Table 4.5: Energy Consumption of various MWV Treatments

Treatment Type	Energy Consumption (MJ/kg)	
	MWV (Fresh)	**MWV (MWODS)**
10%	15.6 ± 0.2 a	10.6 ± 0.4 b,c
20%	8.9 ± 0.4 c,d,e,f	8.5 ± 0.2 d,e,f
30%	9.4 ± 0.4 c,d	8.3 ± 0.3 d,e,f
40%	8.6 ± 0.3 c,d,e,f	7.2 ± 0.0 e,f
50%	7.2 ± 0.2 f	7.1 ± 0.5 f
20/10%	12.2 ± 0.1 b	10.6 ± 0.1 b,c
30/10%	9.5 ± 0.1 c,d	7.6 ± 0.1 d,e,f
30/20%	8.0 ± 0.2 d,e,f	7.4 ± 0.0 e,f
40/10%	9.3 ± 0.1 c,d,e	7.6 ± 0.1 d,e,f
40/20%	8.3 ± 0.1 d,e,f	8.2 ± 0.2 d,e,f
40/30%	7.0 ± 0.1 f	7.9 ± 0.2 d,e,f
50/10%	7.1 ± 0.2 f	8.3 ± 0.1 d,e,f
50/20%	7.8 ± 0.2 d,e,f	7.4 ± 0.1 d,e,f
50/30%	7.3 ± 0.2 e,f	8.0 ± 0.2 d,e,f
Air Dry		4.54-6.50[20]

Mean values with standard deviation and Tukey groupings (95% confidence interval) shown: means that do not share a letter are significantly different

Comparing the fresh berries to MWODS pre-treated samples, the energy required per unit mass of moisture removed is generally lower for the pre-treated berries than for the fresh. This trend is evident despite the fact that the initial moisture content of the MWODS pre-treated berries is lower than the fresh berries. Previous work has found that lower starting moisture content actually increased energy consumption, an effect attributed to the fact that the ability of a product to absorb energy decreases with moisture content, resulting in less efficient use of applied energy (Yongsawatdigul & Gunasekaran, 1996a). This likely indicates an effect of the MWODS process itself, where the treatment would both migrate moisture towards the outer layers of the sample and

promote the destruction of the cell walls, where microwave heat treatments have previously been found to disrupt cell walls of plant material (Funebo et al., 2000). These effects would allow water molecules to be more readily evaporated during finish-drying which would in turn reduce the drying time and energy consumption. This is supported by the fact that MWODS pre-treated samples maintained a higher rate of moisture removal during the early minutes of the process regardless of power level (Figure 4.4) despite the lower amount of moisture present to begin with. In comparing the drying efficiencies over the course of the whole process, the decrease between the fresh and MWODS samples erodes and actually reverses slightly at the higher range of power settings. This is largely attributed to the uneven reduction in finish-drying times as with constant power setting the energy consumption is dependent on drying time. For instance, whereas the MWODS treatment decreased the MWV drying time of the 10% sample from 182 to 95 min (a reduction of nearly 50%), whereas at higher power levels the impact was more mixed where for instance using the 50% process there was no difference between the two sample types. This indicates that these processes are intensive enough to overcome any benefit of the MWODS pre-treatment, either in terms of destruction or reduced initial moisture content.

In previous studies on microwave vacuum drying, energy consumption has been calculated in several ways. In bench-top scale setups, the required power for all the components are typically estimated separately, summed, and then expressed per unit mass moisture removed, while in studies using larger commercially built pilot scale equipment and larger sample loads, the power draw by the entire system is typically used. More to the point, in prior bench top scale studies the contribution to the energy consumption by the vacuum pump has typically been omitted. This is largely because laboratory vacuum pumps like the one used in this study are designed to run continuously at full capacity, whereas the energy required to maintain a vacuum will be less than that required to initially evacuate the chamber. Also, the size or capacity of the pump is likely too large for a bench top scale MWV setup to begin with. As a result, including this energy consumption in its entirety will vastly overestimate total energy use. For example, in looking at the continuous 10% process for which total drying time was 180 min or 10800s. In this case, the magnetron (204W incident power) is on for only $1/10^{th}$ of the total drying time (1080s), this represents a total of 0.221MJ incident on the sample over the duration of the process. In contrast, the 125W vacuum pump would consume 1.35MJ over this same timeframe. When converted to a MJ/kg moisture removed basis, this increases the total energy consumption from about 12 (with

no vacuum pump) to around 88 MJ/kg (continuous vacuum pump), which far exceeds previous estimates, which range from 2.98-3.67 MJ/kg (Yongsawatdigul & Gunasekaran, 1996a) to 2.8-7.7 MJ/kg (Sunjka et al., 2004).

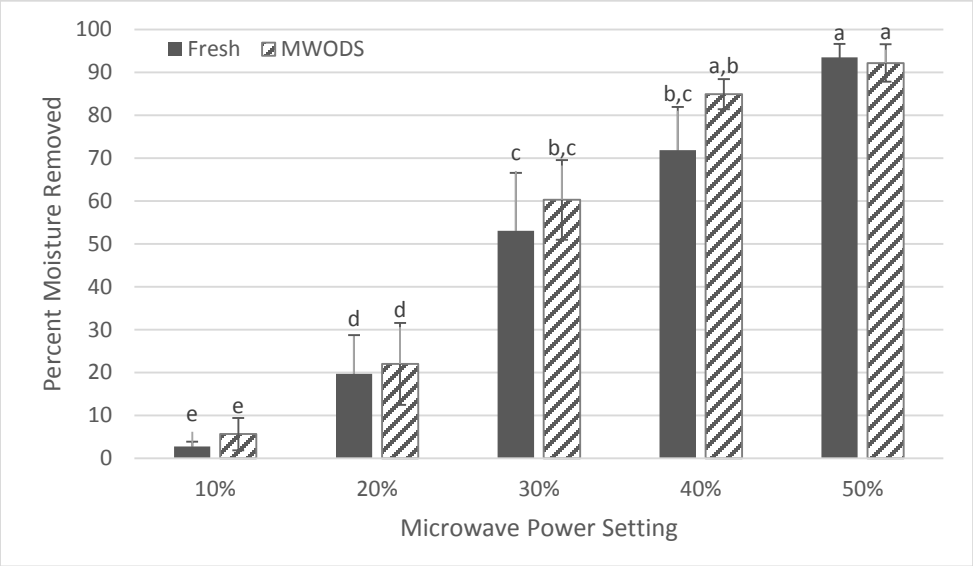

Figure 4.4: Amount of Moisture Removed from Sample in First Ten Minutes as Fraction of Total Moisture to be removed

Mean values with standard deviation and Tukey groupings (95% confidence interval) shown: means that do not share a letter are significantly different

As a result, a new method to compare energy consumption was developed. As previously mentioned, the loss of vacuum due to leaks in the system was minor and therefore this new method assumed that the pump would only have to work to re-establish the vacuum as it was broken by the creation of water vapor. By calculating the volume of vapor created and the flow rate the pump is capable of, a more accurate picture of the contribution of the pump towards the total energy consumption was developed. In fact, while energy consumption values in this study (Table 4.5) were found to be higher than those previously reported for MWV drying of cranberries the comparison is still valid, particularly when allowing a margin for the different experimental setups, initial moisture contents and the fact that including the vacuum pump increased EC values by 22-69%.

Generally speaking, the energy consumption of the lower power setting processes (particularly the 10% process) exceeded previously published values by a larger degree than the more intensive treatments. Overall, it's likely that in order to optimize the energy consumption, modifying the duty cycle alone is not enough and must be combined with altering applied power as well. Additionally, the value for the vacuum pump included is likely lower than the 'real' energy required, both because of the leaks in the system but also because it was assumed the pump was operating at 100% of the manufacturer rated capacity when establishing the vacuum conditions, which is likely not the case. Regardless, these values do provide some insight into the substantial contribution of the pump to the total energy consumption of the process.

In order to compare the energy consumption of MWV and conventional air drying, energy consumption values for cranberries were assumed to be equivalent to pre-existing values for prunes due to their similar physical properties (Yongsawatdigul & Gunasekaran, 1996a). In this case, the cited values for conventional air drying were estimated at 4.54-6.50 MJ/kg (Thompson et al., 1981). This is likely an underestimate, however, when it is considered that this comparison was established for sliced berries, whereas in the present study the berries were left whole. As cranberry skin is known to be an effective moisture barrier, this likely had the effect of extending air drying times. The average of ≈22.4h was much longer than those in previously published reports, which is typically around the 12.6h reported in one previous study (Beaudry et al., 2004). However, a more accurate estimation of energy consumption is difficult due to the fact that the sample size used is typically much smaller than the air dryers maximum load, and therefore values pertaining to energy consumption are unsuitable for making comparisons (Yongsawatdigul & Gunasekaran, 1996a). Therefore, while it is difficult to claim outright that the MWV process is more energy efficient than air drying in this case, the fact that the MWV energy consumption is within the same range as previously published suggests that this would hold true in this case, particularly if the berries were left whole. Moreover, the comparison of the techniques is clouded when considering other impacts such as the cost of electrical energy required for microwave generation versus other sources that can be used to produce heat alone (e.g. burning biomass), as well as the ability of air drying to recapture expended energy as part of multi-stage processes. Finally, it must also be pointed out that these values do not include the energy consumption of the osmotic pre-treatment and therefore the values presented in Table 4.5 should be used for comparing the various finish-drying treatments only.

4.4 Conclusions

Overall the MWODS and MWV combination process was found to be suitable for the rapid production of dried cranberries. By enhancing or eliminating the longest parts of the dehydration process (conventional osmotic dehydration and convective air drying), the process allows for rapid dehydration of both fresh and MWODS pre-treated whole cranberries. Overall, it was found that the 10%, 20/10%, and 30/10% treatments were most amenable to finish-drying of the MWODS pre-treated berries while remaining free of visible damage (scorching), where higher intensity treatments reduced energy consumption by reducing finish-drying times. Furthermore, the MWV process could be used as a standalone method without osmotic pre-treatment, particularly where the berries would be further transformed or integrated into a manufactured product and therefore the increased solids content promoted by osmotic treatments would be of no benefit. In this case there is a wider range of applicable power settings, where the absence of added sugar enables higher intensity MWV treatments. When fitting drying kinetic models, the empirical Page model was the best fit and was able to suitably predict the finish-drying kinetics of both fresh frozen and MWODS pre-treated whole cranberries under both MWV and air drying conditions. While further investigation of the effects of the processes on the quality of the dried berries is required, the groundwork has been laid out in order to design a process that balances the two main advantages of the combination process: energy consumption and product quality.

CONNECTIVE STATEMENT TO CHAPTER 5

More and more, consumers are not only shopping with their eyes but also with their health in mind. By maintaining levels of heat sensitive compounds such as anthocyanins, which also produce the characteristic red color of cranberries, an important step is taken in developing the process by assuring a high quality product. These chemical markers are valuable as quality indices because of their susceptibility to degradation. Therefore, in following the developments of the previous chapter where energy and drying kinetics were determined for various MWV treatments, the next step was to determine the effects of the process on quality parameters. Initially only observed visually in order to determine the maximum treatment intensity, in the following chapter the samples are tested after each run for their quality indices, including texture, color, and several chemical indices: total monomeric anthocyanins, total phenolics, and DPPH radical scavenging activity. By comparing MWV to a gentle but more expensive process such as freeze drying, we can obtain a good idea of where a new drying process compares in terms of quality maintenance.

Parts of Chapter 5 have been adapted for presentations and publications as follows

Wray, D and Ramaswamy, H.S., 2014. Development of Microwave-Vacuum Finish-drying for Whole Cranberries Pretreated by Microwave-Osmotic Dehydration under Continuous Flow Spray (MWODS) Conditions. Northeast Agricultural and Biological Engineering Conference (NABEC) 2014. July 27-30th, 2014, Kemptville, Ontario.

Wray, D and Ramaswamy, H.S. The Effect of Process Intensity on Quality Attributes of Microwave-Vacuum Finish Dried Fresh and Microwave-Osmotic Pre-Treated Whole Cranberries *(Vaccinium Macrocarpon)*. *(Submitted)*

CHAPTER 5

THE EFFECT OF PROCESS INTENSITY ON QUALITY ATTRIBUTES OF MICROWAVE-VACUUM FINISH DRIED FRESH AND MICROWAVE-OSMOTIC PRE-TREATED WHOLE CRANBERRIES (*VACCINIUM MACROCARPON*)

Abstract

A novel combination of drying techniques for whole frozen-thawed cranberries was developed employing microwave osmotic dehydration under continuous flow medium spray (MWODS) conditions as a pretreatment coupled with microwave-vacuum (MWV) finish-drying. Fresh and MWODS pre-treated berries were dried under a range of treatments employing continuous and decreasing microwave power settings. Physical quality indices (color and texture) as well as chemical indicators (total phenols, total monomeric anthocyanins, and radical scavenging ability) were monitored in order to determine optimal treatment types for both test samples. All physical and chemical indicators were found to decrease with increasing process intensity, but several MWV treatment types were identified as having good potential for the production of high quality dried berries. Overall the MWODS-MWV was found to better maintain product quality than air dried samples, and in many cases the MWODS-MWV dried product approached the standard set by freeze dried samples. The MWODS-MWV combination process was therefore found to be a suitable rapid method to produce high quality dried cranberries.

5.1 Introduction

Dehydration is one of the most widely used preservation methods employed within the food industry. The primary goal is to remove moisture in order to reduce the water activity of the product to a level lower than 0.7 in order to stop microbial growth and limit degradation during storage. Drying also allows the transformation of a fresh crop into a shelf stable commodity, lower storage and transportation costs by reducing weight and eliminating the need for refrigerated storage, and the possibility of adding value to processed foods (Orsat et al., 2007). However, drying is also energy and cost intensive due to its simultaneous mass and heat transfer process accompanied by a phase change as water evaporates (Fernandes & Rodrigues, 2007). This is a particular concern with conventional air drying, a method which results in shrunken products with tough texture, severe browning, and low nutritive value (Deng & Zhao 2008b). Quality losses typical of dehydration include degradation of color and flavor as well as loss of nutritional profile, effects which are largely attributed to exposure to high temperatures for long periods of time (Alibas, 2007). Therefore, there is considerable interest in developing novel dehydration techniques that produce higher quality dry food products. This is of particular interest with cranberries as these berries possess a wide range of phytochemicals that are thermolabile and subject to degradation during processing (Pappas & Schaich, 2009). These phytochemicals (primarily flavonols, flavan-3-ols, anthocyanins, tannins, and phenolic acid derivatives) have been implicated in a wide range of health positive functions in the body including prevention of cardiovascular diseases, various cancers, urinary tract infections, and pylori-induced stomach ulcers, as well as promoting dental health (Côté et al., 2010b). Because of the wide range of health positive functions, there is particular interest in modernizing processes to promote their retention during dehydration.

Microwave-vacuum (MWV) dehydration has been suggested as one technique to dry cranberries, where retained antioxidant activity approaches that of freeze dried berries (Leusink et al., 2010). MWV has been successfully applied to various food products in order to reduce volatile loss, accelerate moisture removal and slow heat transfer to the solid phase due to absence of convection (Drouzas & Schubert, 1996). Initially, the application of vacuum was suggested as one strategy for alleviating physical damage typically caused during microwave drying such as scorching, off-color production and uneven heat distribution (Gunasekaran, 1990). Another suggested approach was to cycle magnetron power during drying both because continuous

application of microwave energy generally does not accelerate the rate of water removal once a critical moisture content has been reached and also because pulsed application of microwave provides energy benefits over continuous heating (Yongsawatdigul & Gunasekaran, 1996a). Power cycling also allows better redistribution of the temperature and moisture profile within the product during power off times (Sunjka et al., 2004). Application of vacuum allows water to vaporize at lower temperatures and therefore the drying operation can be maintained at much lower temperatures, offering higher product quality (Raghavan & Orsat, 2007). Moreover, because air is excluded during drying, oxidation reactions are minimized (Gunasekaran, 1990). This is particularly important with a product such as cranberry where biologically active antioxidants are easily oxidized and degraded. By combining these principles, the microwave vacuum process then allows a dried product with better color, texture and flavor, making it advantageous to use this process despite high installation and operating costs (Yongsawatdigul & Gunasekaran, 1996a).

Microwave osmotic dehydration under continuous flow medium spray (MWODS) conditions has been described as a method to accelerate moisture loss from fruit while limiting solids gain (Azarpazhooh & Ramaswamy, 2010c). This technique has also been applied to whole cranberries where it was found that the process was able to overcome the moisture barrier property of cranberry skin with no skin pre-treatment (Wray & Ramaswamy, 2013). This alleviates the problem encountered in prior work on conventional osmotic dehydration of cranberries which suggested it is necessary to disrupt the skin prior to osmotic treatment where chemical, thermal, mechanical or combined techniques have been tested (Grabowski et al., 2007).

The monitoring of polyphenolic content has been used in various berry products such as jams, juices, and canned berries (Howard et al., 2010; Fang et al., 2006; Chaovanalikit & Wrolstad, 2004). This type of monitoring is of increasing importance with dried products as well, where there is an increasing consumer awareness of the health positive effects of phytochemical rich fruits such as cranberries. Therefore, when designing a process, efforts should be made to monitor the levels of these health positive compounds during dehydration with the end goal of preserving the phytochemical integrity of the product. Studies featuring such testing procedures for dried products have been applied to phytochemical rich products such as green tea (Hirun et al., 2014), sour cherries (Wojdyło et al., 2013), and also cranberries (Leusink et al., 2010).

After an osmotic pre-treatment, products still need to be transferred to a finish-drying step to remove further moisture to limit the water activity of the product. Finish-drying has traditionally

been accomplished using hot air drying, even when employing a microwave-osmotic pre-treatment (Azarpazhooh & Ramaswamy, 2011a; Azarpazhooh & Ramaswamy, 2011b). Moreover, previous work (Chapter 4) had focused on energy concerns and drying kinetics of MWV drying of frozen-thawed and MWODS pre-treated berries. Therefore, the objective of this study was to screen MWV drying treatments by monitoring quality parameters and chemical markers of fresh (frozen-thawed) and MWODS pre-treated berries. In combining the primary osmotic treatment (MWODS) with secondary MWV drying, the goal was to develop a novel technique to rapidly produce high quality dehydrated cranberries.

5.2 Materials and Methods

5.2.1 Cranberries

Previous work indicated that frozen-thawed whole cranberries were suitable for drying with no skin pre-treatment necessary (Wray & Ramaswamy, 2013). Therefore, IQF whole cranberries (Atoka Cranberries Inc., Manseau, QC, Canada) were kept frozen (-21 to -27°C) until use, at which point the berries were thawed by floating 200g batches in room temperature tap water for 1 h. During this time the berries were sorted, where only whole, undamaged, and ripe cranberries of medium size (approximately 10-15mm diameter) were selected. Under-ripe (white), broken, crushed or otherwise damaged berries were discarded. Surface moisture was then removed by blotting before samples were weighed and transferred either directly to the MWV setup or first to the MWODS pre-treatment. The average moisture content of the frozen-thawed berries was found to be 89.1 ± 1.02%.

5.2.2 MWODS Pre-Treatment

The experimental setup employed for the MWODS pre-treatment was the one previously developed (Wray & Ramaswamy, 2013; Azarpazhooh & Ramaswamy, 2010c), which was further refined with a new spray head as outlined in Chapter 4. MWODS parameters (50°C, 50°B, and 30 min) were selected as this represented the midpoint of the previously established CCRD design (Wray & Ramaswamy, 2013). In this process, the sample was held inside the microwave cavity under a spray head which continually showered the product with osmotic solution which was circulated and maintained at a constant temperature (50°C in this case). This setup allowed for the product to be treated in a thin layer of osmotic solution allowing good temperature maintenance

and moisture removal while still facilitating the majority of the microwave energy to be absorbed by the product itself. The system used a solution-to-sample ratio of approximately 30:1 as in previous work (Azarpazhooh & Ramaswamy, 2010c). As the midpoint of the CCRD design, this represented a medium intensity treatment meant to be representative of MWODS on the whole for purposes of selecting suitable MWV treatment to follow a wider range of microwave osmotic treatments in subsequent studies.

The method employed for MWODS was also similar to the previously published works (Azarpazhooh & Ramaswamy, 2010c; Wray & Ramaswamy, 2013) with a couple modifications. Briefly, accurately weighed portions of cranberries were placed in the MWODS setup, where the osmotic syrup was previously equilibrated at 50°C with the help of an external heat exchanger. Once the osmotic solution was circulating the microwave was turned on at full power for 30 min after which the samples were removed, shaken to remove excess sugar solution, and allowed to cool at room temperature for 10 min. In order to accurately determine the moisture content of the samples set to undergo finish-drying, half the post-MWODS berries were taken to determine the moisture content by oven drying to constant weight (approximately 24 h) at 105°C (AOAC, 1975). The other half of the sample was sealed and held at 4-6°C until the next day when their moisture content could be estimated from the previously dried half of the sample. This method was able to accurately predict (R^2 = 0.96) the moisture content of the half-sample to be finish dried when verified by the same AOAC method. Overall, the moisture content of the cranberries post-MWODS varied from 77-82% (wet basis).

5.2.3 Microwave-Vacuum Finish-drying

The purpose built bench-top MWV setup employed a commercial domestic microwave and glass vacuum chamber which was suspended from a balance, allowing regular mass measurements without interrupting the process. Drying times ranged from 12-95 min for MWODS pre-treated samples and 12-180 min for frozen-thawed berries. Initial power density was determined to be approximately 10.2 W/g and magnetron duty cycles ranged from 3s on/27s off for the 10% setting up to 15s on/15s off for the 50% setting. Full details of the microwave vacuum construction, operation, and characterization has been given in Chapter 4.

During the actual test, approximately 20g of fresh or MWODS pre-treated cranberries samples were accurately weighed and spread in a single layer into Pyrex petri dishes lined with

food grade silicone. The chamber pressure was then lowered to the operating pressure (6 kPa absolute), the initial mass recorded, and the microwave set at the prescribed power level. When combination run types were employed the initial power level (e.g. the 50% in a 50/10% process) was applied for the first ten minutes of the process and then the power was changed to the secondary level in order to reduce the magnetron power on time as the sample mass decreased. The mass of the sample was monitored and once the sample reached the required target mass to achieve a moisture content of 20% (dry basis), the microwave was stopped and the vacuum was partially relieved to a level of 13 kPa abs for approximately 5 min in order to allow the sample to cool in a reduced oxygen atmosphere. The sample was then removed, weighed, and sealed in a plastic bag for further analysis.

5.2.4 Convective Air Drying

MWODS pre-treated cranberries were air dried using a domestic drying oven (Equi-Flow Food Dehydrator, Marysville, WA) which was modified with a digital thermostat to maintain conditions of 60 ± 1°C, 0.64 ± 0.02m/s and a RH of approximately 15%. Berries were arranged in a single layer on a metal mesh and suspended from a balance in the drying chamber, where they were subjected to constant horizontal airflow. The mass of the sample was recorded every 10 min and four times during the process the door was quickly opened and the sample container rotated 90° so as to alternate the side of the sample exposed to the oncoming hot air. Air drying is the method typically used to finish dry cranberries and other products in industrial settings and therefore was employed as a comparative standard for the MWODS pre-treated samples.

5.2.5 Freeze Drying

As in other studies, freeze drying was employed as 'best case' scenario in terms of maintaining quality attributes during dehydration (Azarpazhooh & Ramaswamy, 2011b). Both fresh and MWODS pre-treated berries were freeze dried in order to produce comparative standards (Fresh FD and MWODS FD, respectively) for quality analysis. Samples were frozen overnight at -30°C and then dried at approximately 13 Pa at room temperature for approximately 24 h using a pilot scale freeze dryer (SP Scientific/Virtis MR-145BA, Warminster, PA).

5.2.6 Quality Analysis

Quality measurements were categorized into physical (color, texture) and chemical (total phenolics, total monomeric anthocyanins, and radical scavenging activity) based tests. All treatment types were performed in duplicate and physical characteristics of the berries were measured the same day, while for chemical analyses the samples were kept frozen at -30°C until extraction, a maximum of one week.

5.2.7 Color Measurement

Color values of fresh and dried samples were determined in the L^*, a^*, b^* system using a tristimulus Minolta Chroma Meter (CM-500D, Minolta Corp., Ramsey, NJ, USA). The Chroma Meter was warmed up 30 min prior to use and calibrated against a white standard. Eight measurements were taken with each sample and the values averaged in order to obtain the L^* (lightness), a^* (green (-) to red (+)) and b^* (blue (-) to yellow (+)) values of the individual trials. The ΔE (total color change) was also determined according to the following equation (Azarpazhooh & Ramaswamy, 2011b):

$$\Delta E = \sqrt{(L_0 - L)^2 + (a_0 - a)^2 + (b_0 - b)^2} \qquad (5.1)$$

where the L_0, a_0, and b_0 values refer to fresh freeze-dried berries (Fresh-FD) and L, a, and b represent the values of the samples dried via either the MWV or air drying processes. The Fresh-FD standard was used as the zero values for total color change in order to represent the total differentiation from a best case scenario dried product.

5.2.8 Texture Analysis

A simple compression test was used in order to monitor the peak hardness of the sample using a TA.XT*Plus* Texture Analyser with a flat bottom probe (TA-11ss); (Stable Microsystems, Surrey, UK). The analysis was performed with eight replicates of each run with a pre-test speed of 1mm/sec, and a test and post-test speed of 5 mm/sec. The target was 50% deformation of the berries, which generally resulted in the complete fracturing of the product.

5.2.9 Chemical Indicators

In this study, assays to determine the total phenolics, total monomeric anthocyanins and radical scavenging activity of the samples were employed and used as chemical markers of the intensity of the process. In order to prepare the samples for the chemical assays, the berries were

ground to a fine powder in a consumer grade spice grinder using short bursts of power to limit the effect of heat buildup. The samples were then freeze dried for 24 hours in order to eliminate any variations of moisture content of the dried berries on subsequent analyses. After freeze drying, the phenolics were extracted from the powder using a method previously applied to cranberries (Zheng & Wang, 2003). In this case 0.1 g portions of the ground samples were accurately weighed and placed in 15mL centrifuge tubes, to which 10mL of 80% acetone and 0.2% v/v formic acid (Fisher Scientific, Montreal, QC) was added and the tubes vortexed for 10 s. The tubes were then allowed to stand for 10 min at room temperature with 2 additional vortex mixings after which they were centrifuged at 20,000 x *g* for 20 min. The supernatants were then kept at -20°C until ready for analysis, a maximum of one week.

5.2.10 Total Phenolics

The phenolic content of the berry extracts was measured using a Folin-Ciocalteu based method (Lim & Murtijaya, 2007). Briefly, 0.3 mL aliquots of the extract were placed in test tubes to which 1.5mL of 0.2N Folin-Ciocalteu Reagent (MP Biomedicals, Santa Ana, CA) and 1.2mL of 7.5% w/v sodium bicarbonate (Fisher Scientific, Montreal, QC) was added. The test tubes were then capped, vortexed briefly, and allowed to stand for 30 min at room temperature before measuring absorbance at 765 nm. Each sample was analyzed in duplicate for a total of 4 measurements for a given drying treatment. Gallic acid (Sigma-Aldrich, Oakville, ON) was used as the standard and results are expressed in mg gallic acid equivalents (GAE) per gram dry matter (GAE/g dm).

5.2.11 Total Monomeric Anthocyanins

The measurement of total monomeric anthocyanins was completed as suggested for cranberries by Zheng and Wang (2003) and as outlined by Lee et al. (2005). This assay takes advantage of the fact that anthocyanins reversibly change color with pH, where the oxonium ion form is brilliantly red at highly acidic pH values, whereas the colorless hemiketal form predominates at and beyond pH 4.5 (Lee et al., 2005). For this analysis, 0.8mL of the acetone-formic acid extract was mixed with 3.2 mL of buffer at either pH 1 (0.025M KCl acidified with concentrated HCl; Fisher Scientific, Montreal, QC) or pH 4.5 (0.4M sodium acetate acidified with glacial acetic acid; Fisher Scientific, Montreal, QC) was added to the cuvette. The cuvettes were allowed to stand for 20 min and then absorbance was measured against the appropriate buffer blank

at both 520 and 700 nm. Each sample was analyzed in duplicate for a total of four replicates for each process treatment and results expressed as milligrams of cyanidin-3-glucoside equivalents according to the following equation (Lee et al., 2005):

Total Monomeric Anthocyanins (cyanidin-3-glucoside equivalents, mg/L) =

$$\frac{A \times MW \times DF \times 10^3}{\in \times 1}$$

where $A = (A_{520nm} - A_{700nm})_{pH1.0} - (A_{520nm} - A_{700nm})_{pH\ 4.5}$; MW is the molecular weight of cyanidin-3-glucoside (cyd-3-glu); DF = dilution factor; 1 = path length in cm; $\in$ is the molar extinction coefficient for cyd-3-glu (26 900 L mol^{-1} cm^{-1}) and 10^3 is the conversion factor from g to mg.

5.2.12 Radical Scavenging Activity

Anti-oxidant activity was assessed using the electronic transfer based colorimetric assay that monitors the degradation of the stable free radical DPPH using the procedure outlined by (Lim & Murtijaya, 2007). In this case, 100µL of the extract was added to 3 mL of 0.15mM DPPH (Sigma-Aldrich, Oakville, ON) in methanol (Fisher Scientific, Montreal, QC). The mixture was allowed to stand for 30 min in the dark at which point the absorbance was measured at 517 nm against a methanol blank and the antioxidant activity was determined as a percentage of DPPH decrease using the following equation:

$$AA(\%) = [(A_{control} - A_{sample})/A_{control}] \times 100 \qquad (5.2)$$

where $A_{control}$ is the DPPH˙ solution diluted with 100µL of methanol instead of the phenolic extract.

5.2.13 Data Analysis

Experiments were performed in duplicate and mean values with standard deviation are presented. The ANOVA function of Minitab v16.1 (Minitab Inc., State College, PA, USA) with Tukey groupings were used to compare results on a 95% confidence interval.

5.3 Results and Discussion

Data for each comparative standard (Fresh-FD, MWODS-FD, MWODS-AD, and Fresh) is plotted on the relevant graph. Data for all the comparative standards can be found in Table 5.1. In this section, the effects of process parameters on each quality index will be discussed as they compare both to literature values as well as the employed standards (control anchors) as a means to determine the effects of the individual processes and treatments.

5.3.1 Color

Cranberries have a characteristic vibrant red color that is instantly recognizable to consumers, making it an important attribute in terms of consumer acceptance. Moreover, the loss of color implies destruction of the anthocyanins responsible for the color. Moreover, because the appearance of anthocyanins is pH-dependent and is intensified as acidity increases, the loss or destruction of organic acids from the flesh of the fruit would likely reduce the level of pigmentation. The recent focus on health promotion through diet places increasing demand on understanding the effects of processing on these active phytochemicals (Pappas & Schaich, 2009). Furthermore, overheating and charring of samples has been widely discussed as a drawback of microwave based dehydration techniques in various studies (Gunasekaran, 1999). Therefore by monitoring changes in the appearance of the product, the development of these negative characteristics can be monitored, allowing for a determination of optimal power settings for MWV finish-drying of fresh and MWODS pre-treated berries.

Of primary importance in monitoring the color of cranberries is the *a**-value, which in its positive form denotes the redness of the sample. The air dried MWODS pre-treated sample (MWODS-AD) was as red as the fresh (full moisture) sample and many of the other processes actually produced samples that were even redder than the fresh sample (Figure 5.1). This is not uncommon in dehydrated samples and indicates that natural pigments have been concentrated during drying, which has the effect of intensifying product color (Chiralt & Talens, 2005). The *a**-value generally decreased in with increasing process intensity, results that confirm previously published reports (Sunjka et al., 2004). The redness of the samples declined below the MWODS-AD and fresh-frozen comparative standards as power levels exceeded 20% for the constant power processes. There was more variability in the split level processes, indicating that processes employing settings with longer power-on time initially were still capable of maintaining the redness of the dried sample, provided the finishing power setting did not exceed 20%.

This trend was true for both the fresh and MWODS pre-treated samples, however, in general, the fresh samples proved to be redder than their MWODS counterparts except in the case of very intense processes (e.g. 50% or 50/30%). It is interesting to note that in terms of *a** values 40/10% > 30/10% > 20/10%, and a similar trend was seen in the case of 40/20% > 30/20% > 20%. These trends appear to indicate that even though the processes finished at the same power setting (10% and 20%, respectively), more rapid processes better maintained the redness and anthocyanin

content of the sample, despite the higher temperatures that would be induced through the longer magnetron power-on times. These findings mirror previous findings where anthocyanin retention increased as a function of decreasing drying time, even with increased power density or power-on time (Yongsawatdigul & Gunasekaran, 1996b). However, this trend was not always true as samples dried via too intense a treatment (i.e. those finished at 30%, or under any combination of the 50% setting), showed no such trend. The 10% process produced substantially more red dried cranberries than any other MWV treatment, where redness decreased only slightly and samples were not significantly different (p>0.05) from their respective standards (Fresh-FD and MWODS-FD), indicating the relative gentle nature of the 10% MW power treatment. In the case of MWODS pre-treated berries, the 10%, 30/10%, and 40/10% processes were found to produce samples with redness exceeding that of the MWODS-AD standard, while the 20/10% was slightly lower but not significantly different from the standard. For the un-treated (fresh) berries, the same processes were found to be suitable but the 20/10% was found to be substantially more red in this case. In both cases this indicated the suitability of the MWV process for producing samples that were at least as red as those produced by the conventional method in significantly less time.

Similar conclusions can be drawn from lightness (L*) values (Figure 5.1), where samples were generally darker as process intensity increased. All dried samples were significantly lighter than the fresh (frozen-thawed) berries, which agrees with previous work which found that lightness tended to increase through dehydration, an effect attributed to the partial degradation of color compounds (Nsonzi & Ramaswamy, 1998b). Unlike in the case of a*-values that showed some combined effect from temperature and process time, the L* values tended to decrease in line with process intensification with the MWODS pre-treated samples. A similar trend was found in another study where higher power density or shorter magnetron power-off times lowered L* values in osmotically pre-treated cranberries (Sunjka et al., 2004). However, the opposite was true in another study where results indicated that increased power on times and power densities had no effect on the lightness of the sample (Yongsawatdigul & Gunasekaran, 1996b). In a third study, there was no lightness trend found between any of the combinations of power densities and magnetron cycling periods, where in this case, the lack of correlation between colorimetric and visual data was attributed to variation within the samples themselves (Beaudry et al., 2003). This disagreement of data goes to show the variability inherent to microwave based drying techniques, as they are dependent on the experimental setup and sample preparation. Regardless, the 10% and 20/10%

MWODS pre-treated samples nearly matched the lightness of the MWODS-FD standard, indicating very little darkening of the product in these more moderate treatments, avoiding the development of brown or black coloring that is typical of processes with application of excessive energy. Furthermore, other treatment types (e.g. 20%, 30/10%, 30/20%, 40/10%, and 40/20%) were found to produce significantly lighter samples than air dried samples (MWODS-AD), indicating their suitability in terms of lightness value. In the case of fresh berries, the 30/10% and 30/20% processes exceeded that of the 10% sample, although not significantly so. These treatment types presented L^* values approaching that of the Fresh-FD sample, which was the lightest of all the samples tested. Higher lightness values for fresh as compared to pre-treated berries likely indicates that the increased sugar content makes the berries more susceptible to darkening during MWV.

The b^* value (Figure 5.1), which indicates yellowness (+) to blueness (-), showed the most dramatic changes in the colorimetric data. Interestingly, in the MWODS-FD standard there was an increased evidence of yellow coloring (indicated by larger b^* values) as compared to the Fresh-FD sample. This indicated that the MWODS process promoted the retention of yellow flavonoids over the red anthocyanins, the former being the second main class of compounds responsible for the color of cranberries (Yongsawatdigul & Gunasekaran, 1996b). This also suggested that anthocyanins were lost either due to their heat labile nature or their polarity, which would result in leaching into the osmotic solution. When present, this yellowness was largely maintained by the MWV process as in general Fresh-MWV samples had higher b^* values, where they were either more or as yellow as any of the comparative standards (MWODS-FD, MWODS-AD, and Fresh-FD) in all cases except for the most extreme condition (50%). On the other hand, MWODS pre-treated samples had lower b^*-values than the Fresh-MWV samples, indicating a loss of that yellow hue during finish-drying. This effect was particularly evident at high power levels of MWODS pre-treated samples, which can be attributed to the increased amount of sugar present in the samples. Samples more rich in sugars contributed to a much darker (browning) sample which masked the lighter yellow hues that were still visible after more moderate treatments. This was empirically evident in the samples through the darkening and charring in samples where the b^*-value was severely impacted such as the 40% and 50% processes. Like with a^*- and L^*-values, the 10% and 20/10% treatments were found to be most suitable for the MWODS pre-treated samples. The fresh samples with lower sugar content were less affected by increasing process

Table 5.1: Values for Comparative Standards for Various Quality Indices

Sample Type	*L**	*a**	*b**	*ΔE*	Hardness (N)	Total Phenolics (mg GAE/g dm)	Total Monomeric Anthocyanins (mg cyd-3-glu/g dm)	DPPH (% Inhibition)
MWODS-AD	24.6 (0.5)	31.1 (0.5)	7.6 (0.4)	14.3 (0.3)	36.9 (6.1)	10.7 (0.7)	0.087 (0.001)	8.73 (0.3)
MWODS-FD	31.9 (0.7)	36.6 (0.6)	7.7 (0.3)	5.5 (0.6)	30.6 (4.3)	22.9 (0.4)	0.67 (0.02)	20.2 (1.0)
Fresh-FD	35.1 (0.5)	40.8 (0.9)	6.62 (0.3)	-	30.6 (3.5)	26.2 (0.6)	1.27 (0.01)	23.9 (0.6)
Fresh (thawed)	5.8 (0.4)	30.6 (0.9)	9.9 (0.6)	-	-	-	-	-

Average values with (standard deviation) shown

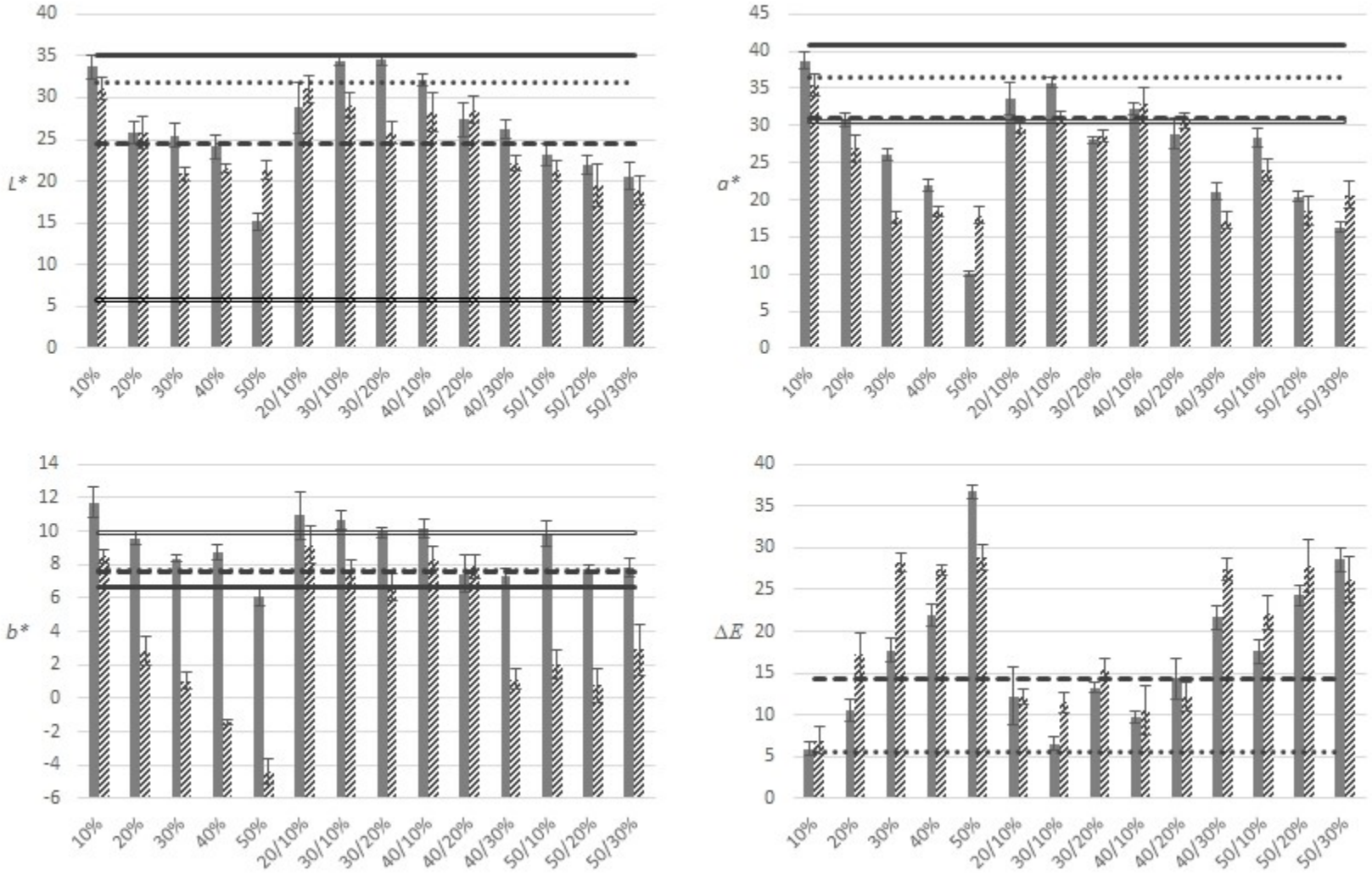

Figure 5.1: Colorimetric Data for MWV Finish Dried Fresh and MWODS Pre-treated Berries

Where:

intensity and had a wider range of acceptable samples. In fact, some of the samples were more yellow (larger b^* value) than the Fresh-FD sample, indicating the development of moderate browning/yellow coloring that has been produced by increasing power levels and duty cycle (Yongsawatdigul & Gunasekaran, 1996b). On the other hand, no significant change for b^*-value was found with increasing process intensity (power density or duty cycle) in another work (Sunjka et al., 2004).

In combining the three main color indicators, the total color change (ΔE; Figure 5.1) is widely used as an indicator of product color changes that take place throughout processing (Azarpazhooh & Ramaswamy, 2011b). In this case ΔE was calculated as deviations from the Fresh-FD type sample in order to provide a comparison to samples dried via what is considered to be a 'best case scenario' of drying techniques, but also one that is both expensive and time consuming and therefore only applies to niche products or high value applications. The MWODS-FD and MWODS-AD sample values were plotted along with the MWV dried samples, which allowed for a comparison of color changes in samples produced by the MWODS process itself as well as the air drying process. In observing the MWODS-FD sample, it's clear that the pre-treatment did moderately impact the product color. Previous work done on MWODS of cranberries indicated that there was no significant change of color attributes with intensifying MWODS process parameters (Wray & Ramaswamy, 2013). This was attributed to the fact that either the MWODS process did not introduce any significant color change or that even the minimal treatment made some impact but that increasing treatment severity did not amplify this damage over the base amount. In light of results in this study, where there is a significant deviation from the Fresh-FD sample in terms of ΔE, the latter of these two possible conclusions seems more viable. Moreover in most cases besides the most intense treatments, the MWODS pre-treated samples generally have larger total color differences than their fresh counterparts, which runs contrary to various studies that have cited the protective effect of sugar incorporation in subsequent drying steps by increasing the stability of natural pigments in subsequent drying steps (Azarpazhooh & Ramaswamy, 2011b). This effect was further investigated by using samples that had been rinsed of excess sugar solution from the surface of the berry (Table 5.2) which significantly reduced the solids gain of the product. In this case, it was found that excess sugar on the surface of the berry did generally produce samples with lower ΔE-values than those that had been rinsed, particularly at lower power levels. This also indicated that the protective effect of sucrose was likely present and that the larger ΔE

values for the MWODS pre-treated samples were likely due to both the heating of the product during the osmotic treatment as well as the leaching of natural pigments into the osmotic solution, an effect which has been shown to be substantial in osmotic dehydration processes (Osorio et al., 2007).

Total color change (ΔE values) tended to increase with process intensity, results that mirror previous studies (Sunjka et al., 2004; Yongsawatdigul & Gunasekaran, 1996b). Overall, the 10% power setting was the best performer in terms of maintaining color for both sample types, where there was no significant change in ΔE between the fresh and pre-treated 10% samples and their respective standards (Fresh-FD and MWODS-FD, respectively). However, the combination processes that were finished at the 10% level (20/10%, 30/10%, and 40/10%) also maintained the color better than the air drying process for both sample types.

Table 5.2: Total Color Change (ΔE) of Rinsed & Unrinsed MWODS-treated berries after MWV

MWV Power Level	Rinsed	Unrinsed
10%	7.0 ± 1.7	12.5 ± 0.3
20%	17.2 ± 2.7	19.5 ± 0.9
30%	28.2 ± 1.0	28.4 ± 1.0
40%	27.4 ± 0.6	29.9 ± 0.9
50%	28.8 ± 1.5	33.2 ± 2.1
Solids Gain (%)	**1.85 ± 0.24**	**4.86 ± 0.1**

Average values with Standard Deviation shown

This implied that they could be suitable from a color based perspective, particularly in applications where the berries were to be coated or integrated into a more complex product and color may not be favored as much as other factors. Similarly, the MWV process could be used alone (without pre-treatment) at a wide range of power levels if the berries were to be used in an instance where there was no benefit to additional sugar incorporation. The 40/10% and 30/10% treated samples had a lower ΔE than the more moderate 20/10% process, indicating that there was a benefit to decreased drying time and not only power. This trend was only true until a certain point as MWODS pre-treated samples dried using treatments that ended at or above 20% were found to

provide a ΔE exceeding that of the air dried sample, while for fresh berries this threshold was found at 30%. Clearly, as process intensity increases so too will the deviation from a visually appealing dried product, and therefore in order to produce an end product of acceptable quality care must be taken in order to avoid scorching and darkening of the sample.

5.3.2 Texture

Regardless of duty cycle or treatment type, the appearance and texture of the berries were similar to a freeze dried product as they were puffed and somewhat became more round in shape. This puffed appearance has been attributed to the fast evaporation of water that pushes the steam outwards very quickly, resulting in larger pores in the product (Leusink et al., 2010). Moreover, a crispy and brittle texture is characteristic of low water activity products (Marzec et al., 2010). In this case, water activity values of the berries did not indicate any meaningful trend and varied between 0.172-0.229 for the MWODS pre-treated berries and 0.146-0.214 for the un-treated berries, as compared to 0.183 for the freeze dried and 0.226 for the air dried berries, indicating that the berries could be dried to a lesser extent in future work, while still maintaining a safe water activity (below 0.7). Hardness was the only texture parameter with any significant trend, where there were issues with repeatability even with relatively large (8-10 berry) sample sizes. Texture results were characterized by large standard deviations that can be attributed to variations in shape, surface irregularities and internal structure diversity of the biomaterial (Marzec et al., 2010). Regardless, when considering the means of the sample hardness values (Figure 5.2), results indicated that overall the MWODS pre-treated samples were generally softer than the untreated berries, matching trends that suggest osmotically treated samples are softer than their fresh counterparts (Nsonzi & Ramaswamy, 1998b). Moreover, samples generally become softer with increasing MWV process intensity, where similar trends were identified in the case of apple, particularly when dried at higher temperatures (Marzec et al., 2010).

Specific to osmotically treated cranberries, increasing power density or decreasing power-off times appeared to make the samples softer in either microwave-convective or microwave-vacuum finish-drying techniques (Sunjka et al., 2004). On the other hand, this trend was opposite to those identified in another previous study on osmotically pre-treated cranberries where increased hardness of cranberries dried under continuous versus pulsed application of microwave energy was attributed to the higher temperatures attained during the process (Yongsawatdigul &

Gunasekaran, 1996b). These inconsistencies are perhaps attributable to the differences in power density and product temperatures, where a significantly higher power density was used in this study. The MWV finish-drying process was able to significantly soften the texture of the berry, where hardness values lower than that of the air dried sample (MWODS-AD) was attainable by processing employing power settings above 20%, which still maintained malleability of the berry. However, higher power treatments (>30% for both sample types) produced an increasingly brittle product, where, the berries tended to fracture when contacted with the face of the texture probe, which was very similar to the behavior of the freeze dried sample. Therefore, while the process could be tailored to target a softer or harder product as required depending on the specific treatment applied, it may be a narrow window that produces berries of desirable textural characteristics.

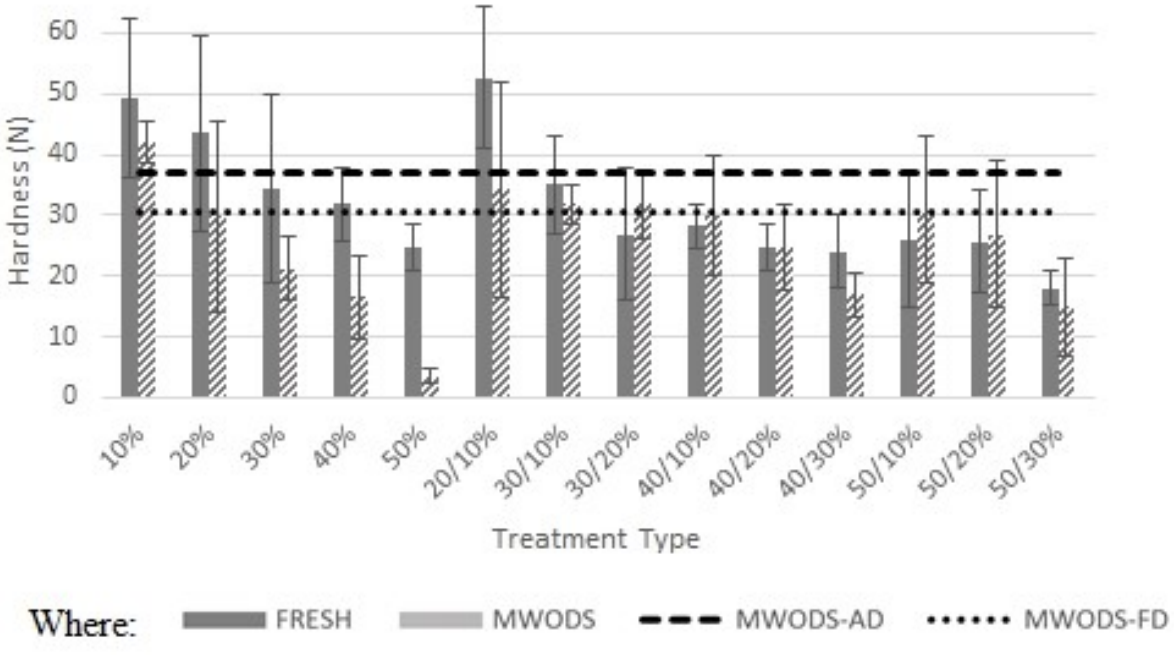

Figure 5.2: Hardness of samples MWV Finish Dried Fresh and MWODS Pre-treated Berries

5.3.3 Total Phenolics

The total phenolic (TP) content of fresh freeze dried cranberries was found to be 26.2 ± 0.6 mg GAE/g dry matter (Figure 5.3) which is within the range previously published for various cultivars of cranberries as compared on a dry weight basis (Gunes et al., 2002; Çelik et al., 2008; Zheng & Wang, 2003). A decreased TP content for the MWODS-FD sample (Figure 5.3) indicated a loss of phenolics during the osmotic pre-treatment, likely due to both heating and leaching into the osmotic solution. Like with other quality indices observed in this study, both the fresh and MWODS-pretreated samples exhibited a trend of decreasing phenolic content with increasing MWV process intensity. This indicates that the phenolics present in cranberry are thermolabile in nature, which agrees with prior work that described temperature as the most important factor in cranberry phenolic stability (Pappas & Schaich, 2009). In all cases the phenolic content of the MWV produced samples were second only to the freeze dried samples, which mirrors results found for Saskatoon berries (Kwok et al., 2004). For osmotically pre-treated berries the 10%, 20/10%, and 30/10% processes were found to produce samples with the highest levels of phenolics and were not significantly ($\alpha = 0.05$) different from each other, indicating they were the best match for osmotically pre-treated samples. For fresh berries a wider range of process treatment types were found to be suitable, where the 10%, 20%, and 30% samples were all in the highest grouping and thus indicate the best processes for retention of phenolics. Interestingly, a split power process such as the 30/10% process was found to have lower TP than the 30%, despite being finished at a lower power setting. This could be attributed to the fact that the 30/10% process was about twice as long as the 30% process (Table 4.3), and therefore the longer process time degraded the phenolic compounds more so than the shorter yet more intensive 30% process. Overall, the MWV produced samples far exceeded TP levels of the MWODS-AD sample, indicating that the process was much more proficient at maintaining phenolic compounds than air drying.

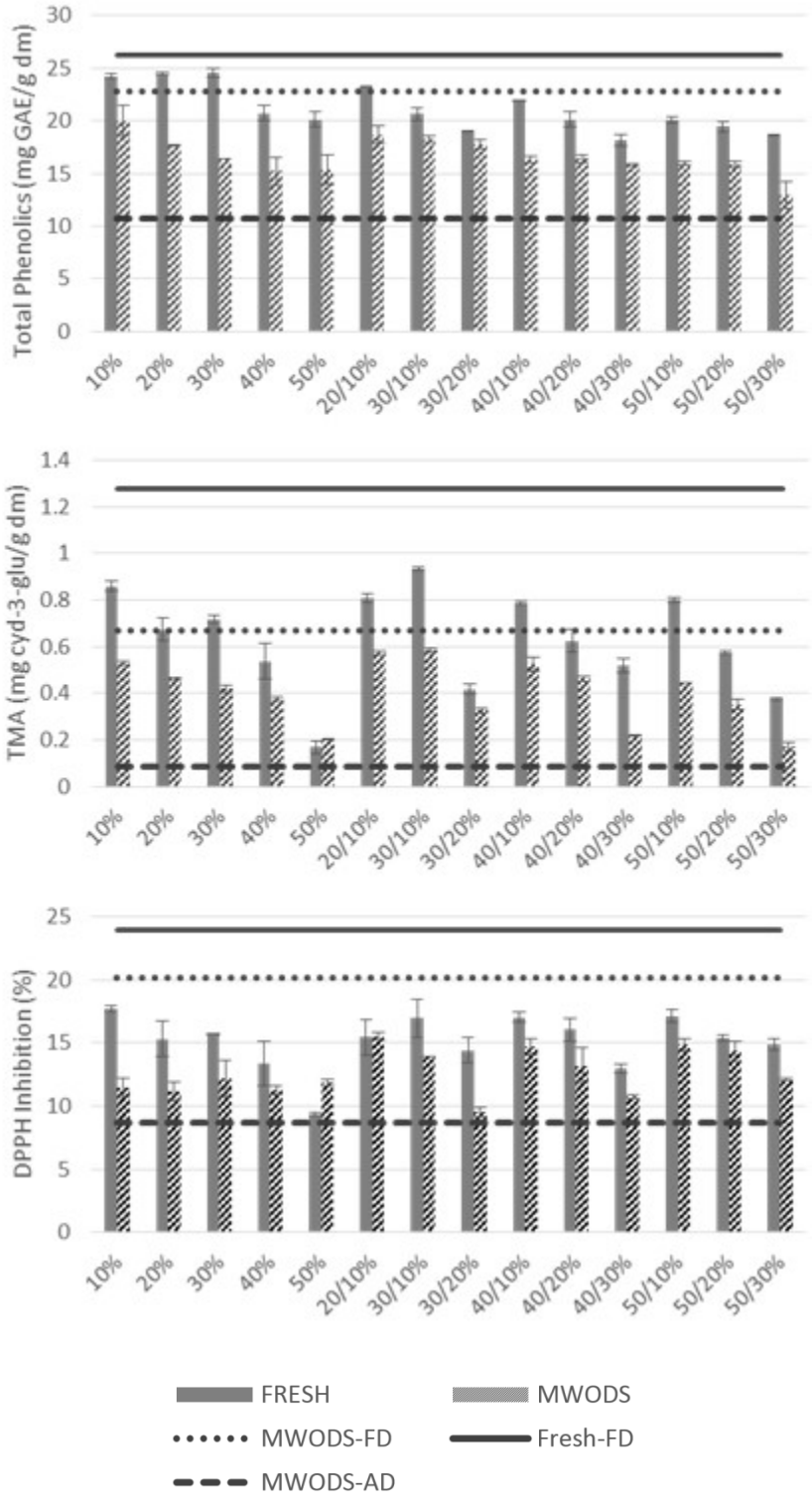

Figure 5.3: Chemical Quality Markers for Monitoring Process Intensity

5.3.4 Total Monomeric Anthocyanins (TMA)

The total monomeric anthocyanin (TMA; in cyanidin-3-glucoside equivalents) found for the fresh freeze dried samples (1.28 ± 0.02 mg cyd-3-glu/g dry matter) was within the range found in previously published reports (Zheng & Wang, 2003; Çelik et al., 2008; Gunes et al., 2002), where variations can be attributed to growing and storage conditions as well as standards used in the TMA assay. There was a substantial reduction in anthocyanins during the MWODS process (Figure 5.3), where nearly half of the anthocyanins were lost. Despite the loss of significant levels of anthocyanins, the redness of the berries remain relatively high (Figure 5.1), and the berries still appeared visually bright red, which speaks to the intensity with which anthocyanins produce the red color that is so typical of cranberries. Anthocyanins are particularly sensitive to losses during osmotic dehydration due to both thermal degradation as well as leaching into the osmotic solution (Mundada et al., 2010). This can be attributed to their polar and thermolabile nature, where the thermal sensitivity is further evidenced by the dramatic decreases of TMA with increasing process intensity during MWV finish-drying, which is evident in both the fresh and pre-treated berries through both the continuous and split power level processes. Similar to the total phenolics, the 10%, 20%/10%, and 30/10% treatments best maintained the anthocyanin content of the dried berries, where because of the steeper decline at increasing power settings the need for a lower (10%) finishing power level to maintain TMA content was evident. This is particularly visible when examining the fresh untreated berries where there is only a small decrease in TMA content in the processes finishing at 10% and in the case of 30/10% there is actually an increased retention. The fact that the 20/10% and 30/10% treatments maintain similar or higher TMA content than the 10% process for both MWODS and fresh berries indicates that despite the treatment intensity the shorter drying time is beneficial to anthocyanin retention, results that agree with prior reports (Yongsawatdigul & Gunasekaran, 1996b). This trend is more mixed with processes ending at the 20% setting and disappears above this level, indicating that processes that exceeded the 10% power setting to completion were not beneficial to TMA retention. Overall, results indicate the MWV process is significantly better than the air drying process for maintaining anthocyanin content, results that confirm previous work where it was found that dehydration by freeze drying or MWV both better retained anthocyanins as compared to air drying (Leusink et al., 2010). Moreover in many cases the MWV process was able to maintain TMA level at or above levels seen in the MWODS-FD standard.

5.3.5 Radical Scavenging Ability by DPPH

Results for radical scavenging ability of DPPH (Figure 5.3) were similar to those seen for total phenolics by Folin-Ciocalteu Reagent (FCR). This is attributed to the fact that the DPPH reagent functions on the same chemical basis as FCR, where both reagents use an electron transfer based mechanism to quench free radicals (Huang et al., 2005). Moreover, prior studies suggest there is also a strong correlation between radical scavenging activity and total phenolics, despite the fact that anthocyanins have been found to be the most powerful antioxidants in cranberry (Pappas & Schaich, 2009). Much like the two other chemical indices, DPPH scavenging activity was better retained by more moderate processes. The radical scavenging activity was generally found to be higher in the fresh berries then the MWODS pre-treated berries as well, indicating either an effect of the MWODS process itself or an interaction between the phenolics measured and the sugar added through the pre-treatment. Furthermore, the decrease between the Fresh-FD (23.9 ± 0.6%) and MWODS-FD (20.2 ± 1.0%) standards (Figure 5.3) is much closer to the decrease seen for the TP (26.2 ± 0.6 to 22.9 ± 0.4 mg GAE/g) than for the TMA (1.27 ± 0.01 to 0.67 mg cyd-3-glu/g dry matter), where nearly 50% of the TMA content was lost. Despite the similarity between the TP and DPPH results, there are some differences, particularly that MWODS pre-treated berries exhibited a more visible decrease with increasing finishing power settings (e.g. from 40/10% through 40/30% or 50/10% through 50/30%), a trend that is not as evident in the TP assay. Taking into account the TMA results, this suggests that the degradation of anthocyanins at these later stages of drying was largely responsible for the loss of scavenging activity. Similarly, the fact that the 20/10% and 30/10% samples provided scavenging activity higher than the 10% further complements results seen in the TMA assay, which confirms both the importance of anthocyanins as free radical scavengers as well as the notion that anthocyanins are better retained by faster processes within certain temperature limits. Therefore, the recommended treatment level for MWODS pre-treated berries is 20/10%, which significantly exceeded the radical scavenging levels seen in other treatment types. For fresh berries there is again a wider range of acceptable treatments, where the 10% and 30/10% provided the highest level but also where the 20/10%, 40/10%, 40/20%, and 50/10% produced samples with similar scavenging activity. In these cases, the radical scavenging ability retained is much higher than that found for the air dried sample (MWODS AD), which agrees with previously published reports on vacuum microwave dried cranberries (Leusink et al., 2010).

5.4 Conclusions

Overall the MWODS-MWV combination process was found to be suitable as a rapid method for the production of high quality dried cranberries. By enhancing osmotic dehydration and eliminating air drying, the process allows for higher throughput and a sample with better color, texture, and retention of health positive effects that are of increasing concern to consumers. Overall, it was found that with this experimental setup the 10%, 20/10%, and 30/10% treatments were most amenable to producing a high quality MWODS pre-treated berry. Furthermore, the MWV process could be used as a standalone method, particularly where the berries would be further transformed or integrated into a manufactured product and therefore the increased solids content promoted by osmotic treatments would be of no benefit. In this case, there is a wider range of power settings application in this setup, where generally speaking in the absence of added sugar higher intensity treatments are capable of producing a high quality product. It is also worth noting that the product was also easily ground, indicating that the process could easily be employed to create a dried cranberry powder with properties rivalling that of freeze dried samples in much less time. In considering the chemical indicators employed in this study, the total monomeric anthocyanin content showed the most dramatic decrease with increasing process intensity, and therefore monitoring TMA content of cranberries is a sensitive and reliable method to employ as a chemical indicator of losses during dehydration and potentially other processing methods. While optimal MWV used in the future will depend on the properties (particularly solids content) of the osmotically treated berries, the groundwork has been laid out in order to design a process that balances the two main advantages of the combination process: drying efficiency and product quality.

CONNECTIVE STATEMENT TO CHAPTER 6

While the previous two chapters used a moderate MWODS treatment for the purposes of determining the effects of MWV treatments on quality and energy considerations, there is a need to expand the experimental design to determine the effects of input MWODS process variables such as concentration, temperature, contact time on the final quality of the berries. Moreover, while the experimental design for the following chapter was based on the CCRD in Chapter 2, the flow rate effect was not included in the earlier work and hence it was expanded to include the effect of flow rate in this study. In considering a wide range of MWODS treatments in combination with a MWV treatment suited to finish-dry them (20/10% process), these effects can be explored. The CCRD design allows the effects of each process parameter to be tested individually and the development of a predicting model which can then be experimentally validated. Additionally, center points from this design are used to compare the effects of different finish-drying treatments on properties of the final product.

Parts of Chapter 6 have been adapted for presentations and publications as follows

Wray, D and Ramaswamy, H.S., 2014. Development of a Rapid Dehydration Technique for Cranberries *(Vaccinium macrocarpon)*. Institute of Food Technologists Annual Meeting and Food Expo, June 21-24, New Orleans, Louisiana

Wray, D and Ramaswamy, H.S. Microwave-Osmotic/Microwave-Vacuum Drying of Whole Cranberries: Effects on Quality and Comparison with Other Methods. *(In preparation)*

CHAPTER 6

MICROWAVE-OSMOTIC/MICROWAVE-VACUUM DRYING OF WHOLE CRANBERRIES: EFFECTS ON QUALITY AND COMPARISON WITH OTHER METHODS

Abstract

A novel drying method for frozen-thawed whole cranberries was developed by combining microwave osmotic dehydration under continuous flow medium spray (MWODS) conditions with microwave vacuum finish-drying. A central composite rotatable design was used to vary temperature (33-67°C), osmotic solution concentration (33-67°B), contact time (5-55 min), and flow rate (2.1-4.1 L/min) in order to determine the effects of MWODS input parameters on the quality of the dried berry. Quality indices monitored included colorimetric and textural data in addition to anthocyanin retention and cellular structure. Overall it was found that the MWODS-MWV process was able to produce dried cranberries with quality comparable to freeze dried samples in much shorter time. Additionally, cranberries dried via the novel process exhibited much higher quality than those dried via either vacuum or convective air drying in terms of color, anthocyanin content, and cellular structure.

6.1 Introduction

As the oldest and still one of the most widespread processing operations in the food industry today, dehydration can account for up to 15% of all industry energy usage (Fernandes et al., 2006). The major contributor for this excessive energy consumption is traditional convective hot air drying, both because it relies on air as a heat transfer medium and because water removal is accomplished with a phase change such that the latent heat of vaporization must be provided. Convective air drying exposes a product to high temperatures for long periods of time, leading to wide ranging quality losses such as loss of color, flavor and nutritional profile (Alibas, 2007). As a result, much research in recent years has gone into technologies that could be employed to supplant air drying as the industry standard. Among the most popular, approaches have been to incorporate electromagnetic (EM) radiation, where EM radiation has several properties that provide benefit to drying processes. Of primary importance is the ability to penetrate into a sample and heat the product from within. Microwave radiation in particular has a strong effect on dipolar molecules such as water, which has a strong permanent dipole and makes up the bulk of fresh fruits and vegetables. As a result, microwave energy is particularly effective at selectively heating moisture molecules within the product, resulting in enhanced moisture removal rates and shorter drying times. When compared to traditional techniques, EM-based drying allows for higher quality product in shorter periods of time, where often the quality obtained can even approach that produced by freeze drying. Freeze drying is often referred to as the gold standard of drying methods (Azarpazhooh & Ramaswamy, 2011b). Industrially, however, the process is limited to high value products industrially because of its high installation and operation costs (Duan et al., 2007).

Typical issues associated with microwave heating include uneven heating, which can lead to runaway heating and charring in some locations while other portions remain under-dried. As a result, variations on microwave based techniques are typically designed to address these issues, by equalizing temperatures using an airflow, mixing the sample using a spouted or fluidized bed or to decreasing the boiling point of water so that less energy can be applied to the sample while still evaporating moisture by drying under a vacuum (Beaudry et al. 2003; Wang et al. 2014; Jiang et al. 2014; Yongsawatdigul & Gunasekaran 1996b). This latter approach is of particular interest to this work, where various studies have looked at the effects of power density, magnetron duty cycle, and vacuum levels as a means to control product temperature and therefore product quality

(Yongsawatdigul & Gunasekaran, 1996a; Yongsawatdigul & Gunasekaran, 1996b; Sunjka et al., 2004).

Another approach to limit damage to products during finish-drying is to reduce the amount of time required in the process by applying a pre-treatment to remove the initial bulk of moisture from the product. One of the most popular primary drying operations is osmotic dehydration (OD), which has been described as a power efficient means to decrease moisture content, increase dry basis yield, as well as allow the creation of novel food products through incorporation of solutes (Ramaswamy & Tola, 2014). Osmotic dehydration is, however, a relatively slow process - at ambient temperatures it is typically used for anywhere from 12-24 h depending on the product and desired solids content. As a result, much work has gone into employing pre-treatments prior to osmotic dehydration in order to increase mass transfer rates and reduce the process time. These treatments include skin treatments, application of ultrasound, pulsed electric field, and high hydrostatic pressure, among others, and have the common aim of disrupting the plant tissue in order to make it easier for moisture to be removed and solids to be taken into the product. Beyond pre-treatments, another approach has been the application of microwave during osmotic treatments. Apple cylinders were originally treated in an immersion based setup (Li & Ramaswamy, 2006c), which later progressed to a spray based system (Azarpazhooh & Ramaswamy, 2010c). The spray based technique (known as microwave-osmotic dehydration under continuous flow medium spray conditions, or MWODS) was found to produce samples with the highest moisture loss and lowest solids gain along with excellent product quality once finish dried (Azarpazhooh & Ramaswamy, 2010c; Azarpazhooh & Ramaswamy, 2011b). Later studies proved that the MWODS process could be applied to whole frozen-thawed cranberries with no need for skin pre-treatment (Wray & Ramaswamy, 2013).

In the earlier studies, MWODS pre-treated samples were hot air dried (Azarpazhooh & Ramaswamy, 2011b; Azarpazhooh & Ramaswamy, 2011a). Additionally, initial screening work has been done on developing a microwave-vacuum (MWV) based drying technique for both fresh and MWODS pre-treated berries using a single moderate MWODS process to screen for suitable MWV treatments (Chapters 4 and 5). The objective of this work is to therefore expand the scope of previous studies by determining the effects of MWODS input variables on product quality as well as to compare the finished product to cranberries dried via traditional techniques such as convective, freeze, or vacuum drying.

6.2 Materials and Methods

6.2.1 Experimental Design and Data Analysis

A central composite rotatable design (CCRD) was designed using Design Expert v6 (Stat-Ease Inc., Minneapolis, MN). The process variables included temperature, concentration, contact time, and flow rate in order to create a set of 31 experiments that allowed the testing of each input parameter individually (Table 6.1). Despite being described as of minor influence in prior work (Azarpazhooh & Ramaswamy, 2012), flow rate was included again in the CCRD design because of the change of spray head as well as the possibility that a different product could be affected differently.

Data pertaining to MWODS-MWV samples prepared as part of the CCRD were analyzed using the ANOVA function integrated in the program, and fitted with regression curves in order to create the contour plots displayed in this work. For the comparison of the drying methods, results were tabulated manually and compared using the one-way ANOVA function of Minitab v16.1 (Minitab Inc, State College, PA) and compared using the Tukey method for determining statistically different groups on a 95% confidence interval.

6.2.2 Microwave Osmotic Drying (MWODS)

Full details of the MWODS pre-treatment steps can be found in Chapter 4. Briefly, small batches of approximately 200 g were defrosted by floating in an excess (≈2L) of room temperature tap water for about one hour. During this time, under ripe, broken, or otherwise damaged berries were discarded. Two samples (24-25g each) were then blotted dry of surface moisture, weighed, and then placed on the sample stage in the MWODS setup under the spray head. The pump was set at the desired flow rate which began the circulation of the commercial grade sucrose based osmotic syrup which had been previously equilibrated at the run temperature using an external steam jacketed water bath with digital thermostat. The microwave was then turned on at maximum power for the allocated time, after which the pump was stopped and the samples removed. Once shaken slightly to remove excess osmotic syrup, the berries were then allowed to cool for 10 min at room temperature, were weighed again, and then transferred to an oven at 105°C and dried until constant weight for moisture content determination (AOAC, 1975). When intended for finish-drying, the 50 g samples were divided in half after MWODS. The moisture content of the first half was determined by the AOAC method. Meanwhile, the other half was sealed in a plastic bag and

held at 4°C to await finish-drying the next day when its moisture content could be estimated from the results of drying the first half to completion by the AOAC method. This method allowed the prediction of the moisture content of the second half with good precision ($R^2 = 0.96$) and allowed the moisture content of the sample prior to finish-drying to be known.

Compositional changes of the berries during MWODS were monitored using the moisture loss (ML) and solids gain (SG) of the products using the equations outlined here:

$$\%\mathrm{ML} = 100\frac{\mathrm{M}_0 x_0 - \mathrm{M}_t \mathrm{x}_t}{\mathrm{M}_0} \qquad (6.1)$$

$$\%\mathrm{SG} = 100\frac{\mathrm{M}_0 \mathrm{s}_0 - \mathrm{M}_t \mathrm{s}_t}{\mathrm{M}_0} \qquad (6.2)$$

where M_0 and M_t are the total sample mass as time 0 and time t, respectively; x_0 and x_t are the moisture fractions (kg/kg wet basis) at time 0 and time t, respectively; and s_0 and s_t are the solid fractions (kg/kg wet basis) at time 0 and time t, respectively. These equations assume a one way mass transfer of sucrose into the product and that any leaching of solids from the sample into the solution was insignificant on a mass basis.

6.2.3 Microwave-Vacuum Drying (MWV)

Full details of the system and process can be found in Chapter 4. As an overview, MWODS pre-treated berries were spread in a single layer in a pre-weighed glass petri dish lined with consumer grade silicone to prevent sticking. The petri dish was then transferred to a glass vacuum chamber which was in turn suspended from a balance to allow weighing of the sample without breaking vacuum/interrupting the process. The vacuum pump was then engaged and allowed to bring the setup to operating pressure (about 6kPa absolute), which took approximately one minute. The microwave was then turned on at the prescribed power level and the sample mass monitored using the integrated balance. The process was stopped once the target mass for 25% (db) was reached, at which point the vacuum was partially broken for 5 min to allow the product to cool slightly in a reduced oxygen atmosphere. The product was then removed, weighed with an analytical balance to verify final mass, and finally sealed in a plastic bag to await quality analysis. The water activity for all dried samples was found to be between 0.55-0.61.

Prior work focusing on both the energy (Chapter 4) and quality aspects (Chapter 5) determined the several suitable MWV treatments for MWODS pre-treated berries using this bench top setup. From this prior work it was determined that the best treatment for both quality and energy considerations was the 20/10% process, which initially involved applying the 20% power

for the first 10 min and then the 10% power setting until completion. In this study, the process was adapted slightly so that the 20% setting was employed until the product reached a moisture content of 50% (wb), which was visually determined to be the point beyond which product charring would begin to occur. At this point, the power setting was maintained at 10% until the target mass was reached. The initial power density in this setup for a 20 g sample was found to be 10.2W/g, where the duty cycle decreased from 6s on/24s off for the 20% process to 3s on / 27s off with the 10% setting (Chapter 4). Drying times ranged from approximately 55-70 min, depending on MWODS pre-treatment and corresponding initial moisture levels in the samples.

Additional samples were treated using the center point of the CCRD design (50°C, 50°B, 30 min, and 3.1 L/min) to compare the different drying methods in terms of final product quality. The methodology employed for the different finish-drying methods are outlined below.

6.2.4 Freeze Drying

Freeze drying was employed as 'best case' scenario in terms of maintaining quality attributes during dehydration (Azarpazhooh & Ramaswamy, 2011b). MWODS pre-treated samples were frozen overnight at -30°C and then dried at ≈13 Pa at room temperature for approximately 24 h using a pilot scale freeze dryer (SP Scientific/Virtis MR-145BA, Warminster, PA, USA). The resulting sample is denoted MWODS-FD in this study.

6.2.5 Vacuum Drying

MWODS pre-treated berries were weighed and transferred to a Fisher Scientific IsoTemp vacuum oven which had been pre-heated to 60°C. The pressure was reduced to 6kPa abs using a model 100EX laboratory vacuum pump (Emerson Motors, Markham, ON). The drying process took about 6 h to reach a final moisture content of 25% (db), where every 30 min the vacuum was broken and the samples weighed using an analytical balance. The resulting sample is denoted MWODS-VD.

6.2.6 Hot Air Drying

MWODS pre-treated cranberries were air dried (MWODS-AD) using a domestic drying oven (Equi-Flow Food Dehydrator, Marysville, WA) which was modified with a digital thermostat to maintain conditions of 60 ± 1°C, 0.64 ± 0.02m/s and a RH of approximately 15%. Berries were arranged in a single layer on a metal mesh and suspended from a balance in the drying chamber,

where they were subjected to constant horizontal airflow. The mass of the sample was recorded every 10 min, and four times during the process the door was quickly opened and the sample container rotated 90° so as to alternate the side of the sample exposed to the oncoming hot air. Samples were removed when their moisture content reached 25% (db) and sealed in plastic bags for further analysis.

6.2.7 Quality Analysis

Once finish dried, the berries were then subjected to quality analysis in terms of color, texture, and total monomeric anthocyanin (TMA) content. Texture and color analysis were performed within 24 h, while for TMA samples were held at -30°C for up to one week before being prepared for analysis. Samples for microscopic analysis were held for up to 48 h at 4°C.

6.2.8 Color Measurement

Color values of fresh and dried samples were determined in the L^*, a^*, b^* system using a tristimulus Minolta Chroma Meter (CM-500D, Minolta Corp., Ramsey, NJ, USA). The Chroma Meter was warmed up 30 min prior to use and calibrated against a white standard. Five measurements were taken with each sample and the values averaged in order to obtain the L^* (lightness), a^* (green (-) to red (+)) and b^* (blue (-) to yellow (+)) values of the individual trials. The ΔE (total color change) was also determined according to the following equation (Azarpazhooh & Ramaswamy, 2011b):

$$\Delta E = \sqrt{(L_0 - L)^2 + (a_0 - a)^2 + (b_0 - b)^2} \qquad (6.3)$$

Where the L_0, a_0, and b_0 values refer to fresh freeze-dried berries (Fresh-FD) and L, a, and b represent the values of the samples in question. The Fresh-FD standard was used as the zero values for total color change in order to represent the total differentiation from a best case scenario dried product.

6.2.9 Texture

A simple compression test was used in order to monitor the peak hardness of the sample using a TA.XT*Plus* Texture Analyzer with a flat bottom probe (TA-25); (Stable Microsystems, Surrey, UK). For this analysis 5-6 berries of equivalent size were placed in a rigid glass container and the probe allowed to contact all of them to obtain an averaging effect. Tests were performed in triplicate with a pre-test speed of 1 mm/sec, and a test and post-test speed of 5 mm/sec, and

results averaged. The target was 50% deformation of the berries.

6.2.10 Total Monomeric Anthocyanins (TMA)

The total monomeric anthocyanin content of the samples was employed as a chemical marker of the intensity of the process because of its previously established sensitivity to drying treatments (Chapter 5). In order to prepare the samples for the chemical assays, the berries were ground to a fine powder in a consumer grade spice grinder using short bursts of power to limit the effect of heat buildup. The samples were then freeze dried for 24h in order to eliminate any variations of moisture content of the dried berries on subsequent analyses. After freeze drying, the phenolics were extracted from the powder using a method previously applied to cranberries (Zheng & Wang, 2003). In this case 0.1g portions of the ground samples were accurately weighed and placed in 15mL centrifuge tubes, to which 10mL of 80% acetone and 0.2% v/v formic acid (Fisher Scientific, Montreal, QC) was added and the tubes vortexed for 10 s. The tubes were then allowed to stand for 10 min at room temperature with periodic mixing before being centrifuged at 20,000 x *g* for 20 min. The pellets were then discarded and supernatants kept at -20°C for a maximum of one week.

The measurement of total monomeric anthocyanins was completed using a differential pH method as suggested for cranberries by Zheng and Wang (2003) and as outlined by Lee et al. (2005). This assay takes advantage of the fact that anthocyanins reversibly change color with pH, where the oxonium ion form is brilliantly red at highly acidic pH values, whereas the colorless hemiketal form predominates at and beyond pH 4.5 (Lee et al., 2005). For this analysis, 0.8mL of the acetone-formic acid extract was mixed with 3.2mL of buffer at either pH 1 (0.025M KCl acidified with concentrated HCl; Fisher Scientific, Montreal, QC) or pH 4.5 (0.4M sodium acetate acidified with glacial acetic acid; Fisher Scientific, Montreal, QC) was added. The samples were allowed to stand for 20 min and then transferred to cuvettes and absorbance was measured against the appropriate buffer blank at both 520 and 700nm. Each sample was analyzed in duplicate for a total of four replicates for each process treatment and results expressed as milligrams of cyanidin-3-glucoside equivalents per gram dry matter (mg cyd-3-glu/g dm) as outlined in Section 5.2.11.

6.2.11 Light Microscopy

Light microscopy was employed to compare the effects of the MWODS treatment as well as the various finish-drying methods on the cellular structure of the berries using a method adapted

from prior work on cellular structure during drying (Fernandes et al., 2008). Sections (≈5 mm) from the equatorial region of the berries were sliced using a razor blade and then placed in fixative buffer (4% paraformaldehyde and 1% glutaraldehyde in pH 7.2 0.1M phosphate buffer) for 24 h at 4-6°C. Samples were then dehydrated in a graded ethanol series (1 h each in 20, 50, 70, 95, 100, 100% EtOH) before being transferred to two toluene baths for 30 min each. The samples were then transferred to liquid paraffin wax and kept at 55°C overnight. Once embedded, a Leica RM 2125 rotary microtome (Leica Biosystems, Concord, ON) was then used to section 8 μm slices which were then affixed to a slide and stained using 0.1% w/v toluidine blue at pH 4. Slides were observed using a Leica Axiostar*plus* light microscope and MicroPublisher RTV digital camera (QImaging, Surrey, BC) using Northern Eclipse v5 software (Empix Imaging Inc., Mississauga, ON).

6.2.12 Rehydration Capacity

Rehydration capacity was determined in triplicate using the procedure described by Azarpazhooh and Ramaswamy (2011b). Dried samples were accurately weighed and soaked in excess distilled water for 14 h at room temperature (23°C). Once removed from the water the samples were then subjected to slight suction for approximately 1 min to remove surface moisture. The rehydration capacity was then determined according to the equation (Azarpazhooh & Ramaswamy, 2011b):

$$RHC = \frac{W_r - W_d}{W_d} \qquad (6.4)$$

where W_r and W_d are the masses of the rehydrated and dry material (in g), respectively.

6.1.13 Bulk Density

Bulk density was measured by placing approximately 25 g of berries in a 250 mL graduated cylinder and gently tapping it three times to settle them. The mass of the berries was divided by the approximate volume taken up by the berries and expressed in kg/m^3. Tests were performed in triplicate.

6.3 Results and Discussion

6.3.1 Effects of MWODS Process Parameters

In this section, the effects of the individual process parameters will be discussed as they affected the various responses (Figures 6.1-6.3; Table 6.2), namely the moisture loss, solids gain, a^*-value, total monomeric anthocyanin (TMA) content, colorimetric parameters and texture (hardness) of the product. The predicting model, sign and statistical significance of each input parameter for each response is shown in Table 6.3.

6.3.2 Temperature

Temperature was found to be the most important variable in determining both the performance of the process as well as the quality of the final product, where it was highly ($p < 0.0001$) significant in the case of moisture loss and significant ($p < 0.05$) in the case of solids gain (Table 6.3). Temperature was the largest contributor to changing TMA content, b^*-value, and ΔE and second largest contributor (behind contact time) to moisture loss, solids gain, and a^*-value as determined by the sum of squares. In not being the largest influence on moisture loss, this study conflicts with prior reports that have found that osmotic dehydration is largely dependent on temperature (Li & Ramaswamy, 2006a). However, even though contact time was found to have a larger influence, higher temperatures did tend to increase moisture loss and solids gain to their maximal values (Figure 6.1), and therefore the overall trend seen agrees with these prior reports. During conventional osmotic dehydration, elevated temperatures enhance moisture loss by promoting moisture diffusion within the product itself, increasing solution-sample contact, and increasing cell membrane permeability (Sereno et al., 2001; Ito et al., 2007; Li & Ramaswamy, 2006a). Prior work on microwave-osmotic dehydration in both immersion and spray configurations confirm this behavior (Li & Ramaswamy, 2006c; Azarpazhooh & Ramaswamy, 2011b; Wray & Ramaswamy, 2013).

Higher temperatures tended to degrade quality parameters, having a negative effect on the color (L^*, a^*, and b^* and ΔE), as well as the anthocyanin content and firmness of the cranberries, providing either a significant or highly significant effect in each case (Table 6.3). The loss of red color at higher temperatures (Figure 6.2) was likely due to the loss of responsible anthocyanins and through thermal degradation or leaching into the osmotic solution as they are known to be both thermolabile and polar (Côté et al., 2010a). This effect is confirmed by the TMA content,

where the highest levels are found at the lowest temperatures (Figure 6.3A-C). The effects of temperature on both redness and TMA content were found to be highly significant ($p < 0.0001$). Of particular interest is that in comparing the plots for TMA and a^*-value, the maxima and minima are much sharper in the case of TMA. This could provide some benefit in terms of optimizing the process as it would provide a much narrower area of suitable treatments to target. However the correlation between a^*-value and TMA content combined with the simplicity and rapidity of colorimetric analysis implies that this technical advantage may not be of any real benefit. For conventional osmotic dehydration, it was found that anthocyanin content is reduced by 10% by a conventional osmotic treatment (Grabowski et al., 2002). In Table 6.5, however, it can be seen that the MWODS-FD sample contained only about half that of the Fresh-FD sample. Assuming no losses during freeze drying, it can be concluded that the MWODS process is harsher on the anthocyanins than conventional OD, an effect most likely attributed to higher product temperatures and perhaps the flowing nature of the osmotic solution which would help prevent equilibrium conditions from developing at the surface.

Similar trends could be seen in terms of the total color change, or ΔE of the sample (Figure 6.2J-L). This parameter takes into account not only the redness (a^*) but also the contributions of Lightness (L^*) and blueness-yellowness (b^*). Therefore, the deviation from the color of the freeze dried sample was due to changes in all three color components, where the decrease in both L^* and b^* values are likely related as the loss of the brighter yellow color (positive b^* value) to the darker blue (negative b^* value). This indicates that intensifying MWODS process parameters also have a deleterious effect on yellow flavonoids, which are the second main class of compounds responsible for the color of cranberries (Yongsawatdigul & Gunasekaran, 1996b). Moreover, the general darkening of the sample is likely caused by browning both during MWODS and during subsequent treatments.

Finally, increasing temperature tended to decrease the hardness of the sample (Figure 6.3D-F), likely through increased solids uptake or destruction of cellular structure, both of which have been theorized as being the causes of softening during osmotic dehydration, and which is likely desirable in some products requiring a chewy structure (Wray & Ramaswamy, 2013).

Table 6.1: Central Composite Rotatable Design with Real and (Coded) Variables Shown

Run	Temperature (°C)	Concentration (°B)	Flow rate (L/min)	Contact time (min)
1	40 (-1)	40 (-1)	2.5 (-1)	15 (-1)
2	40 (-1)	60 (+1)	2.5 (-1)	15 (-1)
3	60 (+1)	40 (-1)	2.5 (-1)	15 (-1)
4	60 (+1)	60 (+1)	2.5 (-1)	15 (-1)
5	40 (-1)	40 (-1)	3.7 (+1)	15 (-1)
6	40 (-1)	60 (+1)	3.7 (+1)	15 (-1)
7	60 (+1)	40 (-1)	3.7 (+1)	15 (-1)
8	60 (+1)	60 (+1)	3.7 (+1)	15 (-1)
9	40 (-1)	40 (-1)	2.5 (-1)	45 (+1)
10	40 (-1)	60 (+1)	2.5 (-1)	45 (+1)
11	60 (+1)	40 (-1)	2.5 (-1)	45 (+1)
12	60 (+1)	60 (+1)	2.5 (-1)	45 (+1)
13	40 (-1)	40 (-1)	3.7 (+1)	45 (+1)
14	40 (-1)	60 (+1)	3.7 (+1)	45 (+1)
15	60 (+1)	40 (-1)	3.7 (+1)	45 (+1)
16	60 (+1)	60 (+1)	3.7 (+1)	45 (+1)
17	50 (0)	33 (-1.68)	3.1 (0)	30 (0)
18	50 (0)	67 (+1.68)	3.1 (0)	30 (0)
19	33 (-1.68)	50 (0)	3.1 (0)	30 (0)
20	67 (+1.68)	50 (0)	3.1 (0)	30 (0)
21	50 (0)	50 (0)	2.1 (-1.68)	30 (0)
22	50 (0)	50 (0)	4.1 (+1.68)	30 (0)
23	50 (0)	50 (0)	3.1 (0)	5 (-1.68)
24	50 (0)	50 (0)	3.1 (0)	55 (+1.68)
25	50 (0)	50 (0)	3.1 (0)	30 (0)
26	50 (0)	50 (0)	3.1 (0)	30 (0)
27	50 (0)	50 (0)	3.1 (0)	30 (0)
28	50 (0)	50 (0)	3.1 (0)	30 (0)
29	50 (0)	50 (0)	3.1 (0)	30 (0)
30	50 (0)	50 (0)	3.1 (0)	30 (0)
31	50 (0)	50 (0)	3.1 (0)	30 (0)

Table 6.2: Data for CCRD Responses *(Mean Values with Standard Deviation Shown)*

Run	Moisture Loss (%)	Solids Gain (%)	*L**	*a**	*b**	Δ*E*	TMA (mg cyd-3-glu/g dm)	Firmness (N)
1	20.4 (1.87)	0.86 (0.06)	36.7 (0.5)	39.2 (0.2)	8.4 (0.1)	4.9 (0.4)	0.57 (0.03)	82.6 (12.6)
2	20.8 (0.38)	3.21 (0.51)	32.8 (2.3)	36.3 (1.3)	10.9 (0.3)	9.5 (2.2)	0.63 (0.07)	55.5 (8.4)
3	21.3 (0.05)	1.85 (0.49)	36.2 (0.7)	29.2 (0.4)	8.1 (0.1)	18.6 (0.7)	0.51 (0.02)	63.6 (20.5)
4	24.8 (0.72)	4.98 (0.62)	39.4 (0.2)	30.1 (0.2)	5.6 (0.1)	11.7 (0.2)	0.46 (0.09)	39.4 (7.2)
5	18.7 (2.50)	0.35 (0.35)	34.7 (1.4)	33.1 (1.0)	9.9 (0.7)	8.1 (1.2)	0.63 (0.01)	87.3 (14.4)
6	18.9 (1.47)	1.43 (0.18)	38.0 (1.2)	36.6 (0.9)	10.0 (0.4)	10.1 (1.1)	0.60 (0.09)	58.4 (2.9)
7	21.5 (0.20)	4.12 (0.76)	35.9 (0.2)	37.9 (0.3)	9.2 (0.1)	6.6 (0.3)	0.42 (0.02)	68.2 (11.6)
8	24.7 (1.54)	2.56 (0.31)	35.2 (0.3)	38.2 (0.7)	12.1 (0.2)	8.6 (0.6)	0.39 (0.04)	44.3 (17.3)
9	26.3 (3.20)	0.66 (0.10)	38.4 (0.8)	35.1 (0.6)	11.8 (1.1)	8.2 (0.2)	0.31 (0.02)	69.6 (18.6)
10	27.4 (2.69)	0.84 (0.11)	33.9 (0.1)	33.7 (0.3)	6.3 (0.1)	10.2 (0.2)	0.71 (0.07)	39 (11.6)
11	31.3 (0.70)	5.38 (0.41)	34.4 (0.4)	34.9 (0.2)	6.1 (0.1)	9.0 (0.4)	0.19 (0.01)	57.5 (12.9)
12	32.7 (1.85)	9.18 (1.06)	38.9 (0.7)	30.7 (0.3)	10.9 (0.5)	12.2 (0.2)	0.20 (0.05)	29 (30.1)
13	26.3 (1.14)	3.01 (0.59)	36.0 (0.6)	33.1 (0.1)	9.2 (0.4)	7.0 (0.3)	0.49 (0.01)	73.6 (4.1)
14	26.6 (2.03)	2.90 (0.33)	36.1 (0.7)	37.3 (0.4)	7.5 (0.1)	6.2 (0.2)	0.77 (0.12)	37 (16.1)
15	29.1 (0.59)	4.58 (0.22)	34.9 (0.7)	27.8 (0.2)	6.8 (0.1)	16.8 (0.4)	0.37 (0.09)	63.8 (7)
16	33.7 (2.32)	14.9 (1.38)	38.5 (0.5)	33.5 (0.3)	9.5 (0.3)	9.7 (0.3)	0.19 (0.04)	32.3 (30.5)
17	28.3 (0.51)	2.74 (1.94)	35.7 (0.7)	35.6 (0.2)	6.3 (0.1)	7.7 (0.5)	0.27 (0.12)	103.0 (24.1)
18	23.3 (0.83)	3.46 (0.07)	40.9 (0.5)	33.1 (0.4)	6.4 (0.1)	12.0 (0.6)	0.51 (0.08)	32.7 (11.6)
19	20.1 (0.24)	0.62 (0.01)	33.6 (0.5)	34.4 (0.4)	5.6 (0.2)	9.9 (0.2)	0.66 (0.11)	93.5 (11.5)
20	29.3 (0.46)	6.97 (1.15)	37.4 (0.3)	34.7 (0.3)	9.4 (0.2)	10.7 (0.1)	0.44 (0.05)	39.4 (8.7)
21	27.8 (0.46)	2.06 (0.32)	35.3 (0.1)	37.4 (0.1)	6.5 (0.3)	6.7 (0.1)	0.34 (0.09)	31.2 (8.1)
22	22.5 (0.78)	4.40 (0.69)	37.0 (0.9)	36.4 (0.2)	10.3 (0.5)	9.3 (0.6)	0.52 (0.04)	49.4 (3.6)
23	20.6 (0.48)	1.30 (0.31)	31.8 (0.1)	36.0 (0.2)	11.0 (0.1)	10.4 (0.1)	0.60 (0.17)	98.2 (14.3)
24	30.3 (3.41)	5.65 (0.26)	36.2 (0.7)	34.3 (0.4)	10.5 (0.2)	9.6 (0.5)	0.27 (0.07)	36.6 (13.9)
25	22.4 (0.31)	1.81 (0.69)	35.6 (0.5)	35.6 (0.1)	7.8 (0.2)	7.9 (0.3)	0.41 (0.11)	61.7 (43.9)
26	23.4 (2.17)	1.50 (0.26)	35.0 (0.4)	33.5 (0.1)	7.4 (0.2)	9.9 (0.3)	0.63 (0.09)	49.8 (18.5)
27	25.4 (1.19)	1.12 (0.14)	36.6 (0.3)	35.9 (0.4)	5.3 (0.3)	7.0 (0.5)	0.45 (0.09)	44.9 (8.5)
28	23.7 (0.65)	1.43 (0.22)	32.8 (0.5)	33.8 (0.2)	7.2 (0.2)	11.0 (0.2)	0.64 (0.09)	46.1 (5.3)
29	23.0 (0.07)	2.09 (0.53)	32.5 (0.2)	38.0 (0.1)	11.2 (0.2)	10.2 (0.1)	0.46 (0.02)	39.8 (7.1)
30	23.4 (0.53)	1.77 (0.50)	38.8 (0.6)	34.6 (0.2)	9.3 (0.1)	10.4 (0.4)	0.51 (0.10)	45 (12.6)
31	25.1 (0.04)	1.54 (0.52)	36.2 (0.5)	34.7 (0.4)	8.2 (0.3)	8.4 (0.5)	0.51 (0.07)	52.5 (12.9)

Table 6.3: Predicting Equations and Compiled ANOVA Results for CCRD Responses

Response	Model	Pred-R^2	Lack of Fit	Predicting Equation in Terms of Actual Variables
ML	**Quadratic**	0.93	0.448 (NS)	= 52.75 - **0.66C** - **0.32T** - *0.01F* - **0.18t** + *0.01C²* + *0.001T²* + *8.09x10⁻⁷F²* + 0.01t² + *0.01CT* + *8.5x10⁻⁶CF* + *0.001Ct* + *2.49x10⁻⁵TF* + *0.003Tt* + *3.65x10⁻⁶Ft*
SG	**Linear**	0.84	0.175 (NS)	= -1.84 + 0.02C + 0.03T + *5.72x10⁻⁵F* + **0.03t**
*L**	Quadratic	0.85	0.548 (NS)	= 45.36 + 0.21C - **0.73T** - *0.02F* + 0.32t - *0.01C2* + 0.01T² + *5.5x10⁻⁷F²* + 0.01t² + *0.01CT* + *7.0x10⁻⁵CF* - *0.01Ct* + *3.35x10⁻⁵TF* - 0.01Tt + *3.60x10⁻⁶Ft*
*a**	**Linear**	0.80	0.702 (NS)	= 49.55 - 0.09C - **0.13T** + *2.61x10⁻⁴F* - **0.15t**
*b**	Quadratic	0.86	0.103 (NS)	= 88.83 - 0.97C - 1.07T - *0.01F* - 0.04t + 0.01C² + 0.01T² + 2.71x10⁻⁶F² + 0.003t² - *0.01CT* + *1.51x10⁻⁵CF* - *0.01Ct* + *2.88x10⁻⁶TF* + *7.91x10⁻⁵Tt* + *2.82x10⁻⁵Ft*
Δ*E*	Quadratic	0.81	0.478 (NS)	= 76.08 - 1.32C - 1.09T - *0.004F* - 0.54t + *0.01C²* + *0.01T²* + *1.57x10-6F²* + *0.002t²* + 0.01CT - *1.85x10⁻⁵CF* + *0.03Ct* - *8.38x10⁻⁵TF* + 0.01Tt - *3.73x10⁻⁵Ft*
TMA	Interaction	0.87	0.487 (NS)	= -1.48 + 0.04C + **0.04T** + *0.002F* - 0.01t - 0.001CT - *4.11x10⁻⁶CF* + *0.001Ct* - *2.67x10⁻⁶TF* - *0.002Tt* + *3.64x10⁻⁶Ft*
Firmness	**Linear**	0.74	0.087 (NS)	= 186.03 - **1.62C** - 0.90T + *0.01F* - 0.61t

where C is Concentration (°B), T is Temperature (°C), F is Flow Rate (mL/min), and t is contact time (minutes). Note that highly significant ($p < 0.0001$) models and variables are in **bold**, significant ($p < 0.05$) are normal type, while non-significant ($p > 0.05$) factors are *italicized*

6.3.3 Concentration

Increasing concentration tended to increase moisture loss as well as solids gain (Figure 6.1A, D). In the case of moisture loss, this effect was found to be highly ($p < 0.0001$) significant, while it was significant on an $\alpha = 0.05$ level in determining solids gain. In comparing the sum of squares from the ANOVA analysis, concentration had the largest contribution to firmness and the second largest contributor to lightness (L^*-value) and yellowness (b^*-value). Increasing the concentration of the osmotic solution will have the effect of increasing the osmotic pressure across the cell membrane. As a result, higher concentrations tend to promote both moisture loss and solids gain (Azarpazhooh & Ramaswamy, 2012). However, it has been found that concentration tends to have a larger effect on solids gain than moisture loss (Nsonzi & Ramaswamy, 1998a), an effect that was also seen in this study. In previous work with cranberries, the effects of concentration were found to be minimal, an effect attributed to the mass barrier properties of the cranberry skin (Wray & Ramaswamy, 2013). The same conclusion cannot be made in this study, however, as concentration was found to have a significant effect on drying performance. The sole difference from these results and those from the prior study is the change in spray head, where the new spray head is slightly larger and provides more complete coverage of the berries than the earlier iteration. As a result, the better solution-to-sample contact would likely allow for larger changes in response to take place for a given change in concentration, thus allowing these changes to be noticed.

Except in the case of very high concentrations, the solids gain (Table 6.2) was generally lower than prior results seen for cut fruit (Azarpazhooh & Ramaswamy, 2011b). This has been attributed to the mass transfer barrier property of the cranberry skin which would prevent large fluxes of solids from the solution into the flesh of the berry (Wray & Ramaswamy, 2013). On the other hand, the solids gain in this work is higher than that previously observed for cranberries, likely attributed to the better spray and more even solution distribution in this iteration of the setup. Moreover, since a large portion of the solids gain is due to solution remaining on the surface of the berry (Table 5.2), rinsing or further shaking of the berry could be useful in terms of further controlling solids gain.

Higher solution concentrations did tend to produce significantly ($p < 0.05$) redder samples, an effect that can be seen in Figure 6.2D. It has been stated before that sucrose incorporation will exhibit a protective effect on natural pigments in food products (Chiralt & Talens, 2005). This

effect is confirmed by the total monomeric anthocyanin content (Figure 6.3A), where higher sucrose concentrations resulted in higher anthocyanin content, an effect that was significant on an $\alpha = 0.05$ level (Table 6.3). Total color change (ΔE) also tended to increase with increasing concentration, despite the maintenance of anthocyanin content and red color. This is largely attributed to significant decreases in L^* and b^* values (Figure 6.3 A and G, respectively), where increased sugar concentrations in the berries tended to produce substantially darker samples, likely due to increased browning and charring during finish-drying.

Finally, concentration also provided the only highly significant ($p < 0.0001$) variable for firmness, where increasing concentrations tended to decrease the firmness of the product (Figure 6.3D), an effect that agrees with various prior studies on osmotic dehydration where sugar uptake has been found to product softer, chewier products (Monsalve-Gonzalez et al., 1993; Telis et al., 2005). This effect was also seen in earlier work with cranberries were it was found that increasing process intensity tended to lead to loss of firmness in the post-MWODS intermediate moisture product (Wray & Ramaswamy, 2013).

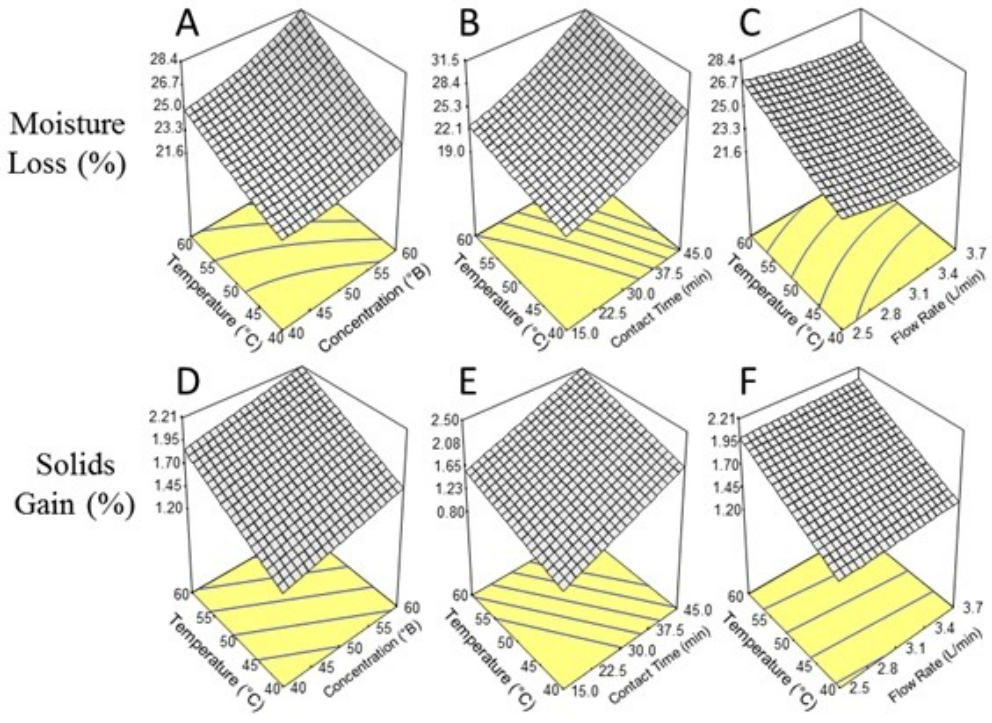

Figure 6.1: Response Surface Curves for Moisture Loss and Solids Gain.
(When not a variable, inputs were fixed at their center point: 50 °C, 50°B, 30 min, and 3.1 L/min)

6.3.4 Contact Time

Contact time was found to be a highly significant ($p < 0.0001$) contributor to moisture loss, solids gain, and a^*-value, while it was significant ($p < 0.05$) in the case of L^*, b^*, ΔE, anthocyanin content, and firmness. In comparing the sum of squares, contact time had the largest effect on moisture loss, solids gain, and a^*-value. More specifically, longer contact times tended to increase drying responses (ML and SG; Figure 6.1B, E), by allowing more time for moisture and solids diffusion to take place. The importance of contact time in this work agrees with conclusions in prior studies, where for cranberries contact time was found to be statistically significant but less so than temperature (Wray & Ramaswamy, 2013). On the other hand, MWODS of apple have found contact time to be the most important parameter in determining the moisture loss of the sample (Azarpazhooh & Ramaswamy, 2010b). Similar results were also drawn for conventional osmotic dehydration, where contact time was also the most significant influencer of solids gain (Li & Ramaswamy, 2006a; van Nieuwenhuijzen et al., 2001). These varying conclusions highlight the impact of different samples types, where the cut nature of the apple cylinders used in these two prior works could make them more susceptible to mass transfer over time.

Just as longer contact times allow for more moisture loss and solids gain, they also tended to decrease redness and TMA content (Figure 6.2E and 6.3B, respectively), likely due to increased destruction or leaching of anthocyanins. The loss of anthocyanins was visually evident in berries subjected to longer processes, where there was almost a bleaching effect and post-MWODS were much lighter in appearance. This effect is confirmed in Figure 6.2B, where particularly at low temperatures, longer processes tended to increase the lightness of the sample on an $\alpha = 0.05$ level (Table 6.3). This effect was tempered at elevated temperatures, suggesting that the loss of anthocyanins was in effect sped up by the increased temperatures to the point where longer process times had little effect. The b^*-value (Figure 6.2H) showed a general decrease with increasing process time, likely indicating that over time there was a progressive loss of yellow flavonoids from the berries. These changes contribute to the significant ($p < 0.05$) effect of contact time on total color change (Figure 6.2K). Of particular interest in this case, however, is the particularly large influence on ΔE that contact time has at higher temperatures, an effect confirmed both by the slope of the curve (Figure 6.2K) as well as the statistical significance ($p < 0.05$) of the time-temperature interaction effect (Table 6.3). This indicates that longer processes were more destructive to color when they were performed at higher temperatures as compared to low

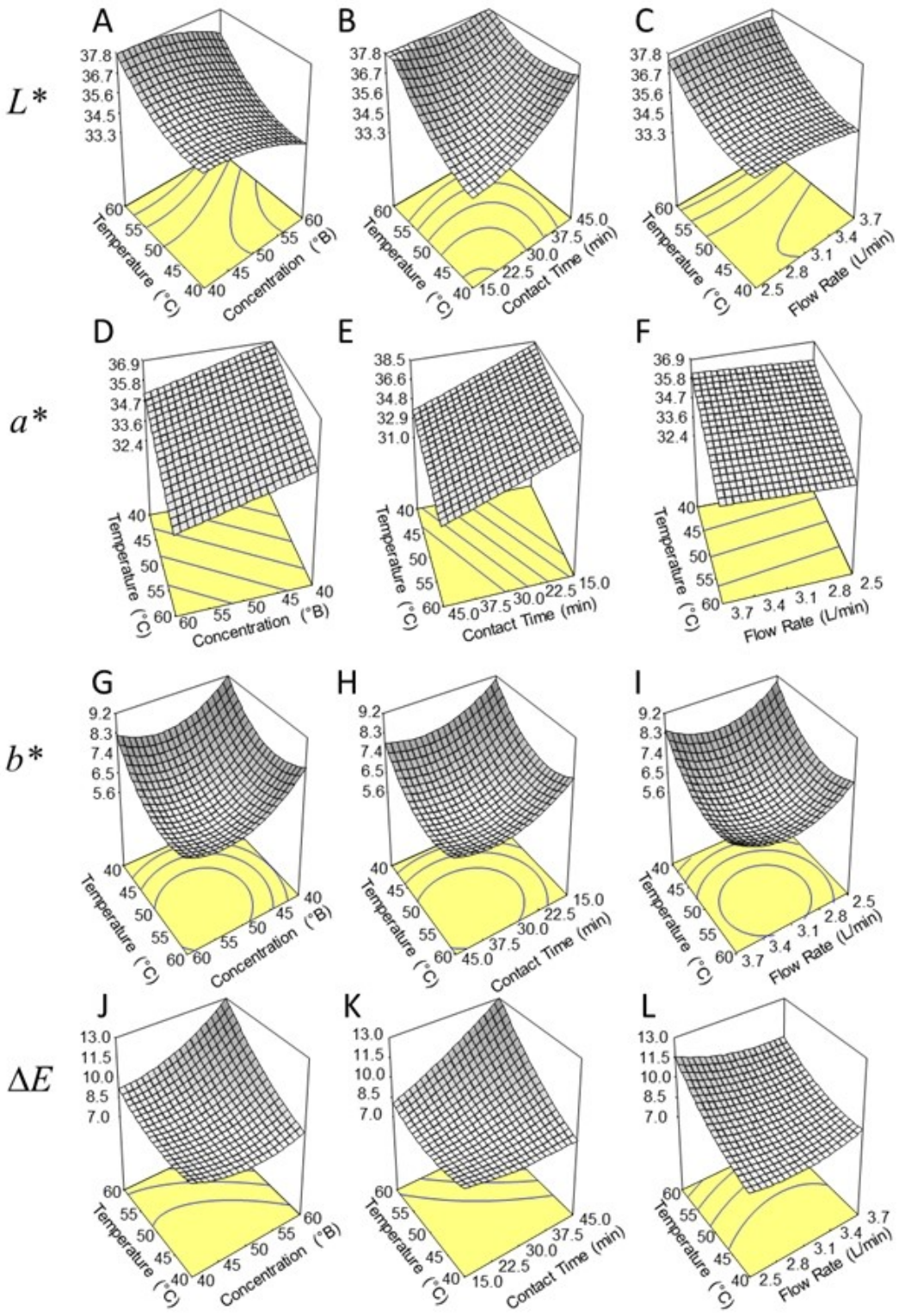

Figure 6.2: Response Surface Plots for Selected Colorimetric Parameters.
(When not a variable, inputs were fixed at their center point: 50 °C, 50°B, 30 min, and 3.1 L/min)

temperatures. This would be due to the fact that phenolics are particularly susceptible to degradation at higher temperatures, but also that hotter osmotic solution over longer periods of time would also incorporate more sugar, which would in turn cause darkening during finish-drying. The elevated sugar uptake would also explain the fact that longer MWODS tended to make the sample softer (Figure 6.3E).

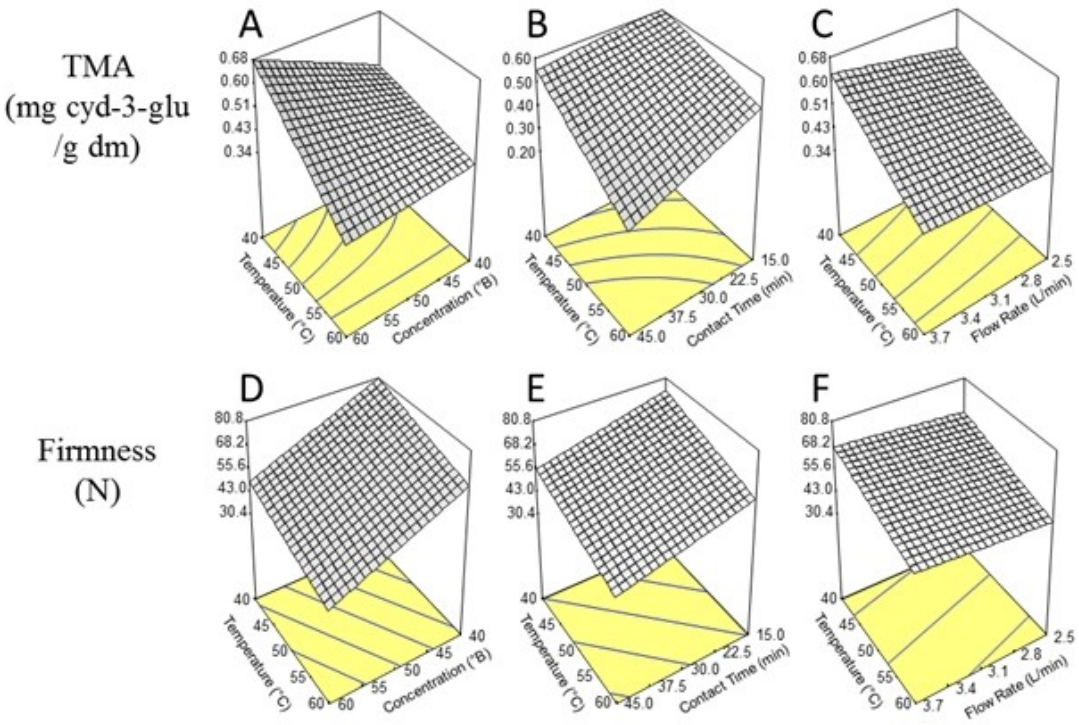

Figure 6.3: Response Surface Plots for Total Monomeric Anthocyanins (TMA) and Firmness. *(When not a variable, inputs were fixed at their center point: 50 °C, 50°B, 30 min, 3.1 and L/min)*

6.3.5 Flow Rate

Flow rate had the smallest impact of any of the input variable, where it was statistically insignificant and had the smallest sum of squares in all cases. This conclusion agrees with prior work on apple (Azarpazhooh & Ramaswamy, 2012). Even if insignificant, changes in flow rate did tend to have small effects on the process. For instance, increasing flow rates tended to slightly increase solids gain (Figure 6.1F), which could be attributed to faster removal of moisture and re-

establishment of concentration differentials that fuel the osmotic exchange at the surface of the fruit. Interestingly, higher flow rates tended to decrease moisture loss (Figure 6.1C) and ΔE (6.2L) while it increased TMA retention (6.3C), a^*-value/redness (6.2F), and firmness (6.3F). Considering all of these trends, it seems likely that increasing the flow rate has a slight cooling effect on the samples, where enhanced flow rates would be able to more quickly remove the heat created by the microwave application, thereby lowering the effective temperature of the sample and decreasing moisture loss and promoting quality retention. The lack of statistical significance suggests these effects are small, but could warrant further investigation as a means to control product temperature during MWODS.

6.3.6 Optimization and Model Validation

The term optimization as it pertains to drying processes can be difficult to assess, simply because the intensive operating conditions that would promote drying rate would tend to be destructive to product quality. Regardless, an attempt was made to verify the accuracy of the predicting model output by Design Expert by validating it with experimental data. Numerical optimization was performed by setting the input parameters of concentration, temperature, flow rate, and contact time to be 'in range', while the responses set to 'maximum' included moisture loss, TMA, and a^*-value. Conversely, total color change (ΔE) and firmness were set to 'minimize'. The resulting solution with the highest desirability (0.683) was found to be a process at 41.8°C, 50.9°B, 3.2 L/min, for 30 min. The relatively low desirability shows the impact of the two opposed requirements of the constraints outlined above—i.e. a process with maximal moisture loss while also minimizing quality loss. For comparison, removing the ML requirement while leaving all other constraints increased the desirability of the output solution to 0.871. The predicted values (and relevant confidence intervals), along with experimentally determined data can be seen in Table 6.4. While there was some deviation between predicted and experimental results, there was appreciable correlation between the two especially considering the relatively low desirability of the function to begin with and the inherent variability of working with a biological product (though the berries were all taken from the same batch). Therefore it was determined that the model predicted the experimental output well. It is worth noting, however, that this predicting model could only be used to predict outputs for this product within these ranges, and not be extrapolated outside of the ranges of the CCRD design.

Table 6.4: Predictive Model Validation

Response	Predicted	CI Low	CI High	Observed
Moisture Loss (%)	27.5	25.8	29.0	29.4 (1.2)
Solids Gain (%)	2.06	1.74	2.37	1.80 (0.3)
a*	32.9	31.8	34.0	35.1 (0.6)
ΔE	8.4	5.8	10.5	9.0 (0.7)
TMA (mg cyd-3-glu/ g dm)	0.71	0.59	0.83	0.60 (0.05)
Firmness (N)	41.9	30.6	50.2	50.6 (7.0)

Mean values with (standard deviation shown). CI: Confidence Interval (95%)

6.3.7 Comparison with other Methods

Comparing the novel process to established methods is a way to benchmark the process on the basis of quality parameters. As can be seen in Table 6.5, the MWODS-MWV dried berry compared favorably in many ways to both the fresh freeze dried (Fresh-FD) and MWODS pre-treated freeze dried (MWODS-FD) samples. While significantly different from both the MWODS-FD and Fresh-FD in terms of colorimetric parameters (L^*, a^*, b^*, and ΔE), the MWODS-MWV produced sample was much closer to the freeze dried samples than those produced via other methods such as vacuum drying (MWODS-VD) and air drying (MWODS-AD). Similarly, while about half of the anthocyanin content was lost during MWODS, (1.27 vs 0.67 mg cyd-3-glu /g dm for Fresh-FD vs MWODS-FD, respectively), the MWODS-MWV process was found to maintain statistically similar levels of anthocyanin as compared to berries that were freeze dried after MWODS. This echoes previous work where it was found that MWV finish-drying cranberries had similar anthocyanin content and antioxidant activity as compared to freeze dried berries (Leusink et al., 2010). In the case of TMA content, levels decreased significantly in processes that applied higher temperatures, namely vacuum and air drying (VD and AD, respectively). It is worth noting, however, that the precipitous decline to the TMA content of the MWODS-AD sample was likely because the berries were left whole, which led to extremely long (24-26 h) drying times. If sliced, as is the industry standard, then this decrease would likely be mediated by reducing the amount of time the samples were exposed to elevated temperatures. Still, the performance of the MWV finish-drying step and the MWODS-MWV drying process on the whole indicate that it is much better at

maintaining anthocyanin content and color profile as compared to either VD or AD.

It is difficult to draw conclusions from textural data (firmness) because of the inconsistency in the data and the corresponding lack of statistically different groupings. However, comparing on the bases of means, it appears as though higher temperature processes tend to produce harder samples. Moreover, because the vacuum and air drying procedure took place at the same temperature, there appears to be an effect of time or presence of oxygen as well, since the air drying procedure took approximately 4 times longer to complete (6 vs 24 h) and was performed at atmospheric conditions.

Bulk density data (Table 6.5) indicates an overall increase in density between Fresh-FD and MWODS-FD samples, likely due to solids uptake during MWODS and the corresponding increase in mass. The MWV finish-drying process was able to produce a similar puffed appearance and rounded berry to the freeze dried samples, which is evidenced by the two groups (MWODS-FD and MWODS-MWV) being in the same statistical grouping. Despite also being finish dried under vacuum, the MWODS-VD sample exhibited slightly more shrinkage, which contributed to a significantly ($\alpha = 0.05$) higher bulk density. MWV dried samples were closer in size and appearance to the freeze dried samples than those dried via VD, despite being dried at about the same vacuum level (6 kPa abs), which was in turn much lower than the 13-20 Pa employed in the FD process. This can be attributed to the faster rate of moisture diffusion, where the rapid formation of steam within microwave dried samples has been previously described as a contributing factor to the puffed appearance of samples produced this way (Andrés et al., 2004).

In terms of rehydration capacity (RHC) (Table 6.5), the MWV finish dried berries were found to be statistically the same as both freeze dried sample types (Fresh- and MWODS-FD). Similarly, the MWODS-VD samples also had a high rehydration capacity, albeit lower than the FD or MWV dried samples, again likely due to the slightly less puffed structure. Finally, while it is common for air dried samples to exhibit low rehydration capacities, the fact that the MWODS-AD samples exhibited such a low RHC can be attributed to the moisture barrier property of the relatively intact skin in combination with the shrunken nature of the product, which limits the ability of moisture to diffuse back into the sample.

Table 6.5: Comparison of Cranberries Dried via Various Drying Techniques

Response	Treatment Type				
	Fresh-FD	**MWODS-FD**	**MWODS-MWV**	**MWODS-VD**	**MWODS-AD**
L*	35.1 (0.4) [a]	31.8 (0.7) [b]	29.4 (0.4) [c]	24.0 (0.6) [d]	24.6 (0.5) [d]
a*	38.5 (0.9) [a]	37.9 (0.6) [a]	34.3 (1.3) [b]	20.8 (2.7) [c]	11.1 (0.5) [d]
b*	8.6 (0.6) [a]	8.9 (0.3) [a]	8.1 (0.8) [a]	7.6 (1.2) [a]	7.6 (0.7) [a]
ΔE		3.6 (0.6) [d]	5.8 (0.9) [c]	14.3 (2.4) [b]	20.7 (0.3) [a]
TMA (mg cyd-3-glu/g dm)	1.27 (0.01) [a]	0.67 (0.02) [b]	0.70 (0.1) [b]	0.37 (0.02) [c]	0.09 (0.01) [d]
Firmness (N)	30.6 (3.5) [a]	30.6 (4.3) [a]	34.2 (10.6) [a]	35.4 (3.1) [a]	36.9 (6.1) [a]
Bulk Density (kg/m^3)	80.3 (1.3) [d]	87.0 (1.7) [c]	85.6 (1.3) [c]	93.6 (2.1) [b]	139.8 (9.4) [a]
Rehydration Capacity (%)	99.2 (2.0) [a]	101.9 (1.3) [a]	98.0 (2.5) [a]	86.0 (2.1) [b]	25.2 (1.8) [c]

Mean values with standard deviation shown—values that do not share a letter (a,b,c) are significantly different (Determined by Tukey method on 95% confidence interval)

Many macroscopic properties can be explained by changes that take place at the microscopic level during dehydration. For instance, the high bulk density, low rehydration capacity, and relative hardness of the air dried sample makes more sense when comparing the compressed and shrunken cellular structure of the MWODS-AD sample to, for example, open and intact structure of the Fresh-FD sample (Figure 6.5C and 6.5A, respectively). Further, whereas both the Fresh-FD and MWODS-FD samples exhibit a relatively intact and open cellular structure, there is some breakdown in the latter sample (Figure 6.5B). The breakdown of cell walls is a normal occurrence in osmotic dehydration because of loss of cell turgor as cells lose moisture throughout the process (Fernandes et al., 2008). Moreover, the degree to which a product can be rehydrated is inversely proportional to the level of cellular destruction that takes place (Krokida & Marinos-Kouris, 2003). While both the VD and MWV dried samples retained much of the puffed and open cellular structure of the FD samples, there is significantly more breakdown of the cell walls,

particularly with the VD sample; an effect that can likely be attributed to exposure of the product to high temperatures for long periods of time. However, it is worth noting that this breakage may not have occurred during drying and may have occurred during sectioning because of the brittle nature of the dried cell walls. Interestingly, the MWODS-MWV (6.5E) sample shows some evidence of compressed cell structures pressed against the inside of the intact cranberry skin (the dark blue/black line). This is likely caused by the rapid formation of steam within the berry due to microwave application, which forcibly pushes outwards as it exits the fruit (Andrés et al., 2004). As the steam forces its way to the outer layers of the product, it pushes the cellular structure outwards, which in the case of berries would mean the roundness of the berries is maintained. On the other end of the spectrum, the substantially higher bulk density found for the air dried sample can most likely be attributed to its substantial level of shrinkage. The MWODS-AD samples were, as observed on a visual basis, regularly less than half the diameter of those dried under vacuum (particularly FD or MWV).

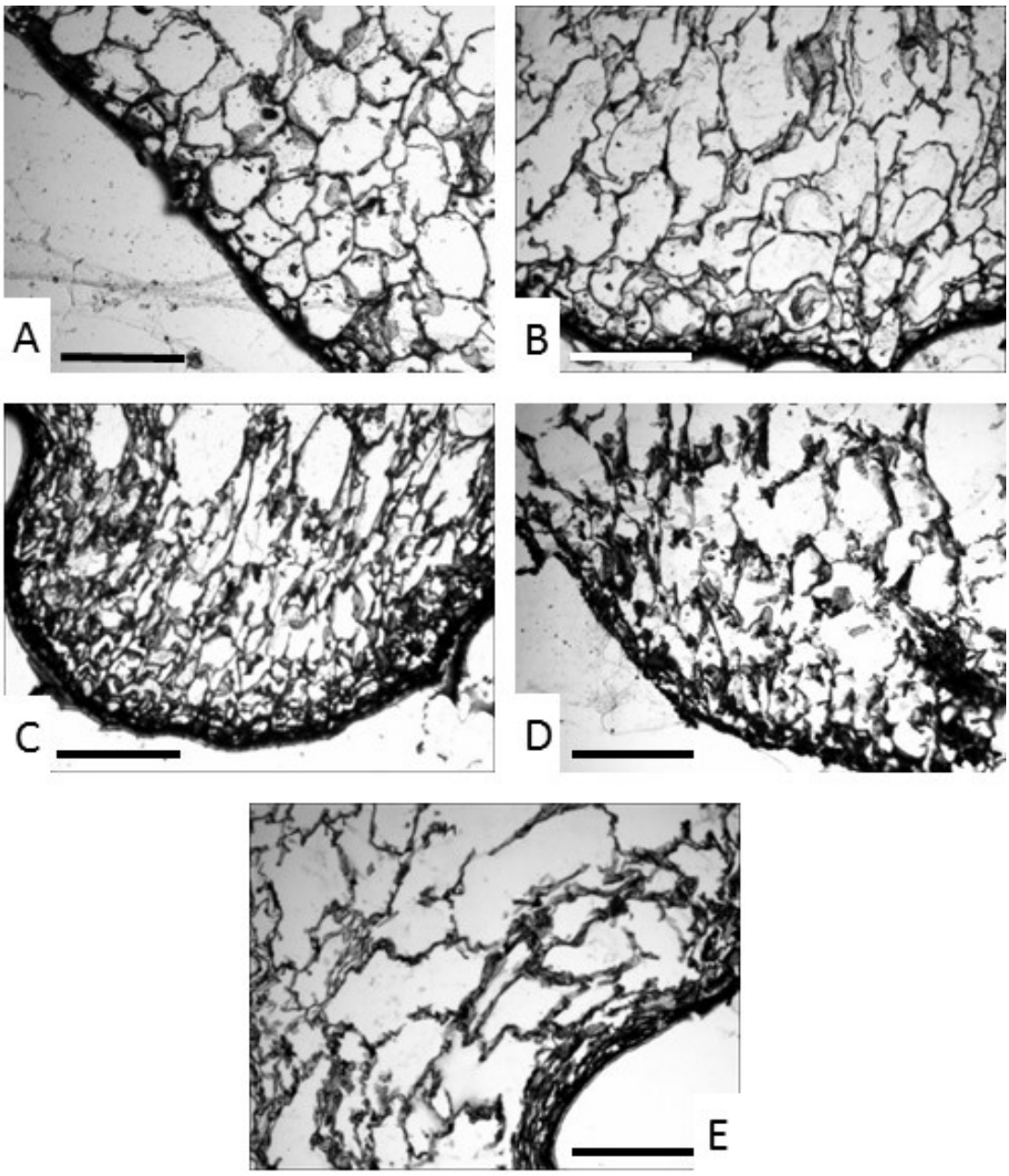

Figure 6.4: Cellular Structure of Dried Cranberries Subjected to Various Drying Techniques. *Where: (A) Fresh-FD; (B) MWODS-FD; (C) MWODS-AD; (D) MWODS-VD, and (E) MWODS-MWV. The bar indicates 100 μm.*

6.4 Conclusions

Overall it was found that the MWODS-MWV process was capable of producing high quality dried whole cranberries with quality indices approaching those of freeze dried samples and far exceeding those dried via either vacuum drying or air drying. While freeze dried samples provided the highest quality, drying times for the novel process were significantly shorter, and additionally the sample would not have to be frozen beforehand, thereby simplifying the process. The MWODS-MWV berries exceeded the quality of those produced by either vacuum drying or air drying by better maintaining the characteristic color of the berry and by creating an open and more intact cellular structure, which in turn allows for lower bulk density and higher rehydration capacity. By varying MWODS input variables such as temperature, concentration, contact time, and flow rate it was found that the process behaved in such a way that increasing any of these process parameters tended to increase moisture loss and solids gain. Increasing temperature or contact time tended to have a negative impact on quality parameters, while increasing concentration or flow rate tended to mediate loss of quality markers through incorporation of solute and an apparent cooling effect, respectively. The predicting model determined in the study was able to adequately predict an experimental outcome, however by its very nature the optimization of drying work is difficult, as often the gains sought in product quality are offset by increasing drying times or energy consumption as these gains are typically achieved by reducing the intensity of the process.

CONNECTIVE STATEMENT TO CHAPTER 7

Despite the relative energy efficiency of osmotic dehydration in removing moisture from food products, there is extensive energy input required to re-concentrate the solution back to its original strength after it has been diluted due to moisture picked up from the product. Other means to regenerate the solution include solute addition, or maintaining the solution-to-sample ratio sufficiently high such that the dilution that takes place has a minimal effect on the overall concentration. While less energy intensive, both involve costs in terms of the cost of solute to add or create the large volume of solution, respectively. As a result, there is interest in determining the ability of the MWODS process to reuse osmotic solutions: the more it can be reused, the more cost effective the process becomes. Further, during osmotic dehydration there are notable amounts of polar components native to the food product that leach into the osmotic solution. Simply discarding the solution will lead to the loss of these components, as well as incur the cost of properly disposing of the solution. Therefore, this chapter focuses on the properties and performance of reused osmotic syrups as well as their potential to infuse the components leached from one product (cranberries) into another (apples), to therefore determine its usefulness in creating a novel food product.

Parts of Chapter 7 have been adapted for presentations and publications as follows

Wray, D and Ramaswamy, H.S. Recycling of Osmotic Solutions in Microwave-Osmotic Dehydration: Effects on Product Quality and Potential for Creation of a Novel Product. *(In preparation)*

CHAPTER 7

RECYCLING OF OSMOTIC SOLUTIONS IN MICROWAVE-OSMOTIC DEHYDRATION: EFFECTS ON PRODUCT QUALITY AND POTENTIAL FOR CREATION OF A NOVEL PRODUCT

Abstract

Despite osmotic dehydration being a cost effective process for moisture removal, the cost implications of making, regenerating, and properly disposing of the spent osmotic solutions contribute greatly to the economic feasibility of the drying operation. The potential for recycling of osmotic solutions and their use for creation of a novel product was explored using microwave osmotic dehydration under continuous flow spray (MWODS) conditions. Identical runs were repeated ten times to determine the progressive physical and compositional effects of the thermal treatment and leaching from the cranberry samples. The microbiological stability and steady drying performance indicates that MWODS would be well suited for employing recycled solutions. Moreover, while the anthocyanin content of the solution never approached that of cranberry juice concentrate, it is demonstrated that the spent syrup still holds potential for infusing these health positive components into another product (apple), enabling creation of novel products.

7.1 Introduction

Osmotic dehydration (OD) is a process used to remove the initial bulk of moisture from a food product and create an intermediate moisture food product. By operating at moderate temperatures and removing water in its liquid form, OD eliminates the need to provide the latent heat of vaporization as required to evaporate water in most drying techniques. Owing to the moderate conditions and lack of exposure to oxygen, the osmotically dried products are typically of better/high quality (Raoult-Wack, 1994). Moreover, OD limits the amount of time that a product has to spend in subsequent finish-drying, thereby limiting quality deterioration in this stage. However, there are some drawbacks to OD which can be attributed to its operating principles. First, by limiting energy input and relying on osmotic pressure differentials, the process is very slow, taking as long as 24-48 h in some settings. Microwave-osmotic dehydration was developed in order to enhance the rate of moisture diffusion from the sample with the goal of reducing process time. Initially, this technique was developed as an immersion based configuration, where apple cylinders were submerged in a continuously circulating bath of osmotic solution and microwaves were applied to the syrup and product (Li & Ramaswamy, 2006c). Later, this process evolved into a spray based setup, where the samples stage were continuously coated in a thin layer of osmotic solution—an arrangement allowed for more microwave power to be incident on the sample itself, resulting in higher moisture loss and lower solids gain during a given process time (Azarpazhooh & Ramaswamy, 2010c). Known as microwave osmotic dehydration in spray configuration (MWODS), in its most recent iteration the process has been applied to whole frozen thawed cranberries with no slicing or skin pre-treatment, and was found to be capable of providing upwards of 30% moisture loss in process times of about 1 h (Chapters 3 and 6).

Another drawback to osmotic dehydration is that the theoretical extent of dehydration depends on the concentration of the osmotic solution, where higher concentrations of the solution allow for lower final product moisture contents. More to the point, the water removed from the sample dilutes the osmotic solution and limits the effectiveness of the solution in subsequent re-uses by slowing the mass transfer rate (Garcia-Martınez et al., 2002). As a result, the solution is typically regenerated to the original concentration by either evaporation or addition of solute (Valdez-Frugoso et al. 1998). However, in many cases osmotic solutions are discarded, creating substantial amounts of industrial waste and substantially increasing overall costs for the operation (Garcia-Martınez et al., 2002). As the resulting spent osmotic syrup can be considered an industrial

waste, recycling the solution is one way to make the process both economical and environmentally friendly (Aachary & Prapulla, 2009). As a result of these considerations, one of the main issues with osmotic dehydration at the industrial scale is management of spent solutions or brines.

During osmotic dehydration the main mass transfers that take place are the flow of moisture out of the product, and flow of solutes from the osmotic solution into the product. However, there is also a more minor flow of solutes naturally present in the food product into the osmotic solution (Torreggiani & Bertolo, 2001). It has previously been stated that discarding the solution without further use (recycling or use in a new product formulation) can result in loss of valuable natural substances such as vitamins and minerals (Garcia-Martınez et al., 2002). In fact, the leaching of health positive components from fruits during osmotic dehydration takes place to such an extent that it has been proposed that the solutions be used as a natural additive to food or pharmaceutical products (Morales et al., 2005). This concept is particularly topical with cranberries, which contain various health positive components including flavonols, flavan-3-ols, anthocyanins, tannins, and phenolic acid derivatives (Côté et al., 2010b). Bioactive compounds in cranberries also exhibit a broad anti-oxidant effect by scavenging reactive species such as the superoxide and hydroxyl radicals (Wang & Jiao, 2000). Moreover, prior studies have established positive effects of consumption of these compounds in terms of reducing the incidence of conditions such as neurodegenerative diseases, cardiovascular disease, cancer, and stroke (Hertog et al., 1993; Knekt et al., 1996; Keli et al., 1996; Knekt et al., 1997).

While various studies have looked at the effects of recycled solutions during conventional osmotic dehydration at the bench top and pilot scale (Garcia-Martınez et al., 2002; Peiró et al., 2006; Bolin et al., 1983; Osorio et al., 2007; Valdez-Fragoso et al., 2002; Valdez-Frugoso et al., 1998), there has been no work on these effects during microwave-osmotic dehydration. Therefore, the focus of this study is to examine the reuse of sucrose based osmotic syrups over a number of successive runs, as well as the potential of using the resulting syrups as a value added sweetener or for the creation of novel food products. This is achieved by monitoring the drying performance and physical parameters of the solution itself as well as the quality indices of the resulting product.

7.2 Materials and Methods

7.2.1 Raw Materials

Frozen whole Cranberries (ATOKA Ltd, Manseau, QC) were kept frozen at -20°C prior to use and were thawed in excess room temperature water and sorted as outlined in Chapter 3. For the apple treatments, Royal Gala apples were purchased locally and kept at 4-6°C for up to 48 h prior to use. Apple cylinders (1.5cm diameter x 1.5cm height) were prepared using an apple corer, avoiding the core and skin portions of the fruit. Cranberry juice concentrate (Ocean Spray Ltd, Lakeville, MA) was purchased locally and kept frozen until a few hours before used when it was thawed at room temperature. Sucrose based osmotic solutions were made using tap water and consumer grade sucrose (Lantic Canada Ltd, Montreal, QC). The soluble solids of all solutions was measured using an Atago PAL-α digital refractometer (Atago Co. Ltd, Tokyo, Japan) after which the value was adjusted for the contribution of the acidity of the solution.

7.2.2 MWODS Treatments

MWODS treatments were performed as described in Chapter 6 using the center point of the previously determined CCRD design (50°C, 50°B, 30 min, and 3.7 L/min). The set of 10 successive runs was done in duplicate, where the osmotic solution was prepared fresh for each set of runs using tap water and consumer grade sugar. A fresh sample (approximately 50g) of berries was placed in the sample holder for each run, after which the samples were removed and finish dried using the 20/10% MWV drying process (Chapter 4). Dried cranberries were subjected to quality analysis within 24h or alternatively were ground, frozen, and lyophilised for chemical analysis.

7.2.3 Monitoring the Osmotic Solution

After each run approximately 25 mL of solution was removed from the sample container and was replaced with 25mL of fresh osmotic syrup in order to maintain total volume. These samples were stored at 4-6°C for 2-3 days during which time the following analyses were performed.

Spectra of the recycled solutions and cranberry juice concentrates were determined by a wavelength scan at 5nm resolution from 260-780 nm using a UV-Vis spectrophotometer (UV-3100PC, VWR International, Montreal, QC) and accompanying ‘UV-Vis Analyst’ software. The

visible portion of the spectra (380-770 nm) were used to calculate the colorimetric properties, including *L**, *a**, and *b** values, of the osmotic solutions and juice concentrates.

Viscosity was measured using a controlled stress rheometer (AR 2000, TA Instruments, New Castle, DE, USA), and data analyzed using the accompanying Rheology Advantage software. Measurements were taken using a shear rate sweep of 0-300 s^{-1} in 3 mins at 25°C, using a 50 μm gap and 0.2 mL of solution.

Microbiological properties were determined according to the procedure described by Garcia-Martinez et al. (2002). Bacteria were determined using Plate Count Agar (Fluka 70152; 48h at 30°C) (PCA) while yeasts and molds were enumerated with Sabouraud Glucose Agar (SGA) with Chloramphenical (Fluka 89579; 72h at 30°C). Results are expressed as colony forming units (CFU) per mL of syrup.

Titratable acidity was determined with 0.01N NaOH standardized against oxalic acid to a phenolphthalein endpoint. Results were expressed as % Citric Acid (CA).

Total monomeric anthocyanins (TMA) and radical scavenging ability by DPPH were determined directly from the solution. TMA content was completed using a differential pH method as suggested for cranberries by Zheng and Wang (2003) and as outlined by Lee et al. (2005). This assay takes advantage of the fact that anthocyanins reversibly change color with pH, where the oxonium ion form is brilliantly red at highly acidic pH values, whereas the colorless hemiketal form predominates at and beyond pH 4.5 (Lee et al., 2005). For this analysis, 0.75mL of the solutions were mixed with 3.25 mL of buffer at either pH 1 (0.025M KCl acidified with concentrated HCl; Fisher Scientific, Montreal, QC) or pH 4.5 (0.4M sodium acetate acidified with glacial acetic acid; Fisher Scientific, Montreal, QC) was added. The samples were allowed to stand for 20 min and then transferred to cuvettes and absorbance was measured against the appropriate buffer blank at both 520 and 700nm. Each sample was analyzed in duplicate for a total of four replicates for each solution and results expressed as milligrams of cyanidin-3-glucoside equivalents per gram dry matter (mg cyd-3-glu/g dm) as explained in Section 5.2.11.

Radical scavenging ability was assessed using the procedure outlined by (Lim & Murtijaya, 2007). In this case, 100 μL of the solution was added to 3 mL of 0.15 mM DPPH (Sigma-Aldrich, Oakville, ON) in methanol (Fisher Scientific, Montreal, QC).

The mixture was allowed to stand for 30 min in the dark at which point the absorbance was measured at 517 nm against a methanol blank and the antioxidant activity determined as a

percentage of DPPH decrease using the following equation:

$$AA(\%) = [(A_{control} - A_{sample})/A_{control}] \times 100 \qquad (7.1)$$

where $A_{control}$ is the DPPH solution diluted with 100μL methanol aliquot instead of the phenolic extract.

Otherwise, soluble solids (°Brix) was monitored using an Atago PAL-α digital refractometer (Atago Co. Ltd, Tokyo, Japan), with solutions equilibrated at room temperature (23°C) prior to measurement. Water activity was read with a Hygrolab-2 (Rotronic Instrument Corp., Hauppauge, NY). Finally, pH of the solutions was determined directly using a pH meter.

7.2.4 Product Quality Analysis

Quality analysis (color, texture, total monomeric anthocyanin content and DPPH radical scavenging activity) was performed according to the procedures outlined below, where full details are presented in Chapter 6. Color of the berries was determined using a colorimeter Minolta CM-500d Chroma Meter with 3 replicates of each duplicate run were analyzed (6 samples total) and averaged. A simple compression test was used in order to monitor the peak hardness of the sample as outlined in Chapter 6.

For chemical analyses, berries were ground in a consumer grade spice grinder using short bursts of power to limit the effect of heat buildup. The samples were then freeze dried for 24 h in order to eliminate any variations of moisture content of the dried berries on subsequent analyses. After freeze drying, the phenolics were extracted from the powder using a method previously applied to cranberries (Zheng & Wang, 2003). In this case 0.1 g portions of the ground samples were accurately weighed and placed in 15mL centrifuge tubes, to which 10mL of 80% acetone and 0.2% v/v formic acid (Fisher Scientific, Montreal, QC) was added and the tubes vortexed for 10 s. The tubes were then allowed to stand for 10 min at room temperature with periodic mixing before being centrifuged at 20,000 x *g* for 20 min. The pellets were then discarded and supernatants kept at -20°C for a maximum of one week before being analyzed as previously outlined for the syrups.

7.3 Results and Discussion

7.3.1 Physical Changes in Osmotic Syrup and Effects on Drying Performance

The osmotic syrup went through dramatic changes throughout the successive runs which can be attributed to compositional changes such as dilution as well as the impact of compounds

leached from the food product (Table 7.1). Viscosity decreased over the course of the repeated runs, where initially the syrup had a viscosity of 0.03151 Pa·s which decreased to 0.02056 Pa·s by the 10th run. This is despite the soluble solids remaining relatively constant throughout the repeated runs once adjusted for the effect of the acidity of the solution. However, the viscosity of the solution in Run 10 is just over two-thirds that of the original solution, despite the relatively stable solution concentration. This is likely due to the effects of sucrose hydrolyzing into glucose and fructose. In prior reports, hydrolysis was found to have an effect on syrup properties but not on drying performance or product organoleptic properties (Bolin et al., 1983). While in the case of lower acid products like apples, increasing levels of reducing sugar was largely attributed to migration from the fruit (Valdez-Frugoso et al., 1998). One study found that the rate of hydrolysis was found to be higher with apricots than apples owing to their higher acidity (Bolin et al., 1983). This latter effect is likely to be true of cranberries, which have a significant acid content. Sugar inversion raises the soluble solids content owing to the increase in the mass of sugars present in the solution. Sugar inversion also reduces viscosity, where a 50.18°B solution that was inverted 50% was found to cause a 15% decrease in viscosity (Cotton et al., 1955). Furthermore, the acid hydrolysis reaction is favored by reduced pH and elevated temperatures (Shachman, 2004), and therefore likely would have proceeded incrementally as acidity increased and with repeated heating cycles.

Solids gain tended to increase towards the second half of the experiments, particularly for Run 6 and beyond, as well as for the cranberry juice concentrate (Table 7.3). In these cases, the mean values of these were higher than the grouping consisting of Run 1 through Run 5, although not significantly. The lack of significantly different groupings is attributed to the relatively high levels of variability, which was previously discussed as a hindrance to modelling the process for cranberries (Wray & Ramaswamy, 2013). Regardless, the increasing solids gain could perhaps be due to the increasing concentration of monosaccharides resulting from hydrolysis. It has been shown before that smaller solutes lead to higher solids gain because smaller compounds are able to more easily traverse the cell membrane (Qi et al., 1998; Raoult-Wack, 1994). This is particularly relevant with whole cranberries, where the waxy skin represents an effective mass transfer barrier.

The water activity of the osmotic solution also increases slightly over the course of the successive runs, perhaps indicating a slight dilution of the syrup. Regardless, there was no clear trend in the drying performance of the setup as it pertains to moisture loss, indicating that this

decrease in concentration is not substantial enough to produce a clear moisture loss trend over successive MWODS runs, despite the previously proven influence of concentration on moisture loss (Chapter 6). Additionally, it has been theorized that acidified osmotic solutions could enhance moisture loss (Moy, 1978). This effect was not seen in this case, likely because in MWODS moisture loss is not only dependent on the composition of the osmotic solution, but the incident microwave power as well.

7.3.2 Composition of the Osmotic Syrup

It has been suggested that spent osmotic syrup could be used as a value added sweetener for other products (Peiró et al., 2006). In the case of cranberries, anthocyanins are of particular interest, and are known to leach into the osmotic solution. In fact, the most significant loss of anthocyanins took place during the osmotic dehydration step of an osmo-convective drying operation due to the intensive mass transfer operations that took place (Grabowski et al., 2007). In the case of MWODS, this loss was found to be approximately 50%, an effect attributed to the elevated temperatures employed in this operation (Chapter 4).

Compositional change can be seen in terms of the different spectra of the solutions (Figure 7.1), which demonstrate the changes that take place during sucrose and cranberry juice concentrate (CJC) based runs. The region in the 500-550nm range which is initially flat grows progressively over the course of successive runs, which is attributed to anthocyanins (mainly galactosides and arabinosides of cyanidin and peonidin) as they absorb light strongly in this region (Côté et al., 2010a). There was a more noticeable increase, however, in the 280-290nm UV region. Absorbance in this area is caused not only by anthocyanins (which also absorb at 278-280nm owing to their phenolic B-ring) but also by phenolic acids (including ferulic, *p*-coumaric, caffeic, ellagic and sinapic acids), along with proanthocyanidins, catechin, and epicatechin, among other compounds (Côté et al., 2010a). Owing to their smaller size, the phenolic acids likely contribute heavily to the absorbance increases at this wavelength as they would be able to more easily traverse the plant tissue and diffuse into the osmotic solution as compared to the larger anthocyanins and proanthocyanidins that also absorb in this region. This increase, along with native organic acids that do not absorb in this range (e.g. quinic, citric, and malic acids), would contribute to the increasing titratable acidity and decreasing pH values over the course of the repeated runs as seen in Table 7.1.

The spectra of the osmotic solutions varied significantly from those of the cranberry juice concentrates, particularly the lack of peaks between 300-400nm. Bioactive compounds that absorb in this range include cyanidin-3-galactoside, quercitin and its glycosides, myricitin and its glycosides, caffeoglucose, and chlorogenic acid, among others (Côté et al., 2010a). Their absence indicates that during osmotic dehydration they aren't leached as easily from the berry, don't absorb as strongly, or are more susceptible to degradation during MWODS. Finally, it is also possible that the compounds responsible for the absorbance in this range are not bioactive and therefore are not described in the aforementioned literature, making their identification more difficult by this method.

The in-solution destruction of anthocyanins during MWODS is evident when comparing the Pre- and Post-treatment CJC spectra, which represent samples taken before use and after two successive center point runs with cranberries as a sample. In this case, the decrease is more distinct in the 500-550 nm region than at 280-290 nm (Figure 7.1), indicating that the loss of anthocyanins is substantial while the organic acids that contribute to the UV peak stay relatively intact. This is confirmed by the results of the relevant assays, where total monomeric anthocyanin (TMA) content drops significantly (15.88 ± 0.07 to 11.80 ± 0.05 mg cyd-3-glu/g dm) between CJC-Pre and CJC-Post solutions while the titratable acidity stays relatively constant 12.1 ± 1.09 and 12.0 ± 0.43 % citric acid. The thermal degradation of the anthocyanins during MWODS is likely promoted by the application of microwave energy, which would increase the temperature of the solution beyond the set point of 50°C while it is in the cavity. As a result, the TMA levels in the syrup likely underestimate the amount being leached as some anthocyanins would be destroyed before analysis. Overall then, while TMA concentration rise, it is not surprising that levels never approach those seen in CJC (3.98 ± 0.04 versus 15.88 ± 0.07 mg cyd-3-glu/g dm for Run 10 and CJC, respectively). Altogether, this also explains why the 500-550nm peak increases more slowly than the UV band over successive sucrose based runs (Figure 7.1), where the larger and more heat labile anthocyanins do not increase as quickly as the smaller organic acids. This is further confirmed by

Table 7.1: Physical and Compositional Changes in Osmotic Solutions over Successive Runs. *Mean values with (standard deviation) shown*

Run	Viscosity (Pa·s)	Concentration (B)	Water Activity (aw)	pH	Titratable Acidity (% CA)	DPPH (%Inhibition)	TMA (mg cyd-3-glu/mL)	PCA (CFU/mL)	SGA (CFU/mL)
0	0.03151 (0.00041)	50.0 (0)	0.951 (0.002)	7.3 (0.27)	0.01 (0.008)	8.13 (0.66)	0	140	-
1	0.02679 (0.00073)	50.0 (0.1)	0.951 (0.005)	4.3 (0.32)	0.19 (0.27)	13.48 (1.75)	0.45 (0.02)	13	1
2	0.02427 (0.00026)	50.0 (0)	0.952 (0.001)	3.9 (0.04)	1.09 (0.17)	16.62 (1.81)	0.82 (0.04)	1	5
3	0.02618 (0.00098)	49.9 (0.1)	0.950 (0)	3.7 (0.01)	2.11 (0.62)	28.10 (0.51)	1.17 (0.05)	-	3
4	0.02522 (0.00174)	50.0 (0.2)	0.952 (0.003)	3.6 (0.06)	2.75 (0.90)	30.53 (0.12)	1.59 (0.03)	-	1
5	0.02550 (0.00026)	50.0 (0.1)	0.954 (0.002)	3.6 (0.01)	2.91 (0.23)	36.16 (1.28)	2.04 (0.01)	-	1
6	0.02329 (0.00029)	50.1 (0.1)	0.955 (0.004)	3.5 (0.03)	4.30 (0.42)	41.22 (0.27)	2.53 (0.10)	-	-
7	0.02170 (0.0037)	49.9 (0.2)	0.955 (0.005)	3.4 (0)	5.18 (0.62)	44.82 (1.35)	2.83 (0.07)	1	-
8	0.02128 (0.00015)	49.8 (0.2)	0.955 (0.003)	3.4 (0.01)	7.30 (0.80)	46.73 (1.42)	3.15 (0.03)	-	-
9	0.02143 (0.00041)	49.8 (0.1)	0.956 (0.010)	3.4 (0.01)	9.60 (0.59)	53.11 (0.21)	3.36 (0.02)	1	-
10	0.02056 (0.00028)	49.7 (0.1)	0.958 (0.002)	3.4 (0.01)	9.87 (1.48)	54.31 (0.73)	3.98 (0.04)	-	-
CJC-Pre	0.02039 (0.00202)	52.3 (0)	0.948 (0)	2.4 (0.02)	12.1 (1.09)	85.42 (0.13)	15.88 (0.07)	-	-
CJC-Post	0.01729 (0.00007)	52.1 (0.1)	0.949 (0.001)	2.5 (0.02)	12.0 (0.43)	80.57 (0.90)	11.80 (0.05)	-	-

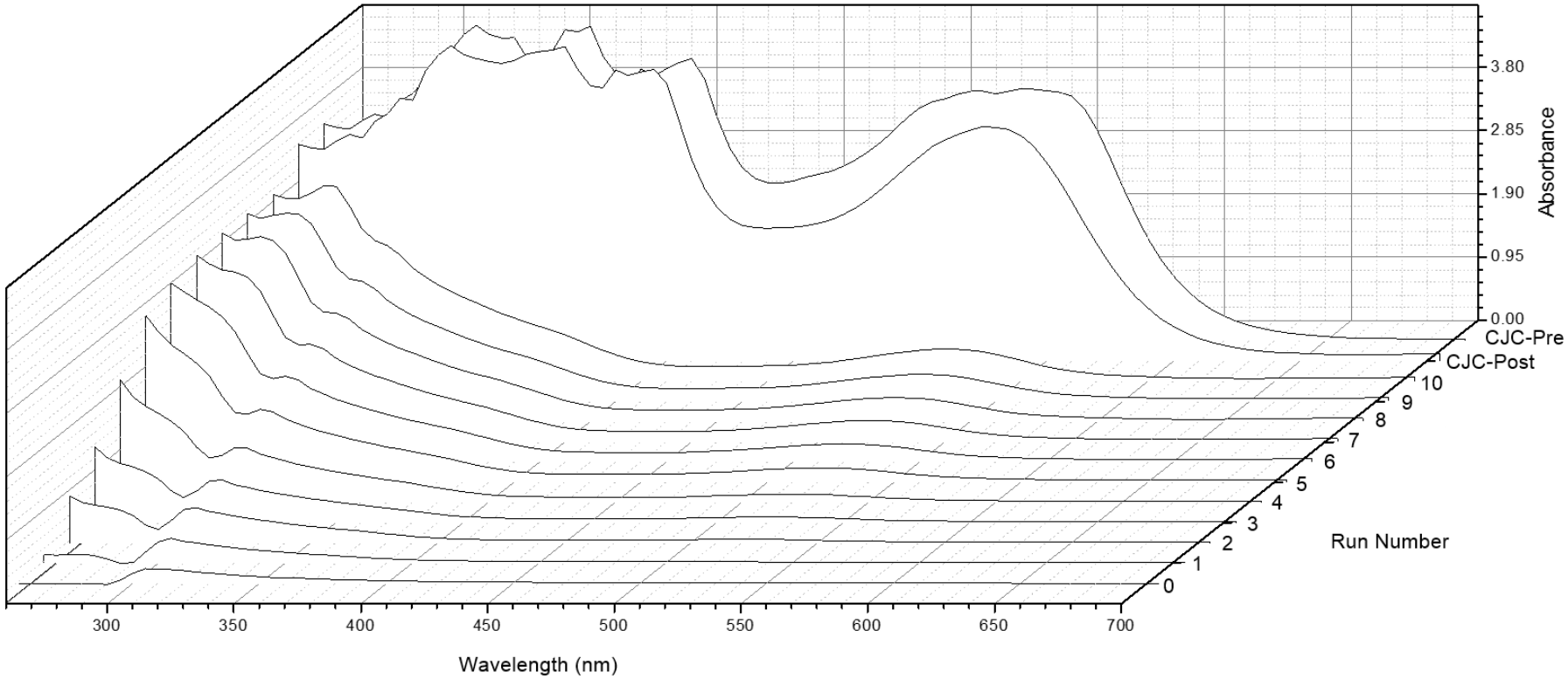

Figure 7.1: Absorbance Spectra of Recycled Osmotic Solutions and Concentrates

the titratable acidity values of 9.87 ± 1.48 and 12.1 ± 1.09 % CA for Run 10 and the pre-use CJC, respectively (Table 7.1), which indicate that the acidity levels are relatively closer as compared to the TMA content of the two solution types. This can also be noted in the colorimetric data (Table 7.2) which indicates the recycled solution becomes redder (larger *a**-value) but never reaches the intensity seen in the concentrate.

Radical scavenging activity by the DPPH method also increases with the number of repetitions. However, since the DPPH method tests the ability of test material to reduce the stable free radical 2,2-diphenyl-1-picrylhydrazyl, the increasing inhibition capability of the syrup is not only caused by the increasing concentration of antioxidants like anthocyanins or ascorbic acid, but also because of the appearance of glucose and fructose which are both reducing sugars and thus capable of reducing DPPH. This is somewhat confirmed by the decrease in DPPH scavenging activity seen after using the concentrate (CJC-Post; Table 7.1). In this case, the scavenging activity decreases by about 5% while the TMA content decreased by approximately 25%, implying the radical scavenging activity is not due to the TMA content alone, where anthocyanins had previously been described as the most powerful antioxidants in cranberries (Pappas & Schaich, 2009).

CIE *L** *a** *b** values calculated from the visible spectrum (Table 7.2) also change dramatically with successive runs. In particular, the lightness (*L**) rapidly decreases, an effect that mirrors changes in the osmotic syrup over repeated runs with andes berry and tamarrilo (Osorio et al., 2007). Moreover, redness (*a**-values) increases dramatically, even with minimal initial anthocyanin uptake (Table 7.1). Interestingly, the *b**-value decreases initially, losing the initial yellow appearance of the virgin osmotic syrup as it darkened with the inclusion of anthocyanins. Beyond Run 2, however, the *b** tended to increase again, likely due to the inclusion of flavonoids, which are the second most prevalent pigment in cranberries (Yongsawatdigul & Gunasekaran, 1996b), as well as due to some evidence of browning of the solution, which introduced a yellow-brown hue to the solution in later runs. Prior reports have also attributed higher *b**-values to acidification of the syrup, where the inclusion of acid was associated with initiating browning during re-concentration, a conclusion that was reached when the same heating cycles had no effect on syrup that had not been exposed to fruit (Bolin et al., 1983). While re-concentration wasn't employed in the current study, over the course of the repeated runs, the solution spent the long periods of time at temperatures close to the reconcentration temperature of 60°C used in the

regeneration cycle of earlier work (Bolin et al., 1983), suggesting it would promote browning during MWODS as well. The relatively lower *b** values for the cranberry juice concentrate are likely due to a much more concentrated and dark nature of the syrup, which would be achieved with minimal browning as it was not subjected to multiple runs. This is supported by the fact that the CJC was significantly darker (lower *L**) than even the Run 10 osmotic syrup, with a substantially higher *a**-value as well. This agrees with an earlier study where 20-60% mixtures of juice concentrate matched those of the spent osmotic syrup in terms of colorimetric properties (Osorio et al., 2007). Finally, the slight decrease in redness between the Pre- and Post- CJC samples demonstrates how powerful a colorant anthocyanins are, as the redness value stays virtually identical even with a 25% loss in anthocyanins (Table 7.1), although as previously mentioned this difference is visible in the spectra of these two samples with the decrease in the peak at 500-550nm (Figure 7.1).

Table 7.2: Colorimetric Data Calculated from the Transmittance Spectra of Osmotic Solutions

Run	*L**	*a**	*b**	*C**	*H°*
0	100.16	2.46	16.5	16.68	261.54
1	7.71	25.14	10.1	27.09	201.9
2	4.4	29.68	9.08	31.04	197.01
3	3.71	36.88	9.11	37.99	193.87
4	3.09	41.82	9.14	42.8	192.33
5	2.67	47.38	9.36	48.29	191.18
6	2.43	50.41	9.54	51.3	190.72
7	2.28	52.78	9.86	53.69	190.59
8	2.17	54.91	9.99	55.81	190.32
9	2.02	55.87	10.71	56.89	190.85
10	1.94	58.32	10.69	59.3	190.39
CJC-Pre	0.71	95.87	7.78	96.18	184.64
CJC-Post	0.74	94.65	6.24	94.85	183.77

7.3.3 Microbiology of the Osmotic Solutions

The microbiological makeup of the osmotic solutions plays an important role in determining the potential for recycling. In considering the total aerobic bacterial count as determined by Plate Count Agar (PCA), the initial samples (Run 0; Table 7.1) were found to have

the highest level of microorganisms (about 140 CFU/mL). These samples were collected after the solution had circulated through the setup but prior to temperature equilibration at 50°C, suggesting that the contamination was caused by the MWODS setup itself, the process or equipment employed to mix the solution, or from the sugar or water that made up osmotic solution. Regardless, after the first cycle (Run 1), the plate count had decreased to about one tenth of that amount, and further decreased over the course of the next two runs before disappearing. This indicates that the MWODS treatment could be considered a mild thermization or pasteurization process, although proper inoculation studies would be required to confirm this effect.

Moreover, colonies observed initially (Run 0) and those present after Run 1 were different in appearance. Initially, colonies were exclusively yellow in color and circular in shape with convex elevation and an entire margin, while those present after the initial run were white, circular, raised, with a filiform margin. This could indicate that either (i) both colony types were present initially, but the white colonies were outcompeted sufficiently by the yellow that they did not produce colonies or that (ii) the microorganisms responsible for the white colonies were introduced by the berries themselves. The occasional reappearance of colonies (Runs 7 and 9; Table 7.1) suggests the latter possibility. In either case, it would appear that the microorganisms responsible for the yellow colonies were more susceptible to destruction by the MWODS treatment (and possible pH), thus allowing the most thermo-, osmo-philic microbes responsible for the white colonies to prevail after subsequent runs. Overall, however, results agree with a prior report on conventional osmotic dehydration of kiwi which found that there was a negligible amount of microbial growth in recycled syrup (Garcia-Martınez et al., 2002).

A different trend was identified for yeasts and molds enumerated with Sabouraud Glucose Agar (SGA; Table 7.1). In this case there was no evidence of initial contamination, indicating that the fungi that accumulated after Run 1 and 2 were introduced by the cranberries themselves. Their subsequent disappearance over the next three runs indicates that either the successive heat treatments or decrease in pH (or some combination of the two) were lethal to the yeasts and molds introduced by the cranberries. This is in contrast to a study on reused syrup in osmotic dehydration of apples, which found that significant numbers of yeasts and molds accumulated in the solution over the course of 20 repeated cycles, which resulting in a suggestion of incorporating a filtration or pasteurization step periodically in order to extend the life of the solution (Valdez-Fragoso et al., 2002). This is despite a similar temperature (50°C) and a higher concentration (60°B) employed

as compared to those employed in this study. The different results seen in that study and those seen here are likely due to the different sample type (where cranberries are substantially more acidic than apple), the shorter process times (10 runs of 30 min each versus 20 runs of 90 min each), as well as the fact that the temperature of the solution increases beyond the set point temperature when subjected to microwave energy, which would enhance the thermal effect.

Contrary to results seen for the sucrose based solutions, neither the virgin nor used cranberry juice concentrate (CJC-Pre and CJC-Post, respectively) showed any evidence of microbial contamination. Possible reasons for this include the low pH/high acidity of the concentrates as well as the likelihood that they underwent some treatment during production. Moreover, there was no fungal growth in the Post-use CJC (Table 7.1) despite evidence that the fungi were introduced by the berries themselves, indicating that the reduced pH of the concentrate would likely be more effective at killing any microorganisms that may have been introduced.

Altogether, this data indicates that whether present initially or introduced by the samples, the MWODS process was able to effectively reduce the microbial load of the osmotic solution, thereby enhancing the potential for longer term use and stability. This was further verified by storing 20mL aliquots of the syrup for one month at 4-6°C, where none of the used syrups (Run 1-10) showed any form of spoilage, while some microbial growth was evident in the Run 0 syrup. All the same, should it be decided as necessary in the future, the MWODS setup could be allowed to run for some time with no sample in order to sanitize the system before use or during a set of runs, an effect that would be particularly relevant in an industrial setting.

7.3.4 Changes in Product Quality

Contrary to the changes seen in the osmotic syrup over the course of the 10 runs, there was less change seen in the product itself (Table 7.3). In terms of colorimetric parameters, the lightness (L^*) values of the berries tended to decrease past the initial two runs. This could be attributed to the promotion of nonenzymatic browning as a result of increasing presence of reducing sugars (Moyano & Zúñiga, 2003). Interestingly, the CJC produced samples tended to have similar lightness to the Run 1 and Run 2 samples of the sucrose solution, indicating that over repeated heating cycles, the solution is affected in such a way that darkens the product in a way that the CJC doesn't. As previously mentioned, there was a brownish hue that developed in the solution over the course of repeated runs which can be attributed to enzymatic and nonenzymatic browning.

Additionally, it was observed that the temperature of the osmotic solution was higher as the runs progressed, initially exiting at 52-53°C and eventually exiting at 55-56°C towards the end of the set of successive runs, which would further increase the rate of browning. This, by extension, also indicates a compositional change in the syrup that altered its dielectric properties and increased its rate of heating under microwave, particularly since the viscosity decreased throughout which implies faster circulation and lower residence time in the microwave cavity. For the recycled solutions the b^*-value decreased significantly after the initial two runs with the recycled syrup. At a glance, the loss of yellow color indicates that the responsible flavonoids are progressively leached into or destroyed by the recycled syrup. However, the cranberry juice concentrate produced samples in the same statistical grouping as Run 1 and 2. More likely then, is that the samples becoming darker could mask the lighter yellow color with a darker hue, as the groupings are the same as those previously identified for the L^* value.

The redness (a^*-value) stayed relatively constant throughout the sequential runs, with the exception of Run 2 and 10, which along with the CJC sample were significantly ($\alpha = 0.05$) higher than the rest of the samples. This perhaps indicates the potential for a solution that is rich in anthocyanins to promote or maintain the characteristic red color of the cranberries. This is in contrast to the TMA content, which remains relatively stable throughout the repeated runs except in the case of the CJC and Run 8. The lack of a clear trend in either of these cases likely indicates that TMA concentration in either solution type wasn't concentrated enough to have a notable effect on the cranberries, which are already rich in these compounds. Conversely, the DPPH radical scavenging activity tends to increase over the course of the repeated runs, which may have as much to do with the increased presence and uptake of reducing sugars as it does with increased uptake of phenolics or anthocyanins. This increased solids uptake should, at least in theory, have a softening effect on the dried berries. In this case, however, there was no identifiable trend or groupings that could lead to conclusions in terms of the hardness of the samples.

The slight changes in the quality of the product led to similar conclusions as prior studies on recycling osmotic solutions, where in the case of kiwifruit it was found that reusing the syrup up to 10 times had no effect on the fruit (Garcia-Martınez et al., 2002). Similarly, there was no change in color or flavor of osmotically dried apricots after as many as 5 repeated reconcentrations (Bolin et al., 1983).

Table 7.3: Changes in Drying Performance and Finished Product Quality over Successive Runs

Run	Moisture Loss (%)	Solids Gain (%)	*L**	*a**	*b**	Hardness (N)	TMA (mg cyd-3-glu/g dm)	DPPH (% Inhibition)
1	25.3 (1.1) [a]	2.10 (0.4)	34.1 (2.0) [a]	31.8 (0.1) [b]	10.5 (0.2) [a]	79.7 (4.1)	0.63 (0.02) [b]	11.82 (0.19) [c]
2	21.7 (1.5) [b]	2.00 (0.3)	31.4 (0.3) [a]	33.0 (0.1) [a,b]	11.1 (0.1) [a]	63.6 (5.5)	0.61 (0.03) [b]	11.95 (0.34) [c]
3	21.3 (1.3) [b]	1.43 (0.7)	22.9 (0.1) [b]	29.0 (0.9) [b]	2.6 (0.3) [b]	73.7 (7.4)	0.61 (0.01) [b]	12.37 (0.84) [c]
4	21.0 (1.8) [b]	2.18 (0.7)	22.4 (0.6) [b]	28.9 (0.5) [b]	1.1 (0.1) [b]	71.4 (7.5)	0.62 (0) [b]	14.46 (0.11) [b,c]
5	26.5 (1.1) [a]	1.11 (0.3)	24.1 (0.8) [b]	31.2 (0.5) [b]	2.2 (1.3) [b]	80.6 (13.6)	0.58 (0.01) [b]	15.42 (0.39) [b]
6	24.8 (0.5) [a,b]	3.13 (0.9)	25.8 (0.7) [b]	32.2 (0.2) [b]	2.7 (0.1) [b]	72.2 (8.0)	0.61 (0.01) [b]	15.15 (0.45) [b]
7	23.5 (1.1) [b]	3.15 (1.2)	25.5 (0.5) [b]	29.7 (0.1) [b]	1.7 (0.1) [b]	64.3 (8.4)	0.65 (0.01) [b]	15.83 (0.10) [b]
8	22.5 (0.7) [b]	2.86 (1.0)	26.5 (0.6) [b]	30.5 (0.1) [b]	2.7 (0.7) [b]	74.8 (10.2)	0.68 (0.01) [a]	16.70 (0.16) [b]
9	22.4 (1.3) [b]	3.24 (1.2)	21.5 (0.3) [b]	29.9 (0.4) [b]	1.7 (0.1) [b]	70.1 (6.9)	0.62 (0.02) [b]	17.94 (0.20) [a,b]
10	20.9 (0.6) [b]	3.49 (1.0)	25.4 (0.4) [b]	35.6 (0.3) [a]	1.0 (0.5) [b]	74.2 (6.5)	0.62 (0.03) [b]	19.58 (0.59) [a]
CJC	26.1 (1.6) [a]	3.05 (0.2)	31.1 (0.3) [a]	34.0 (0.5) [a]	9.4 (0.3) [a]	62.1 (5.6)	0.68 (0.04) [a]	19.02 (0.25) [a]

Mean values with (standard deviation) shown along with Tukey groupings (95% CI): means that do not share a letter (a,b,c) are significantly different; where no letters are present there were no significantly different groupings.

7.3.5 Creation of a Novel Product

Beyond the performance of the recycled solutions with regards to cranberries, the potential of using the recycled syrup to develop a novel food product through the incorporation of solutes was explored. Apples cylinders were selected as the sample because of their lack of native anthocyanins and their cut cylinder preparation allows a large surface area to be exposed to the solution. Overall, using either recycled syrup or cranberry juice concentrate had significant effects on the properties of the product and process performance (Table 7.4). In all colorimetric parameters, the three sample types were significantly different from one another, where the samples got progressively more dark, red, and blue than the virgin syrup when compared to either the solution that had been recycled ten times with cranberry (10x) or cranberry juice concentrate (CJC). Additionally, whereas there were no anthocyanins present in the apple cylinders to begin with, there was a detectable amount after treatment with the recycled solution, which was substantially higher when treated with CJC. Visually, the recycled solution produced sample (10x) appeared pink versus the starkly red CJC sample, where both samples were notably different in appearance when compared to the virgin sucrose sample. Moreover, in a simple taste test performed by the authors, both these samples tasted like cranberry, the 10x sample mildly and the CJC sample more so. The DPPH radical scavenging activity also increased, likely through reducing sugar uptake as well as uptake of bioactive compounds such as ascorbic acid, anthocyanins, and other phenolics that were present in both solution types. The presence of radical scavenging activity in the virgin sucrose produced apple cylinders can be attributed to the natural phenolics, reducing sugars, and other components such as ascorbic acid that are naturally present in apple.

In terms of drying performance, there were significantly different groupings in terms of both moisture loss and solids gain. The highest statistical grouping for moisture loss was seen in the virgin sucrose and CJC based solutions. In reality, however, this could have been due to the slightly lower concentration of the solution when it was applied to the apple cylinders as the solution was reused immediately after the 10 successive runs with cranberries. Although the decrease in moisture loss was small, in the future this could likely be avoided by adding a small amount of sucrose to the solution in order to maintain the concentration.

The virgin syrup provided the highest solids gain, likely due to its higher concentration as compared to the recycled syrup. The lowest solids gain was given by the CJC, which can be

attributed to the presence of higher molecular weight compounds in the cranberry juice such as tannins, pectin, and other polysaccharides. Larger size solutes have been found to promote moisture loss and limit solids gain as their presence increases osmotic differentials but their size limits their ability to actually traverse the cell membrane and be taken into the product (Qi et al., 1998). It is likely that this effect is more visible in the apple than the cranberry samples simply because the solids gain is much higher with lower standard deviations due to its nature as a cut sample and identical particle size.

Table 7.4: Properties of Apple Samples Subjected to MWODS using Virgin Sucrose Syrup, Recycled (10x) Syrup and Cranberry Juice Concentrate

Sample Type	Moisture Loss (%)	Solids Gain (%)	*L**	*a**	*b**	TMA (mg cyd-3-glu/g dm)	DPPH (% Inhibition)
Apple (Sucrose)	49.9 (0.5) [a]	10.3 (0.1) [a]	86.1 (0.1) [a]	2.0 (0) [c]	19.1 (0.1) [a]	0	5.18 (0.18) [c]
Apple (10x)	46.0 (0.4) [b]	8.65 (0.4) [b]	82.0 (0.6) [b]	5.3 (0.2) [b]	17.0 (0.4) [b]	0.02 (0.01) [b]	11.17 (0.10) [b]
Apple (CJC)	50.2 (0.3) [a]	5.42 (0.4) [c]	65.1 (2.0) [c]	19.1 (0.3) [a]	11.5 (0.3) [c]	0.09 (0.01) [a]	15.05 (0.13) [a]

Mean values with (standard deviation) shown along with Tukey groupings (95% CI): means that do not share a letter (a,b,c) are significantly different

7.4 Conclusions

In considering that changes in the final product quality were small and that drying performance was largely unaffected over the course of multiple uses, it can be said that the recycling of an osmotic solution has no appreciable effect on MWODS-treated whole cranberries. Moreover, the stable drying performance when the solution was recycled indicates that this process could likely be repeated several more times at least, although some method for removing the syrup from the system and holding it overnight would need to be implemented. The storage stability of the syrup appears to be good owing to the low microbial counts of the solutions and the apparent microbially destructive effect imparted by the MWODS process. Finally, despite periodic interest at least from an academic standpoint, cost implications dictate that it would likely never be realistic to employ cranberry juice concentrate directly as an osmotic solution. To that end, using recycled syrup on a different food is a viable method both to remove moisture as well as impart some novel characteristics on the product. The ability to infuse leached components into another product while maintaining process effectiveness and safety indicate that the reuse and repurposing of the syrup can contribute to the economic viability of the process. Altogether then, the MWODS process can extend the lifespan of the osmotic syrup and therefore mediate the high cost associated with making, regenerating, and properly disposing of osmotic syrups.

CHAPTER 8

GENERAL SUMMARY & CONCLUSIONS

- Microwave osmotic dehydration under continuous flow medium spray (MWODS) conditions was successfully applied to whole cranberries and was able to overcome the moisture barrier properties of the skin, thereby eliminating the need for a pre-treatment step
- MWODS process parameters were independently tested for their effects on the process and product, where it was determined:
    - Moisture loss and solids gain were increased by increasing temperature, concentration, and contact time, where contact time had the largest effect.
    - Conversely, quality indices (color, texture, anthocyanin content) tended to decrease with increasing temperature or contact time, whereas increasing concentration tended to produce a softer product but increase retention of anthocyanins and their characteristic red color
    - Flow rate had a negligible effect in all cases, but appeared to have a slight cooling influence.
- The central composite rotatable design and model produced from response surface methodology was validated and found to capably predict the outcome of an experimental trial
- For the MWV process, increasing intensity (duty cycles) tended to increase the drying rate and therefore resulted in shorter processes and lower energy consumption.
- In terms of quality (color, texture, and chemical markers), treatments that either employed the lowest 10% power level throughout or split power treatments ending at this level were found to produce samples that approached their freeze dried counterparts.
- In considering the inversely related effects of treatment intensity on energy consumption and product quality, it was determined that the 20/10% process was a valid compromise and was selected for use in further studies.
- Once combined, the MWODS-MWV process was found to rapidly produce high quality dried whole cranberries. When compared to alternate drying techniques, it was found that those produced by the novel process approached the freeze dried berries in terms of properties such as color, texture, rehydration capacity, bulk density, and cellular structure.

- The MWODS process was found to have an effect on cellular structure of the berries, which likely attributed for the higher rates of moisture loss during MWV when compared to fresh berries.
- It was determined that during sucrose based MWODS, the solution could be reused ten times without reconcentration or addition of more solute despite the dilution of the syrup. Throughout these successive runs, the solution underwent considerable compositional and physical changes. Despite this transformation, there was no significant deviation in drying performance or end product quality.
- The microbiological quality of the reused syrup remained good, where the MWODS process employed appeared to have a lethal effect on microorganisms introduced into the solution.
- Various components leached from the berries into the osmotic syrup over the course of the repeated runs, where smaller compounds like organic acids appeared to be favored over the larger anthocyanins.
- Particularly in the case of the anthocyanins, the levels present in reused osmotic syrup never approached those of commercial cranberry juice concentrate. However, both the used syrup and concentrate were able to infuse apple samples with anthocyanins, indicating the potential for use spent osmotic syrup as a means to create a novel food product.

SUGGESTIONS FOR FUTURE RESEARCH

While this work has advanced the state of knowledge in this area, there remain several interesting topics of study, including:

1. Further expanding the use of MWODS in terms of both sample and product type, including:
    a. The extension to vegetable based products
    b. The use of more complex solutions including the effects of including solutes of different sizes in ternary or higher order solutions
2. Model the temperature of the product and investigate the use of temperature feedback control in both the MWODS and MWV process in order to better maintain uniform product temperatures throughout the process
3. As a related work, continue the development of the MWODS and MWV process themselves by incorporating a means to stir the samples or microwave radiation and/or control magnetron power output as methods to better control product quality and energy consumption
4. Further investigate the potential of spent osmotic syrups for their potential use as sweeteners or derivatization into a value-added product, which both present a viable pathway to give value to a waste product. Moreover, the study of compositional and performance changes and smaller solution-to-sample ratios would provide information more relevant to scale up
5. Scaling up the process, with particular attention being paid to creating a continuous or semi-continuous process and the energy implications of microwave-osmotic treatments.

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