AN ABSTRACT OF THE THESIS OF

Tomomi Fujimaru for the degree of Master of Science in Food Science and Technology presented on September 17, 2010.

Title: Experimental Investigation of Carbon Dioxide (CO_2) Laser Perforation as a Potential Skin Pretreatment for Sugar Infusion Process of Frozen Blueberries.

Abstract approved:

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Michael T. Morrissey

The purpose of this research was to examine the feasibility of carbon dioxide (CO_2) laser perforation and its potential utilization as a novel skin pretreatment for the sugar infusion process of IQF (individually quick frozen) blueberries. In the first study, IQF blueberries were treated with varying degrees of laser perforation (i.e., 3 levels of perforation density x 3 levels of perforation depth = 9 treatment combinations) and then subjected to stepwise sugar infusion using low solution concentration increments (5 °Brix/day) to a final °Brix of 70 with a high fructose corn syrup (HFCS) solution. The effects of the perforation density: depth combinations were evaluated against a traditional mechanical treatment in terms of fruit weight change and final product characteristics. A clear, systematic tendency of increasing final fruit weight was observed as the two perforation parameters were increased. The increase in the two parameters also contributed to producing infused blueberries that were maintaining the original shape and appearance with reduced product shrinkage and texture hardening as a result of enhanced solute impregnation. Due to the invasive nature of the treatment, blueberries that were subjected to the

mechanical treatment showed considerable rupture at the end of the infusion process. The second study was carried out under a sugar infusion condition using higher solution concentration increments (10, 20 and 30 °Brix/day). Due to the increased osmotic gradient, the time required for the fruit to reach the target soluble solid content (70 ± 0.5 °Brix) was markedly shortened. A systematic increase in the final fruit weight with increasing perforation density and depth was again observed. However, only the fruit that was subjected to the greatest laser perforation exhibited promoted solute gain, thereby attaining a moderate final process yield with reduced product shrinkage. Overall, the results of the two studies demonstrate the ability of CO_2 laser perforation as a non-contact, minimally invasive skin pretreatment for the sugar infusion of frozen blueberries that significantly enhances solute impregnation, leading to improved process yield, process efficiency, and final product quality.

Experimental Investigation of Carbon Dioxide (CO_2) Laser Perforation as a Potential Skin Pretreatment for Sugar Infusion Process of Frozen Blueberries

By

Tomomi Fujimaru

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I understand that my thesis will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my thesis to any reader upon request.

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Tomomi Fujimaru, Author

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CONTRIBUTION OF AUTHORS

Dr. Qingyue Ling of OSU Food Innovation Center (Portland, OR) was involved in designing the experiments and editing the text presented in Chapter 3 and 4.

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

LIST OF FIGURES

LIST OF FIGURES (Continued)

LIST OF TABLES

LIST OF APPENDIX TABLES

DEDICATION

I dedicate this thesis to those who have guided me, always had faith in me, and had helped mold me into who I am today.

EXPERIMENTAL INVESTIGATION OF CARBON DIOXIDE (CO_2) LASER PERFORATION AS A POTENTIAL SKIN PRETREATMENT FOR SUGAR INFUSION PROCESS OF FROZEN BLUEBERRIES

CHAPTER 1

INTRODUCTION

Native to North America, blueberries (family: Ericaceae, genus: *Vaccinium*) have become one of the most important crops in the United States due to their high economic and nutritional values. Because blueberries have a short harvest season and are highly perishable, a large portion of cultivated blueberries is subjected to freezing, drying, and other processes to ensure year-round availability (Kim and Toledo 1987). Recently, a wide range of processed blueberry products has emerged in order to meet the ever-increasing demands of consumers and food processors.

Based on the immersion of high-moisture materials in a highly concentrated solution that gives rise to the simultaneous countercurrent flow of water and soluble solids (Raoult-Wack 1994), osmotic treatment has been widely utilized to produce minimally processed blueberry products with reduced water content. There are two main types of osmotic treatment: osmotic dehydration (OD) and infusion. The two differ fundamentally in terms of process objectives and final product properties. OD has been primarily described as a dewatering technique with a minimal or controlled amount of solid uptake from the solution, whereas infusion is a solute impregnation process with the objective of maximizing the amount of solute incorporated into the material, hence maximizing the final process yield of the product (Kuntz 1995). Because osmotic treatment can be carried out at moderate temperatures with no phase change involved, it has gained increasing attention as an energy-efficient means of removing moisture from food materials with minimized nutritive and sensory deterioration compared to conventionally dried products (Ponting 1973; Bolin and others 1983; Raoult-Wack 1994; Marani and others 2007).

The waxy outer skin structure of blueberries, originally intended to provide a barrier against transpiration, weather inclemencies, and attacks from insects and parasites, serves as a major obstacle to moisture removal and solute migration during osmotic treatment (Grabowski and Marcotte 2002). This has been traditionally overcome by various physical, thermal and chemical pretreatment techniques; however, these methods may not be ideal in the current food market, where consumers and food processors both seek minimally processed foods with minimal or no use of additives. Furthermore, a typical physical pretreatment involves cutting, halving or abrasion of the fruit (Sunjka and Raghavan 2004; Grabowski and others 2007), which alters the fruit's original shape and structure. Using traditional knives and other tools can also pose a potential source of physical and microbiological contamination, which is to be strictly avoided in the food industry.

Lasers (acronym for *l*ight *a*mplification by the *s*timulated *e*mission of *r*adiation) are non-contact processing tools that produce single-wavelength light that is highly coherent and directional (Cantatore and Kriegal 2004; Ferraz and others 2007). The light beams produced by lasers can be focused into extremely small, energy-intensive spots, which induce site-specific material modification with minimal thermal damage to adjacent areas upon absorption (Cantatore and Kriegal 2004). Laser technology has become essential for materials processing and medical applications due to its process quality, speed, reliability, and ease of integration into existing systems (Ferraz and others 2007; Chen and others 2009b). In the food industry, however, little attention has been paid to fully adopting the technology; its current application is virtually limited to the labeling and etching of product information on the surface of food materials. Although laser processing would undoubtedly have some significant advantages over conventional processing techniques, no other innovative applications have appeared in the food industry.

The general aim of this research project was to examine the feasibility and potential use of laser technology as a novel food processing tool. Specifically, the use of laser perforation as a potential skin treatment prior to the sugar infusion of

blueberries was explored. It was hypothesized that laser-induced microholes in blueberries would serve as open passages for efficient solute incorporation into the fruit while alleviating the osmotic pressure experienced by the fruit during the sugar infusion process, thereby promoting higher process yield and better final product quality. IQF (individually quick frozen) blueberries were chosen as the starting material over their fresh counterparts due mainly to their availability in large quantities irrespective of the harvest season. Among the various types of lasers that are commercially available, a carbon dioxide (CO_2) laser was used in this research. This was because a CO_2 laser is considered to be best suited for processing organic materials that are composed largely of water, as its laser beams are heavily absorbed by water at its operation wavelength (i.e., 10.6 μm).

In this thesis, a literature review on blueberries, the osmotic treatment of food, and laser technology will be presented in Chapter 2. The first study, outlined in Chapter 3, examined the extent of weight gain and final product quality of blueberries that were subjected to laser perforation followed by stepwise sugar infusion with a high fructose corn syrup (HFCS) solution at low concentration increments (5 °Brix/day). To span a wide range of laser perforation conditions, combinations of three different levels of perforation density and depth (3 x 3 = 9 treatment combinations) were tested. To establish a baseline for comparison, mechanical treatment (i.e., typical skin pretreatment in the industry) was included in the first experiment. The second experiment (Chapter 4) was carried out to examine whether laser perforation could be an effective tool under stepwise sugar infusion using higher concentration increments (10, 20, and 30 °Brix/day), which creates conditions more favorable for water removal than solute impregnation due to the increased osmotic gradient. This research project was funded by the U.S. Department of Agriculture (USDA) multi-commodity grant and the Agricultural Research Foundation (ARF). Both experiments were conducted at the Oregon State University Food Innovation Center Agricultural Experiment Station in Portland, Oregon.

CHAPTER 2

LITERATURE REVIEW

2.1. BACKGROUND INFORMATION ON BLUEBERRIES

2.1.1. Blueberry varieties, production and harvesting

Blueberries are perennial flowering plants with dark blue fruit that belong to the genus *Vaccinium*, a group of shrubs or dwarf shrubs in the plant family Ericaceae (Girard and Sinha 2006). The genus *Vaccinium* includes approximately 400 species of blueberries (Strik 2007) and numerous other shrub plants that produce edible fruits such as cranberries, crowberries, bilberries, cowberries and huckleberries (U.S. Highbush Blueberry Council 2002). Among *Vaccinium* plants, blueberries are one of the very few species native to North America, which has long dominated in commercial blueberry production (U.S. Highbush Blueberry Council 2002). In 2003, nearly 85 % of the world's blueberry production was grown in the United States and Canada (Girard and Sinha 2006). Michigan is currently the leading blueberry-producing state in the United States, followed by Maine, New Jersey, Oregon, Georgia, and Washington (Pollack and Perez 2008). Maine is also known as the largest producer of wild blueberries (Girard and Sinha 2006).

The market for fresh blueberries has shown a strong growth in North America and other parts of the world over the past few decades, due mostly to increasing consumer awareness and research interests in the health benefits of blueberries (U.S. Highbush Blueberry Council 2002). In North America, the increase in blueberry production has become significant since 2000, as the total utilized yield of U.S.-cultivated blueberries exceeded 488 million pounds, with per capita consumption of fresh blueberries reaching 0.77 pounds in 2008 (Pollack and Perez 2008). The world acreage of cultivated blueberries has shown a steady increase as well, expanding by 90 % between 1995 and 2005 (Strik 2007). Outside of North America, Poland is the largest blueberry producer, accounting for about 7 % of the world's production in 2003 (Girard and Sinha 2006). Also noteworthy is the increasing interest in blueberry

consumption in Asian countries such as Japan and China in recent years. These countries have been an important blueberry export market for the United States, and the acreage in those regions is expected to steadily increase in the future (U.S. Highbush Blueberry Council 2002).

In the United States, four types of blueberries are commercially grown: northern highbush, southern highbush, rabbiteye, and lowbush (Strik and Finn 2008). Each is unique in its berry and yield characteristics, suitable climates, and commercial values. Northern highbush blueberries (*Vaccinium corymbosum*) grow well in the northern parts of the world due to their high tolerance to severe winter conditions (Strik 2007; Saftner and others 2008). Northern highbush are the most commonly harvested blueberries worldwide and in Oregon (Strik and Finn 2008), and comprise approximately 95 % of the cultivated blueberries in the United States (Girard and Sinha 2006). Although similar in harvesting characteristics, southern highbush varieties have a lower tolerance to chill than their northern counterparts as they were developed to thrive in warmer climates (Girard and Sinha 2006; Strik and Finn 2008). Rabbiteye blueberries (*V. virgatum*, syn. *V. ashei*) are less tolerant to winter cold, are smaller in size, darker in color, and have thicker skins compared to highbush blueberries (Silva and others 2005; Strik and Finn 2008). Despite their harder texture, rabbiteye varieties can be sold for a higher price due to their late fruiting and harvesting seasons (Strik 2007). Lowbush blueberries (*V. angustifolium*), often marketed as “wild blueberries” or “huckleberries”, are produced worldwide for commercial and personal use. Lowbush varieties are smaller in shrub and berry size than highbush or rabbiteye (Girard and Sinha 2006; Strik 2007).

In general, blueberries are self-fertile plants that begin fruit production in their third season. However, cross-pollination is often practiced in commercial settings to ensure good berry size and yield (Strik and Finn 2008). Well-drained soils that are rich in organic matter with a pH between 4.2 to 5.5 are essential in order for blueberry plants to thrive (Girard and Sinha 2006; Strik 2007). Blueberries are susceptible to drought injury due to their shallow roots, which can adversely affect their fruit size

and flavor. Adequate water supply and moisture maintenance are therefore imperative to support the plant's optimal growth (Strik 2007). A typical bush height at maturity varies depending on the species, ranging from 1 foot (lowbush), to 6 to 8 feet (highbush), to 12 feet (rabbiteye) (Strik 2007). In Oregon, the fruiting season of blueberries runs from mid-June through late-September, depending on the cultivars (Strik and Finn 2008). The length of fruit development also differs considerably among the species, typically ranging from 42 to 90 days for northern highbush, 55 to 60 days for southern highbush, 70 to 90 days for lowbush and 60 to 135 days for rabbiteye. The harvesting parameters also vary depending largely on climate, plant vigor, and cultural management practices (Strik 2007).

In North America, the majority of blueberries has long been hand-harvested. In recent years, however, mechanical harvesting has gradually been adopted for the fresh market to minimize labor costs (Strik 2007). One of the drawbacks of mechanical harvesting includes a shorter shelf life of the fruit, which results in limited marketability of the berries (i.e., they cannot be transported to distant markets) (Silva and others 2005). In addition, the quality of machine-harvested berries tends to be inconsistent as a mechanical harvester is not selective for immature, decayed, and/or blemished berries that are unsuitable for consumption (Talcott 2007). To overcome these limitations, new cultivars that yield firmer blueberries with better keeping quality are continuously being developed for mechanical harvesting (Silva and others 2005).

After harvesting, blueberries that are destined for the fresh market are cleaned, sorted for color, defects and damages, and packed for transportation. Blueberries are then transported by refrigerated trucks, airplanes and ships to distant markets (Strik 2007). In the United States, approximately 40 % of cultivated blueberries are consumed fresh and the rest is processed into various products (Girard and Sinha 2006). Details on processed blueberry products are provided later in this chapter.

2.1.2. Physicochemical and nutritional quality of blueberries

As shown in Table 2.1, raw blueberries are a good source of vitamins A and C, minerals, fibers, natural sugars, and are very low in fat and sodium. Organoleptically, blueberries are often characterized as being mildly sweet with a low level of aromatic note and less tartness compared to other berry fruits (Sinha 2007). Ethyl acetate, esters, and 3-isopropyl-butyrate are the compounds that are primarily responsible for the fruity and floral notes of blueberries. Typical total soluble solid (TSS) content and titratable acidity (TA) of highbush blueberries are about 12.0 % and 0.80 % (as citric acid) respectively. However, those harvested in the Pacific Northwest tend to have higher TSS and TA as high as 17.5 % and 1 % (as citric acid), respectively (Girard and Sinha 2006). In contrast, wild (i.e., lowbush) blueberries generally have lower TSS and TA compared to highbush blueberries (Sinha 2007).

Blueberries are known to be rich in various phytochemicals such as anthocyanins, phenolics, tannins, and other bioactive compounds that are beneficial to human health. There has recently been a surge in public and scientific interests regarding the blueberry's high antioxidant capacity due to the presence of these compounds (Lee and others 2002). The rich, eye-appealing dark blue color of blueberries is due to anthocyanin pigments that are concentrated in the skin. The major anthocyanins found in highbush blueberries include malvidins, petunidins, delphinidins, and cyanidins (Girard and Sinha 2006). The color of blueberries is affected by the total anthocyanin content and the surface wax structure, as well as their content (Silva and others 2005). Anthocyanins degrade easily when heated, but they remain fairly stable during frozen storage (Nsonzi and Ramaswamy 1998b). Blueberries and other fruits such as cranberries, grapes and cherry tomatoes are often collectively called "waxy-skinned fruits", due to their unique waxy outer skin structure, which provides protection against various environmental factors such as inclement weather, moisture loss and attacks by parasites and/or insects (Azoubel and Murr 2002; St. George and others 2004).

In the United States, the marketing quality of fresh blueberries is determined by numerous physical attributes such as color, size, shape, and the presence of defects (i.e., mold, decay, scars, broken skin, and shriveling) as specified by the U.S. Department of Agriculture (USDA 1995). Firmness is another physical attribute critical to the marketability of fresh blueberries, as it directly correlates with the fruit's keeping quality and resistance to shipment, the two important fruit qualities for expanding domestic and international markets (Silva and others 2005; Yang and others 2009). The firmness of blueberries varies considerably depending on the species or cultivars; for example, rabbiteye blueberries are firmer than highbush blueberries. The difference in firmness has been attributed to the higher degree of solubilization of pectic compounds that occurs in highbush blueberries, which contributes to softening (Silva and others 2005). Firmness is also affected by cultural management practices such as fertilization, irrigation, and the use of plant hormones and growth regulators (Yang and others 2009). Much effort is being made to improve the firmness of blueberries through breeding (Ehlenfeldt and Martin 2002).

2.1.3. Value-added blueberry products

Blueberries are a highly perishable commodity with a brief harvest season; fresh blueberries typically cannot be kept for more than six weeks (Yang and Atallah 1985; Kim and Toledo 1987; Yang and others 1987). In addition, fresh blueberries tend to succumb to decaying organisms such as molds and fungi, thereby leading to diminished marketability. The vast majority of cultivated blueberries is therefore commercially processed into a variety of products to ensure the year-round availability of good quality fruit. Furthermore, due to growing consumer interests in their health benefits, blueberries are being increasingly incorporated into a number of food products as a healthy ingredient. The following section provides a brief overview of several value-added blueberry products.

IQF blueberries

A large portion of cultivated blueberries is subjected to an individually quick frozen (IQF) process. The process typically involves subjecting sorted, washed, and shake-dried fresh blueberries to a high-velocity cold air blast of - 40 °C in a tunnel freezer for about 12 - 15 minutes until the berries become frozen solid (Abdalla 1966). IQF blueberries are then visually inspected and graded based on the standards for frozen blueberries specified by the U.S. Department of Agriculture (USDA 1995). The IQF process ensures the free flowing characteristic of the product and prevents the agglomeration of berries so that they can easily be used and incorporated into other food products (Abdalla 1966). The fast formation of intercellular ice with small ice crystals upon quick freezing also ensures minimized cell damage and osmotic water loss (Saurel and others 1994).

Although the introduction of IQF technology has enabled the year-round availability of frozen blueberries with a color and shape comparable to fresh blueberries (Abdalla 1966), the storage of frozen blueberries should be limited to six months or less, beyond which freezing-induced textural and other physiochemical changes can become problematic (Sullivan and others 1982). Prolonged freezing causes the loss of original shape and structure, and a pronounced woodiness or grittiness in texture (Sullivan and others 1982; Silva and others 2005). Water serves as a medium for the diffusion of fruit constituents, which can cause further physiochemical deterioration such as off-flavor development and color change (Torreggiani and Bertolo 2001).

Infused blueberry products

Available both in frozen and dehydrated forms, infused blueberry products have become increasingly popular in recent years. They are typically infused with sweeteners or fruit juices to 25 - 45 °Brix. The infused blueberries are then subjected to heat processing and freezing (infused-stabilized frozen blueberries), or to further dehydration, typically to a moisture content of 10 - 15 % and a water activity of 0.40 - 0.60 (infused-dried blueberries) for safety and shelf stability (Girard and Sinha 2006).

Infused-stabilized frozen blueberries remain soft even when frozen, possess excellent keeping qualities against microbial deterioration, and can therefore be used in various products without further processing. Fresh-like characteristics and enhanced sweetness of infused-dried blueberries make them an appealing ingredient or on-the-go snack (Girard and Sinha 2006; Sinha 2007). Sugar infusion is also beneficial from a product formulation viewpoint, as the increased sugar content helps prevent the infused fruit from floating when added to other products (Taiwo and others 2003).

Dried blueberries

Dehydrated blueberries containing 16 - 25% water are often referred to as an intermediate moisture (IM) product. IM products are popular as a convenient snack or ingredient due to their concentrated nutritional content compared to their fresh counterparts, their ready-to-eat texture, and good rehydration performance (Yang and Atallah 1985). Despite a higher cost of processing compared to other drying methods, freeze-dried blueberries have been increasingly used in ready-to-eat cereals in recent years. They are characterized as having a light, crispy texture, and low bulk density and water activity (slightly above 0.20). Freeze-dried blueberries also show minimal shrinking and shriveling of the fruit (Sinha 2007).

Other blueberry products

Blueberries that do not meet quality standards or specifications for premium value-added products described above are transformed into traditional products such as jams, preserves, fruit purees, syrups and juice concentrates (Girard and Sinha 2006; Sinha 2007).

2.2. OSMOTIC TREATMENT OF FOODS

2.2.1. Mechanisms and characteristics of osmotic treatment

Drying is one of the most ancient food processing methods and is still being practiced worldwide as a means of improving shelf life of foods, preserving quality, preventing

moisture-mediated deteriorative reactions, and easing handling, transportation and storage of products (Jayaraman and Das Gupta 1992; St. George and Cenkowski 2008). Drying can take various forms in terms of the energy source employed (i.e., natural and/or artificial energy) and the mode of energy transfer into the material to be dried (i.e., conduction, convection, internal generation, surface radiation, or a combination of several modes) (Grabowski and others 2003).

Among various drying technologies available, osmotic treatment is an example of minimal dehydration for foods (Grabowski and others 2003). Osmosis, the basis of osmotic treatment, is a physical phenomenon driven by a difference in solute concentration of two areas separated by a semi-permeable membrane, causing a movement of water from a low-solute concentration area to a high-solute concentration area through the membrane. When a water-containing cellular tissue is immersed in a hypertonic solution of low molecular substances (e.g., salts, sugars), the concentration difference between the food material and the solution gives rise to two simultaneous counter-flows: 1) the outflow of water from the material into the solution, and 2) the migration of solutes from the solution into the material (Raoult-Wack 1994; Ferrando and Spiess 2001; Shi and Le Maguer 2003). Because of the non-selective nature of the cell membrane, the product's own soluble constituents (i.e., minerals, sugars, organic acids) also migrate out of the product along with the outward flow of water. Although this flow may be quantitatively insignificant compared to the two main types of mass transfer, it may be of great importance to the nutritive value and sensory properties of the final product (Figure 2.1) (Raoult-Wack 1994; Azoubel and Murr 2002; Sunjka and Raghavan 2004). The mass transfer continues until osmotic equilibrium is achieved. It is suggested that the removal of water occurs mainly via diffusion and capillary flow whereas solute uptake by the product and leaching of the product's soluble components are by diffusion only (Shi and others 2009).

During osmotic treatment, a food material typically exhibits a two-phased behavior in terms of water and solute transfer. The dewatering of the material is

known to occur at a rapid rate during the first several hours. The rate of water loss then gradually decreases in subsequent hours (~ 6 hours) and eventually flattens out. On the other hand, the impregnation of solute into the material is negligible at the beginning of osmotic treatment, but the rate of solute gain by the material steadily increases as the dewatering progressively becomes slower (Raoult-Wack 1994).

Early work on the osmotic treatment of foods was reported by Ponting and others (1966), who described the process as a gentle, non-thermal means of dehydration to produce high quality dehydrated fruit while reducing the original weight of the fruit as much as 50 % and preserving color and flavor. Since the publication of their pioneering work, osmotic treatment has attracted considerable research and commercial interests as a practical processing method for fruits and vegetables. Although to a lesser extent, osmotic treatment has also been applied to products of animal origin such as meat and fish. It should be stressed, however, that the osmotic behaviors of animal and plant materials are uniquely different due to the distinctive structures and compositions of the two. This review is therefore based solely on those addressing osmotic treatment of fruits and vegetables. Collignan and others (2001) provide an in-depth literature review on osmotic treatment of fish and meat products.

Osmotic treatment offers several advantages over conventional methods; some benefits include its relative mechanical simplicity, flexible nature of the process, and its low energy requirements because water can be removed without any phase change. In addition, because it is typically conducted at ambient or slightly elevated temperatures, the thermal degradation of color, texture, and nutritive values of the raw material is minimal. Since the material is kept immersed during the process, oxidative reactions and loss of volatile compounds can also be minimized (Raoult-Wack 1994; Marani and others 2007).

2.2.2. Osmotic dehydration vs. infusion

There are two primary categories of osmotic treatment of foods: osmotic dehydration (OD) and infusion. Although the two terms are often used interchangeably (Shi and others 2009) and distinguished ambiguously (Kuntz 1995) in scientific literature, the application and end-product characteristics of the two are fundamentally different. The primary objective of OD is to achieve maximum water removal from the product while limiting or controlling solute uptake from the surrounding osmotic solution. On the other hand, infusion aims at maximizing the migration of external solutes into the food with moderate water removal, thereby maximizing final product yield (Raoult-Wack 1994; Kuntz 1995; Zhao and Xie 2004). The infusion process may also be referred to as "candying", due to the high degree of solute impregnation (Raoult-Wack 1994). Another difference lies in the duration of the process; OD is typically completed within a day, whereas the completion of infusion or candying can take up to several weeks (Zhao and Xie 2004). This is because water removal rapidly takes place at the beginning of the osmotic process and progressively slows, while the rate of solute gain gradually increases. Thus, prolonged immersion tends to yield product with further solute impregnation (Raoult-Wack 1994). The literature review revealed that the vast majority of research efforts have been directed towards OD, and little research has been conducted to explore ways to improve solute gain and infusion efficiency. In fact, methods to prepare good quality infused or candied fruits are often protected by patents (e.g., Mochizuki and others 1971; Kahn and Eapen 1982; Tucker 1997). This is presumably because infusion is a profitable process in which fruits can be impregnated with inexpensive solutes (e.g., sugars) to achieve a considerable increase in product weight and yield (MacGregor 2005).

In contrast, the literature provides a vast amount of information on OD. It is generally acknowledged that OD alone does not offer a dewatering effect sufficient to achieve microbiological stability (Azoubel and Murr 2002). Subsequent drying procedures are therefore necessary when the ultimate objective is to produce a shelf-stable product. A number of investigations have reported OD coupled with conventional and newly emerging dehydration techniques such as air drying,

microwave or convective drying, freeze-drying, microwave-sprouted-bed drying, pulsed-fluidized-bed drying, and infrared radiation heating (Hawkes and Flink 1978; Kim and Toledo 1987; Grabowski and others 2007; Shi and others 2008a). In these reports, using OD as a prestep to subsequent drying was found useful in lowering drying time and energy consumption while enhancing the physical and sensory characteristics of the final product. In addition, Marani and others (2007) recently reported that OD could also be an effective dewatering step to substantially lower the energy required for freezing fruits. By taking advantage of the solute uptake by the material that inevitably occurs during OD, beneficial compounds and additives can be incorporated in order to improve or modify the original nutritional, functional and organoleptic properties of the raw material (Raoult-Wack 1994; Torreggiani and Bertolo 2001). This particular aspect of OD has gained special research attention, and the term “dewatering impregnation soaking” (DIS) has been coined to better describe the nature of the process (Raoult-Wack 1994; Torreggiani and Bertolo 2001).

A considerable amount of research has also been dedicated to investigating the kinetics of dewatering and solid gain, and developing mathematical models in order to characterize and predict osmotic behavior of foodstuff. Such models have been proposed for carrots (Sohdi and Komal 2006), cherry tomatoes (Azoubel and Murr 2004), pineapple rings (Beristain and others 1990), green peas (Kaymak Ertekin and Cakaloz 1996a), and blueberries (Nsonzi and Ramaswamy 1998a). These proposed models are useful in predicting mass transfer phenomena and the influence of various intrinsic and extrinsic factors of the process. However, their applications are limited to materials for which the model was originally developed due to the complexity and diversity of plant materials, and different structural responses of the materials to the osmotic stress (Chiralt and Talens 2005). In addition, despite its mechanical simplicity osmotic treatment is rather complex in its nature with many variables involved, making it simply impossible to develop a model that takes all of the factors into account (İspir and Toğrul 2009). No general theory or equation would therefore be valid without actual experimentation with a particular material.

2.2.3. Effects of process parameters on osmotic mass transfer

The rate and quantity of the simultaneous water and solute diffusions during osmotic treatment and the quality of the final product are largely influenced by numerous process conditions. Some of such conditions that have been well documented in the literature include: types, temperatures and concentrations of osmotic solutions; physical properties and geometry of the material to be treated; mass ratio of osmotic solution to the material; process duration, and the use of solution agitation during the process (Raoult-Wack 1994; Nzonzi and Ramaswamy 1998a; Rastogi and others 2002). The following section provides a literature review on the effects of these factors on osmotic mass transfer and the final quality of osmotically processed products.

Types of osmotic solutions

The type of solutions employed for osmotic treatment of food is of prime importance; not only does it provide an osmotic driving force for the simultaneous counter-flows of water and solute, but it also determines the rate and extent of water removal and solute uptake, as well as the physical and sensory attributes of the final products. Careful selection of osmotic solution is therefore imperative to achieve the required rate for the process and the properties desired for the end products. The stability of solutes in coexistence with other components in food is another important selection criterion (Pan and others 2003). The cost of osmotic solution may also affect the selection, especially in commercial settings.

Although virtually any solute that is miscible with water can be employed, compounds that are commonly used as active osmotic agents include various sugars and sodium chloride (NaCl) (Raoult-Wack 1994). Sugars are mainly used for the osmotic treatment of fruits, and NaCl has been reported as an excellent osmotic agent for vegetables (Contreras and Smyrl 1981; Azoubel and Murr 2004). However, the use of NaCl may not be desirable in some applications because of the salty taste imparted to the product (Lerici and others 1985; Azoubel and Murr 2004). Sugars have been

reported as superior osmotic agents that provide added benefits: they are effective inhibitors of polyphenoxidase, the enzyme that causes oxidative browning in many fruits and vegetables (Ponting 1973). Sugars also exhibit a protective effect against the loss of volatile compounds, which helps to retain the sensory characteristics of the original material (Ponting 1973). The impregnation of materials with sugars further contributes to the pigment stability and better retention of volatile compounds during subsequent drying of osmotically treated products (Ferrando and Spiess 2001).

A combination of different solutes may be used to improve the process and the properties of the final products. The addition of NaCl to sugar solutions in small quantities has been reported to enhance the osmotic driving force due to its low molecular weight and high capability of lowering water activity, which consequently facilitates water loss (Lerici and others 1985; Taiwo and others 2003; Azoubel and Murr 2004). Kaymak Ertekin and Cakaloz (1996a; 1996b) reported that the osmotic treatment of green peas with a sucrose/trisodium citrate solution followed by air drying (65 °C, 10 % RH) enhanced the drying rate and rehydration property of the final product. The authors concluded that the addition of trisodium citrate effectively enhanced the water diffusion. The sucrose/trisodium citrate-treated samples retained a greener color with a slightly more acceptable texture and flavor compared to non-treated samples and those treated with sucrose only (Kaymak Ertekins and Cakaloz 1996b).

The molecular weight of solutes is another factor that governs the rate and characteristics of mass transport: smaller molecular weight solutes (e.g., monosaccharides) penetrate food more readily than larger molecular weight solutes. The use of smaller molecular weight solutes is therefore preferable for the infusion process, during which the void space created by the removed water needs to be filled by the solutes in order to increase the final product yield. On the other hand, higher molecular weight solutes should be selected for OD to ensure high rates of water removal with little solute uptake (Saurel and others 1994; Kuntz 1995). Although solute uptake is generally not a preferred phenomenon for OD, it may be beneficial for

food materials that possess undesirable flavor and taste characteristics when consumed fresh. For example, sugar uptake during OD of cranberries can effectively alter the acidic taste of the fruit (Grabowski and others 2007).

Among different types of sugars, sucrose appears to be the most preferred osmotic agent for OD of fruits. Marani and others (2007) recommended the use of sucrose for OD of kiwifruit cut in disks, which allowed a high degree of water removal with a minimum penetration of solutes. In a study on the sugar infusion of blueberries, Shi and others (2009) found sucrose particularly useful as it increased the final fruit yield, flavor, and textural properties of the infused product. On the other hand, Sunjka and Raghavan (2004) recommend high fructose corn syrup (HFCS) over sucrose for OD of cranberries as it produced higher water loss and solid gain compared to sucrose. In addition to the molecular size difference, the authors suggested that the viscous nature of HFCS could have allowed higher mobility and easier penetration of the solute into the fruit compared to the solution of sucrose solid crystals.

The nature of solute employed for osmotic treatment also greatly affects the osmotic response of the cellular structure. Ferrando and Spiess (2001), in their investigation on the effect of three disaccharide solutions (i.e., sucrose, maltose and trehalose) on cellular shrinkage during OD, observed distinct cell shrinkage profiles between onion epidermis and strawberries. For onion epidermis, the sucrose solution contributed to the highest degree of product shrinkage compared to the other two sugars, while the behavior of strawberry tissues in response to the three disaccharides were not significantly different. This implies that the behavior of a given osmotic agent may depend largely on the nature of the raw material to be treated, and suggests the importance of taking the cell morphology of food materials into consideration when selecting an osmotic agent for the process.

Temperatures and concentrations of osmotic solution

Increasing the temperature at which osmotic treatment takes place markedly increases the rate of water loss and solid gain (Ponting and others 1966; Saurel and others 1994; İspir and Toğrul 2009). A temperature around 50 °C has frequently been used in the literature for the osmotic treatment of fruits and vegetables due to the following reasons: 1) this moderate temperature limits the deterioration of flavor, texture, and thermosensible compounds of the materials, 2) enzymatic browning and flavor deterioration of fruits begin to take place at temperature above 120 °F (49 °C) (Ponting and others 1966), and 3) this temperature is also effective in maintaining adequate viscosity of the solution and sufficient infusion time without compromising the fruit quality. Shi and others (2009) also reported that an undesirable appearance and cooked note of infused blueberries became noticeable at temperatures higher than 50 ºC.

The literature provides somewhat contradictory information about the effects of temperature on solute gain. Rahman and Lamb (1990) reported that temperatures over 50 ºC may not have a favorable effect on solute gain during OD of pineapple with a sucrose solution (sample: solution (w/w) = 1:10). They hypothesized that sucrose molecules may not be able to diffuse as easily as water through the cell membranes at higher temperatures. On the other hand, Shi and others (2009) reported a positive influence of higher temperatures on solute gain during the infusion of blueberries (sample: solution (w/w) = 1:1). The authors suggested that the effect of temperature on solution viscosity and solute diffusivity may be more pronounced in a low-ratio system than in a high-ratio system.

Increasing solution concentrations produces a positive effect on the rate of water loss due to an increase in the osmotic gradient. This has been consistently reported for various fruits and vegetables, such as blueberries infused with different sugars (Shi and others 2009), apricots osmotically dehydrated with various sugars (İspir and Toğrul 2009), and pears dehydrated osmotically with sucrose (Kaymak Ertekin and Cakaloz 1996a; 1996b). An increase in solute gain associated with higher solution concentrations has also been reported (İspir and Toğrul 2009). This has been

attributed to the accumulation of a thick solute layer around the product surface, which slows the water removal and creates a condition more favorable for solute uptake (Nsonzi and Ramaswamy 1998a). The use of higher solution concentrations, however, may adversely affect the final physical characteristics of materials. Yang and others (1987) reported that an increase in the sugar concentration of osmotic solution caused more stickiness and textural hardness in osmotically dehydrated blueberries.

Physical properties and geometry of the material

According to Saravacos and Charm (1962), fruits and vegetables can be broadly divided into three groups based on their structural characteristics: 1) those with a homogeneous structure (e.g., carrots, potatoes), 2) those with a porous structure (e.g., apples, peaches, pears), and 3) those with a waxy outer skin (e.g., grapes, cranberries, cherries). Those belonging to the first and third categories are somewhat resistant to moisture transfer due to the mass of their material and their skin structure. For those in the third category, a special skin treatment is typically employed prior to osmotic treatment as their unique waxy skins greatly hinder osmotic mass transfer. Various skin treatment methods used for osmotic treatment are discussed later in this chapter.

The rate of mass transfer is also substantially affected by the geometry of the materials. At given solution concentrations and other process conditions, the rate of the osmotic process increases with decreased thickness and size of the food. This is due to increased specific surface area (i.e., total surface area per unit mass or volume) available for mass transport and a shorter length of travel for water and solutes. In their investigation of OD for stick-, slice-, cube-, and ring-shaped apples, Lerici and others (1985) found that water loss and solute gain increased in proportion to the ratio of the surface area to the characteristic length of the material. Farkas and Lazer (1969) reported that thinner rings of apples were most effectively dehydrated using a sucrose solution due to the shorter distance for water to travel from the center of the material to its surface.

Material: solution mass ratios

The selection of material: solution ratio for osmotic treatments is largely determined by the process objective and the end product characteristics to be achieved. An increase in sample: solution mass ratio enhances dewatering, resulting in increased weight loss of the material. When the objective of osmotic treatment is to achieve a rapid dehydration of food, it is advisable to use a high material: solution mass ratio (e.g., 1:20) in order to prevent the osmotic solution from becoming overly diluted with the water removed from the material, which can lead to reduced osmotic force (Rastogi and others 2000; Rastogi and others 2002; Azoubel and Murr 2004; İspir and Toğrul 2009). In contrast, much lower food: solution ratios are usually preferred for commercial infusion processes (e.g., 1:1 (w/w)), which favors solute migration into the food over dewatering (Shi and others 2009). Intermediate sample: solution mass ratios may be selected in an application where a moderate water loss and solute gain are needed.

Process duration

In general, longer contact times between the food material and osmotic solution increases the amount of solutes diffused into the food. This is because the diffusion of solutes tends to start slowly and then its rate gradually increases, followed by the rapid water removal at the beginning stage of osmotic treatment (Ponting 1973; Raoult-Wack 1994).

Use of agitation

The purpose of providing agitation to an osmotic treatment system is two-fold. Firstly, agitation ensures uniformity in temperature and concentration of the osmotic solution surrounding the food material (Nsonzi and Ramaswamy 1998a). Water extracted from the material tends to create a localized area of dilution, which weakens the concentration gradient needed for osmotic mass transfer (Ponting 1973). Secondly, agitation prevents the formation of a solute layer surrounding the food material being

processed, which serves as a barrier to the solute uptake and water removal (Azoubel and Murr 2004; Shi and others 2009). Kaymak Ertekin and Cakaloz (1996a) reported that the rate of water loss, solid gain, and reduction in water activity was higher in agitated systems than in static systems in OD of green peas with a sucrose/trisodium citrate binary solution. An increased rate of solute gain was also observed during the infusion of blueberries with a constant shaking of the system compared to a non-agitated system (Shi and others 2009).

Agitation can be provided either by a continuous shaking of the system or by the circulation of solution within the system. Agitation needs to be sufficiently gentle so that physical damage to the food material can be avoided. Shi and others (2009) reported the breaking of fruit in the agitated system during the infusion of blueberries at above 50 ºC. Ponting and others (1966), however, noted that a difference created by agitation might not be economically significant enough to warrant the use of agitation.

2.2.4. Skin pretreatment methods for osmotic treatment

As mentioned previously, the outer structure of waxy-skinned fruits provides a major impediment to mass transport during osmotic treatment. Various skin pretreatments are therefore generally performed to facilitate the movement of water and soluble solids when osmotically treating these fruits. There are three broad types of pretreatment that have been investigated in the literature: chemical, thermal, and physical treatment.

A typical chemical pretreatment involves the dipping of a product into a chemical solution, such as alkaline or acidic solutions of oleate esters (Ponting and McBean 1970; Sunjka and Raghavan 2004). The application of chemicals alters the skin structure of fruits due to the development of fine cracks on the surface of plant tissues (alkaline solutions) and dissociation of the wax platelets on the skin (acidic solutions) (St. George and Cenkowski 2008). Although chemical pretreatment has been proven useful, Sunjka and Raghavan (2004) expressed concerns about the use of chemicals as consumers may hesitate to purchase food products that have been

chemically treated. Additionally, the use of chemicals can result in objectionable off-flavor development unless used at appropriate concentrations (Ponting and McBean 1970).

A typical physical pretreatment involves cutting, ablating, puncturing, or peeling products to increase the area available for mass transport, or to create sites at which mass transport can actively take place (Sunjka and Raghavan 2004). Grabowski and others (2007) reported halving as the best physical pretreatment for OD of cranberries, which effectively brought the core of the fruit in contact with the osmotic solution, resulting in the highest water loss and the most acceptable taste by untrained panels.

Two types of thermal pretreatment are frequently seen in the literature: 1) submitting the food materials to steam or hot water, and 2) freezing the materials. The former is effective in altering skin permeability (Ponting 1973; Grabowski and others 2007) and the latter has been reported to disrupt the integrity of the cellular tissue structure, which favors a higher uptake of solutes by materials (Ponting 1973; Biswal and LeMaguer 1989; Saurel and others 1994). Grabowski and others (2007) noted that because the wax layer of blueberries is thinner than that of cranberries, blueberries are more susceptible to cracks upon freezing and thawing, thereby inducing more pronounced effects on blueberries than cranberries. Yang and others (1987) also reported that considerably less time was needed to osmotically dehydrate IQF blueberries than their fresh counterparts (24 hours vs. 50 hours) to 25 °Brix in 3:1 (w/w) blueberry/sugar ratio system, concluding that IQF blueberries would be a preferable starting material for osmotic treatment. Frozen materials are often used as a starting material in osmotic treatment studies and in actual commercial settings, due largely to the fact that fresh materials are often harder to acquire (Saurel and others 1994).

2.2.5. Effects of osmotic treatment on plant materials

During osmotic treatment, plant tissues undergo a series of synergistic chemical, physical, and structural transformations. These changes are not independent, but complexly interrelated. The next part of this chapter is dedicated to providing a review on various physical and quality changes that take place in fruits and vegetables during osmotic treatment. The methods of measurement that are often used in the literature to quantify such changes are also briefly discussed.

Weight change

The evolution of osmotic treatment is often examined in terms of the two primary osmotic flows, namely, water loss (WL) and solid gain (SG). WL and SG represent the total amount of solid absorbed by and water lost from the material after being osmotically treated for a certain time. They can be calculated using the following equations (Pan and others 2003) to provide a quantitative description of component transfer under osmotic treatment.

$$SG\ (\text{wet basis}) = [M_t \times (1\text{-}MC_t) - M_0 \times (1\text{-}MC_0)]/M_0$$

$$WL\ (\text{wet basis}) = [M_0 \times MC_0 - M_t \times MC_t]/M_0$$

where M and MC are the average wet weight (g or kg) and average moisture content of the material (g/g material or kg/kg material), respectively. Subscripts t and 0 respectively indicate the value at time t and the initial value. Subtraction of WL from SG (SG-WL) at the same time t gives an overall weight change (g/g material or kg/kg material). When calculating WL and SG, it is typically assumed that the two transfers are independent and no leaching of solids out of the materials occurs.

Texture properties and product shrinkage

Inevitable changes in textural characteristics of food occur during osmotic treatment, which is largely attributed to product shrinkage. The literature provides several

osmosis-induced physical transformations as culprits of textural changes and product shrinkage. Rastogi and others (2000) reported an increased osmotic pressure at the surface of food as a major cause of product shrinkage due to progressive diffusion of water. Osmotic pressure eventually reaches a critical value, causing rupture and shrinkage of the cell membrane. Another cause of product shrinkage is the greater degree of dewatering accompanied by lesser degrees of solute uptake. If the space previously occupied by the water does not get refilled with solutes, the deformation of the material occurs due to the contraction of the cellular matrix into the void space (Yao and Le Maguer 1996; Viberg and others 1998; Aguilera 2003). Furthermore, water loss during osmotic treatment causes the detachment of the cell walls from the cell membranes, resulting in the structural disintegration and subsequent reduction in size, as well as the appearance of wrinkles on the product (Rastogi and others 2002).

Since product shrinkage affects various physical properties of materials such as size, weight, volume, density, texture and visual appearance, the literature presents a number of ways to determine the degree of product shrinkage. The extent of product shrinkage can be quantified by a direct measurement of the material size (e.g., diameter determination by a caliper or micrometer) or by measuring changes in related parameters such as product volume, porosity, and density (Moreira and Sereno 2003; Fernández and others 2005; Yadollahinia and Jahangiri 2009). Changes in moisture content, water activity, and solute gain by the material often correlate to product shrinkage (Moreira and Sereno 2003; Yadollahinia and Jahangiri 2009). Since changes in physical properties associated with product shrinkage subsequently alter product texture (Yadollahinia and Jahangiri 2009), textural properties of osmotically treated material are often characterized instrumentally or by human sensory panels. Visual examination of product appearance is also employed as a way to monitor product shrinkage. More recently, computer-based image acquisition and analysis technology has come into use to observe the evolution of material shrinkage and other important morphological changes in a more precise and objective manner than those performed by human eyes (Fernández and others 2005). Scanning electron microscopy (SEM)

analysis is also frequently utilized to evaluate product shrinkage and associated physical changes, as well as to characterize the effect of osmotic treatment on plant tissues at the microstructural level.

Flavor, color, and other sensory properties

Unavoidable losses of flavors and colors that take place during osmotic treatment significantly alter organoleptic and nutritive properties of food. In the literature this has largely been attributed to the leaching of soluble constituents of the material into the osmotic solution. For example, Stojanovic and Silva (2007) observed that approximately 60 % of anthocyanins and phenolics was lost during a 12-hour osmotic treatment of prefrozen rabbiteye blueberries with a 55 ºBrix sucrose solution. The extent of such solute leakage may be quantitatively negligible when considering a material balance, but it may significantly affect the organoleptic and nutritive values of the product (Ponting 1973; Azoubel and Murr 2004). Measurements on total phenolic and anthocyanin contents, color, and antioxidant activity are some of the analytical methods used in the literature to determine any appreciable changes during osmotic treatment of food.

At the end of the commercial-scale osmotic treatment, a large amount of spent osmotic solutions imparted with flavor and color of foodstuffs is left behind (Bolin and others 1983; Raoult-Wack 1994; Kuntz 1995). The spent solution cannot be discharged as wastewater unless properly treated because of its high biochemical oxygen demands (BODs) (Dalla Rosa and Giroux 2001). However, it can be successfully reused in future operations, either by filtering or reconcentrating, or by adding fresh solutes to compensate for the loss in the previous operation (Ponting 1973). Bolin and others (1983) found that the osmotic solutions of high fructose corn syrup (HFCS) or sucrose could be reconstituted and reused up to five times with no objectionable visual or flavor deterioration of the osmotically treated fruit, although some changes in physicochemical properties of solutions (e.g., darkening of solution) were noted.

The use of recycled syrup may also prevent pigment leakage in subsequent operations. Grabowski and others (2007) reported that the amount of anthocyanin, which migrated from blueberries into sucrose syrup during OD (70 °Brix, 50 °C, fruit: solution = 1:5 (w/w)), became increasingly smaller with the repeated use of the syrup and eventually became negligible after being reused more than four cycles. Appropriate control should be taken to ensure the microbiological safety of the recycled syrup (Raoult-Wack 1994; Grabowski and others 2007).

Furthermore, the spent osmotic syrup, which is rich in pigments and fruit flavor, may be processed into various marketable products, such as syrups for fruit fillings or base for beverages (Yang and others 1987; Kuntz 1995; Dalla Rosa and Giroux 2001). In their attempt to formulate a beverage utilizing the spent solution from OD of lowbush blueberries (i.e., blueberry extract (BE)), Camire and Flint (1993) demonstrated that BE could be successfully recycled into a beverage with moderately good consumer acceptability when appropriate levels of BE and citric acid were added to balance the flavor of the beverage. Microbiological stability was also achieved by pasteurizing the formulated beverage (Camire and Flint 1993).

2.2.6. Recent advances to enhance osmotic treatment of plant materials

Osmotic treatment of food is a simple operation in which various processing parameters can be flexibly modified to produce a final product with desired properties. As regards to the speed of the operation, however, it is inherently slow and can only be accelerated to a certain extent by manipulating the process variables (Rastogi and others 2002). To overcome this fundamental drawback of osmotic treatment, much interest has recently been focused to develop novel techniques to enhance the mass transfer rate during the process. Such newly emerging methods include the use of high frequency ultrasound (Simal and others 1998; Stojanovic and Silva 2007), ultra-high hydrostatic pressure (Rasgoti and Nirangan 1998), centrifugal force (Azuara and others 1996), and high intensity electrical field pulses (Rasgoti and others 1999).

High frequency ultrasound

The use of ultrasound creates a two-fold effect when applied in osmotic treatment: 1) the waves of highly intense ultrasound energy produce cavitation, the phenomenon characterized by the formation of vapor bubbles in liquid. This facilitates osmotic diffusions, and 2) the ultrasound waves also cause rapid, continuous compressions and rarefactions of the solid material, promoting dewatering (Simal and others 1998). Simal and others (1998) observed that the rate of water loss and solute gain during the ultrasound-assisted OD of apple cubes at 40 ºC were comparable to those obtained at 70 ºC with mechanical agitation. This suggests that ultrasound may allow higher rates of osmotic transport at lower temperatures, which also helps preserve heat-sensitive constituents. However, Stojanovic and Silva (2007) reported a negative influence of high frequency ultrasound on anthocyanins and phenolics during OD of rabbiteye blueberries followed by air dehydration. The authors noted the cavitation effect of ultrasound might have promoted additional rupture of the fruit and subsequent leakage of cell components.

High pressure treatment

The treatment of pineapple with high pressure prior to OD was studied by Rastogi and Niranjan (1998). Pineapple pieces subjected to varying degrees of high pressure pretreatment (100 - 700 MPa) were osmotically dehydrated with commercial sucrose solution at 50 ºBrix and 40 ºC. The rate of moisture loss and solid gain progressively increased with increasing pretreatment pressures, although there was no significant effect of pressure over 400 MPa. This was attributable to the enhanced cell permeability due to the damaged cell walls by the pressure treatment, which substantially increased the diffusivity rate of water and solute.

Centrifugal force

Azuara and others (1996) surveyed the effectiveness of centrifugal force during OD of potatoes and apples with varying concentrations of sucrose and NaCl solutions. In

comparison to a static system, centrifugal force markedly decreased the solute uptake while affording the same degree of dehydration in both food materials. The authors concluded that centrifugal force could be an effective means of achieving a high degree of dewatering when only minimal solute penetration is allowed.

High intensity electric field pulse (HELP) treatment

The application of high intensity electric field pulse (HELP) has been reported as an effective non-thermal pretreatment for OD. Rastogi and others (1999) reported that the rate of water removal and solute gain of HELP-treated carrot pieces increased with increasing electrical field strength applied during OD with sucrose. An increase in the field strength also markedly contributed to the softening of carrot tissues. The authors attributed these effects to the HELP-induced increase in cell permeability, which also facilitated osmotic transport of water and solute.

2.3. LASER TECHNOLOGY IN MATERIALS PROCESSING

2.3.1. Laser technology basics

Laser, an acronym for *l*ight *a*mplification by the *s*timulated *e*mission of *r*adiation, is a tool that generates highly intense, single-wavelength light. According to Tanzi and others (2003), the origin of laser technology dates back to 1917, when Albert Einstein first introduced the concept of stimulated laser emission. The first optic laser prototype was produced by Theodore Maiman in 1959 using a ruby crystal through which red light was produced at 696 nm wavelength. The ruby laser was quickly expanded to the treatment of various cutaneous pathologies in the 1960's. This further promoted the utilization of lasers with other substrates, facilitating revolutionary advances in the surgical field and a wide range of materials processing over the next several decades (Tanzi and others 2003).

One of the chief advantages of laser technology over traditional processing tools is its ability to allow precise alterations of materials in a flexible manner. Because laser processing parameters (i.e., beam power, penetration depth, speed) are

easily controllable, the area of interest can be precisely targeted, and various types of materials and processing needs can be accommodated (Witteman 1987; Ferraz and others 2007). In addition, because laser is a safe, non-contact processing tool with no equipment wear and tear, material modification to the targeted area can be attained without direct contact of the material with the equipment. This reduces the change of equipment-derived physical and microbiological hazards to virtually zero (Witteman 1987; Ferraz and others 2007).

Laser medium, optical cavity and power source are the three key components of laser beam generation. Laser energy is produced when the molecules of the laser medium are excited by the energy source, which subsequently excites other molecules in a chain reaction within the optical cavity. A beam of light is generated by a photon of energy, which is released upon the return of the energized molecules into their stable state (Cantatore and Kriegel 2004). A light generated by lasers possesses some distinctive properties (Figure 2.2). It is spatially coherent and collimated (Ferraz and others 2007), and it can be propagated over long distances with little divergence of the beam. The light emitted by laser is monochromatic, highly parallel, and can be focused to an extremely small, energy-dense spot. These unique characteristics of laser lights allow a precise, site-specific treatment without causing damage outside of the focus range (Powell 1998). In order for laser beam lights to exert an effect, it has to be absorbed and converted into energy. Transmitted, reflected, or scattered lights are not capable of producing effects (Shalhav and others 1996; Tanzi and others 2003; Cantatone and Kriegal 2004; Sweeney 2008). It is therefore imperative to select a laser that produces a beam of light that can effectively be absorbed by the material of interest.

There are two distinct forms of laser processing that can be achieved upon the absorption of laser energy: photochemical and thermal. In a photochemical process, elevated photon energy brings about the breaking of chemical bonds upon absorption of laser light, which subsequently causes various chemical reactions in the material (Ozdemir and Sadikoglu 1998). In contrast, a thermal process is induced by a rapid

temperature increase due to absorption of laser beams by the material. Rapid heating of materials then causes the evaporation of water, followed by thermal decomposition, carbonization and vaporization of the area surrounding the laser-treated region. Upon completion of the above reaction, a crater at the penetration depth is formed due to ablation of the cellular material (Ferraz and others 2007).

Table 2.2 presents several examples of lasers that are commercially available. Lasers can be broadly classified into three categories based on the types of active laser medium employed. The laser medium can either be a solid (e.g., neodymium: yttrium-aluminum-garnet [Nd:YAG]), a liquid (e.g., dye), or a gas (e.g., argon, carbon dioxide). The laser medium is contained in an optic cavity and acts as a resonator for laser beams. The type of active medium also determines the wavelength at which lasers operate (Cantatore and Kriegel 2004). The laser operational wavelength is of primary importance for laser processing because it also determines the mode of material modification (i.e., photochemical or thermal) and the type of materials that can be treated. Other selection criteria include power level, efficiency, lifetime of the laser medium, and initial investment and operational costs (Ozdemir and Sadikoglu 1998). Despite the relatively large number of laser systems that are currently being commercially used, carbon dioxide (CO_2) and Nd:YAG lasers are the two types that modify materials by thermal means. These two lasers operate at longer wavelengths (i.e., 10.6 µm and 1.6 µm, respectively) than other types of lasers, which don't generate the photon energy sufficient enough for photochemical reactions (Ozdemir and Sadikoglu 1998).

2.3.2. Carbon dioxide (CO_2) lasers

Figure 2.3 depicts a schematic of a typical CO_2 laser system. A CO_2 laser utilizes carbon dioxide gas as its laser medium. Helium (He) and nitrogen (N_2) are the two other gases employed by CO_2 lasers in order to efficiently convert the energy generated by the chain reaction of CO_2 molecules into kinetic energy (Powell 1998). A CO_2 laser is considered an ideal processing tool for biological materials that are

mainly composed of water, as water heavily absorbs the light generated at the wavelength of operation of a CO_2 laser (i.e., 10.6 µm) (Dixon 1988; Bilanski and Ferraz 1991). CO_2 lasers first came into use as a surgical instrument in 1967 (Dixon 1988) and was first utilized for cutting plywood dye boards for the packaging industry in 1971 (Powell 1998). CO_2 lasers are now being utilized in a wide range of materials processing for cutting, welding, and perforating with great process reliability and superior finish. In surgical fields, CO_2 lasers have become an indispensable tool that enables precise, site-specific destruction of living tissues with minimal thermal damage (Dixon 1988; Powell 1998).

In addition to its compatibility with biological materials, CO_2 lasers are relatively affordable and easy to maintain. The lifetime of CO_2 gas is longer compared to other laser mediums, making it more suitable for commercial applications. CO_2 lasers with 5, 6 and 7 kW of power coupled with various automations are commonly used in industrial settings for increasing process speed and efficiency (Bell 2006). A 10 kW CO_2 laser provides sufficient power and energy to easily cut steel plates of several centimeters thickness. In contrast, low-power CO_2 laser systems (i.e., below 100 W) are often used to perform special surgical operations, or micromachining and microsoldering tasks, in which precise processing and material modification without excessive thermal side effects are required (Witteman 1987).

Although CO_2 lasers are generally recognized as safe processing tools, laser-associated hazards are often overlooked (Sweeney 2008). Of four laser classifications specified in the guideline of the American National Standards Institute (ANSI), most industrial and medical lasers including CO_2 lasers fall into Class IV, which can cause severe, permanent damage to eyes or skin if the laser beam accidentally strikes a reflective surface (e.g., a mirror). Therefore, CO_2 lasers must be operated only by trained personnel and appropriate safety precautions must be followed. A warning sign indicating wavelength and maximum energy output must be placed in the area where the laser is in use (Sweeney 2008).

2.3.3. Laser technology in the food industry

Despite rapid advances in the surgical and materials processing fields in the last several decades, there has been little expansion of laser technology in food processing. The investigation of lasers as a potential processing tool for agricultural materials began in the late 1970's, soon after laser technology came into commercial use. The use of laser for sheep shearing, scarification of germinating seeds, and cutting of vines were explored and documented in the late 1970's and early 1980's (Bilanski and Ferraz 1991). Bilanski and Ferraz (1991) were the first to experimentally assess the application of laser energy to foodstuffs, investigating the ablation rates of potato tissues subjected to a CO_2 laser beam. However, such early attempts did not result in the expansion of research interests on the application of lasers for food and other organic materials in the next decades, as evidenced by the fact that virtually no literature on laser-induced food processing was published during this period. In the meantime, laser technology began to be extensively used in the food packaging industry. Lasers have enabled the modification of various packaging materials (i.e., metals, plastics, paper, cardboards, and glass) into precise forms and sizes. Lasers have also been utilized for drilling small holes on a breathable packaging for fresh produces (Ozdemir and Sadikoglu 1998).

Recently, the technology has begun to reappear in food processing. Choi and Li (2006) studied the feasibility of a pulsed Nd:YAG ultraviolet laser as a low-temperature cutting tool for natural cheddar cheese at the wavelength of 335 nm and 266 nm. Coupled with CAD (computer-aided design) software, a laser beam of 266 nm precisely sliced cheese into various complex shapes with minimal material burns, whereas a laser beam of 355 nm caused significant damage. Chen and others (2009a; 2009b) investigated the laser marking of eggshells by a CO_2 pulsed-laser system as a potential replacement for traditional ink marking, for which chemical disposal, its non-permanent nature, and time for ink to dry can often be shortcomings. Surface and cross-sectional examination of the laser-treated eggshells by a scanning electron microscope (SEM) revealed that an effective engraving of Arabic numerals and

graphics was attained at 10.6 µm wavelength and an average power of 30 W. Laser-induced damage was limited to the area surrounding the mark, and no damage to the external or internal structures of the egg was observed.

The low-energy CO_2 laser etching of tomatoes and avocados was investigated by Etxeberria and others (2006). Markings were successfully created in dot matrix letters and numbers with each dot (~200 µm in diameter) formed by pinhole depressions. Microscopic analysis of anatomical and morphological characteristics of the etched marks revealed that considerable structural changes, which the authors called "healing responses" to the laser-induced heat damage (i.e., darkening and thickening of the cell wall, increase in phenolic and lignin deposits in the cell wall) occurred directly underneath the depressed areas after 4 days of storage for both fruits. Using the same principles, Sood and others (2009) performed CO_2 laser etching on grapefruit in order to assess the impact of varying laser exposure times and pinhole sizes on water loss, decay, and quality deterioration from the laser etching site over a 5-week storage period. The authors found no evidence of facilitated water loss or increased susceptibility of decaying microorganisms from laser etching. Although the etched areas slowly deteriorated due to the water loss from the prolonged storage, waxing the etched surface effectively reduced the extent of water loss and enhanced the appearance of the laser-induced label. Also noteworthy is a recent announcement by the Kellogg Company in Britain on their plan to start lasing their signature Corn Flakes. Trial batches of the breakfast cereal are to be produced with their famous Kellogg's logo burned onto individual flakes in order to strengthen their brand image (Alexander 2009). Although the use of CO_2 lasers for food etching has already been approved in some countries (Sood and others 2009), it is still under review in the United States by the Food and Drug Administration (FDA) for commercial use (Stones 2009; FDA 2010).

Although the potential of the CO_2 laser as a viable processing tool has been highlighted in recent literature, its utilization for edible food materials is currently limited to the etching or coding of information. In addition, in the above studies laser

beams were applied only to the surface of food. So far, no research has investigated the effect of laser beams on the internal structure, integrity, and quality of edible materials of plant or animal origins. Nevertheless, the literature review shows that the application of laser technology for food processing would undoubtedly offer several important advantages over conventional methods. First of all, the beam of light generated by lasers can be applied with no direct contact between the equipment and food materials, which minimizes the potential of equipment-derived biological or physical contamination of food (Bilanski and Ferraz 1991). Secondly, lasers offer speedy, safe, and quiet processing with flexible control and adjustment of various process parameters (Powell 1998). The versatility of laser technology would allow processing of food materials that would otherwise be difficult to process with conventional methods (e.g., flimsy materials, materials with irregular shape). One potential drawback of the technology can be the substantial start-up costs associated with equipment installation and personnel training. However, given that process efficiency can be improved significantly, the initial cost could successfully be recovered within a relatively short time, as other industries have witnessed (Powell 1998).

2.4. CONCLUSIONS AND SUMMARY

Blueberries have become an important crop to the United States and the rest of the world due to their excellent nutritional, organoleptic and economic values. Since blueberries are highly perishable and seasonal with a short shelf life, a wide range of value-added blueberry products have emerged as a way of preservation while meeting the ever-increasing demands of consumers and food processors.

Osmotic treatment of food has gained increasing attention as a valuable partial dehydration method that brings about dewatering of the product and incorporation of valuable soluble solids into the product. Based on the immersion of food materials in a hypertonic solution that gives rise to two countercurrent mass fluxes of water and solutes, osmotic treatment allows simultaneous dehydration and compositional

modification of food via iteration of various process parameters. The non-thermal nature of the process also enables energy efficient dehydration with minimal deterioration of the nutritive values and sensory properties of the product. Osmotic dehydration (OD) and infusion are the two main categories of osmotic treatment of foods, with each having a distinct objective and end product characteristics. The literature review indicated that much research effort has been focused on OD, which primary objective is to achieve maximized water removal from food with little to moderate solute uptake. On the other hand, the scientific investigation of infusion, which aims to achieve maximum solute migration into food to increase the final yield, has been relatively scarce and methods to produce good quality infused products are often protected by patents.

Despite the extraordinary success in industrial materials processing and surgical applications over the past few decades, the potential utilization of laser technology for food processing has not been actively sought out. Among various types of lasers that are commercially available, CO_2 lasers are most compatible with organic materials that are composed mostly of water. The literature on the properties, physics, instrumentation, and safety of laser processing proved that the versatile and non-contact nature of the technology would be highly beneficial for the food industry, where materials tend to be highly varied in composition and physical structure, and the avoidance of physical and microbiological contaminations is crucial. In recent years, several studies investigating the use of CO_2 lasers as simple cutting or etching tools for various food products have emerged in the scientific literature. However, no other innovative applications have been pursued and the interaction mechanism of laser beams with food materials is still largely unknown. An experimental investigation that provides the basics of the technology and practical benefits of lasers as a novel food processing tool would be highly valuable to develop a better understanding of the technology among food science professionals, and to facilitate further research on its potential utilization in the food industry.

Table 2.1. Nutrient values of blueberries and blueberry products. Reprinted from Girard and Sinha (2007) with permission from Blackwell Publishing/John Wiley & Sons.

Nutrients/100g	Raw [a]	Canned blueberries in syrup [a]	Infused-dried cultivated blueberries [b]	Infused-dried wild blueberries [b]	Infused-dried organic wild blueberries [b]	Dehydrated blueberries [c]
Calories (kcal)	57.0	88.0	290.0	305.0	280.0	353.0
Calories from fat (Kcal)	3.0	3.0	20.0	19.0	11.0	21.5
Total fat (g)	0.33	0.33	2.19	2.06	1.17	2.39
Saturated fat (g)	0.028	0.027	0.3	0.3	0.1	NA
Polyunsaturated fat (g)	0.146	0.144	0.4	0.8	0.8	NA
Monounsaturated fat (g)	0.047	0.047	1.4	1.0	0.3	NA
Cholesterol (mg)	0.0	0.0	0.0	0.0	0.0	0.00
Sodium (mg)	1.0	3.0	18.0	15.0	22.0	38.0
Potassium (mg)	77.0	40.0	252.0	166.0	144.0	561.0
Total carbohydrate (g)	14.49	22.06	77.9	80.3	78.6	89.0
Total fiber (g)	2.4	1.6	16.6	15.4	15.1	8.19
Total sugar (g)	9.96	20.46	61.2	64.9	60.5	80.80
Sucrose (g)	0.11	NA	NA	NA	NA	NA
Glucose (g)	4.88	NA	NA	NA	NA	NA
Fructose (g)	4.97	NA	NA	NA	NA	NA
Protein (g)	0.74	0.65	2.03	2.43	0.84	4.22
Calcium (mg)	6.0	5.0	255.0	380.0	49.0	38.00
Vitamin C (mg)	9.7	1.1	<0.10	76.0	<0.10	81.90
Vitamin A (IU)	54.0	36.0	14.0	33.0	4.0	630.0
Water (g)	84.21	76.78	16.8	13.8	NA	3.00

NA: Not Available

[a] Data from USDA: http://www.nal.usda.gov/fnic/foodcomposition/cig-bin/list_nut_edit.pl

[b] Data from Graceland Fruit Inc, Frankfort, MI (www.gracelandfruit.com)

[c] Data from Esha Nutritional Database

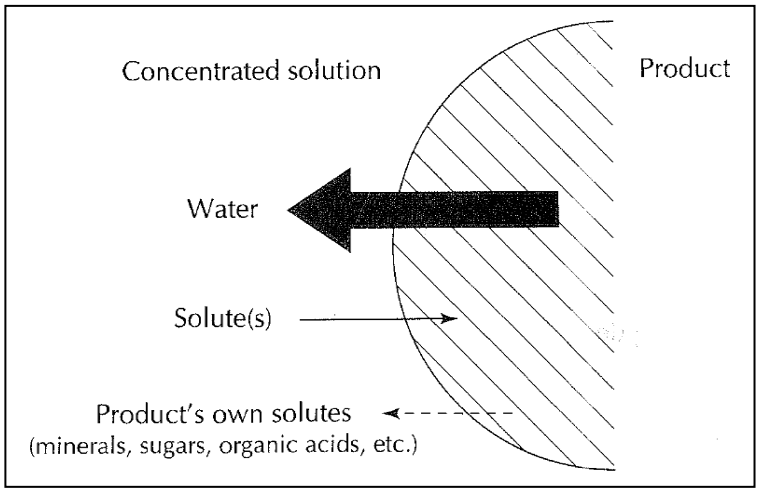

Figure 2.1. Schematic of mass transfer during osmotic treatment. Reprinted from Raoult-Wack (1994) with permission from Elsevier.

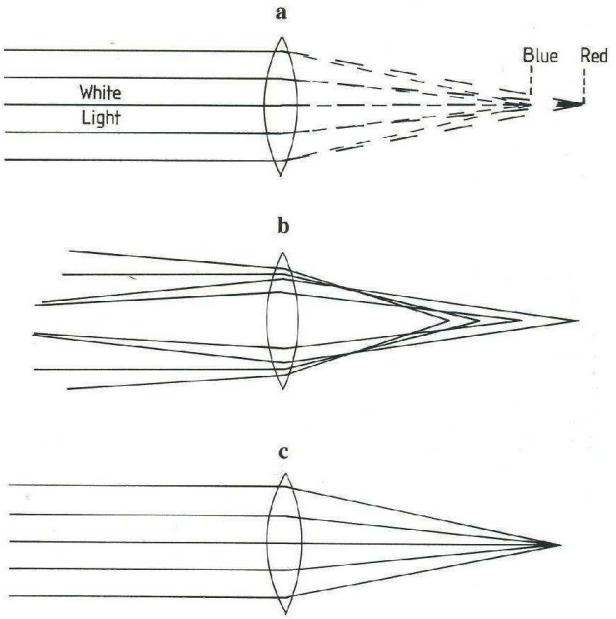

Figure 2.2. Comparison of laser light and lights from other sources. **a.** If white light is focused, a range of focal positions is established as each color focuses at a different distance from the lens. **b.** If non-parallel light is focused, a range of focal positions is established depending on the angles of incidence of the various components of the original beam. **c.** Laser light is monochrormatic (single wavelength or color) and parallel, and it can therefore be focused to a very intense small diameter spot. Reprinted from Powell (1998) with permission from Springer Science and Business Media.

Table 2.2. Examples of commercially available lasers. Reprinted from Hitz and others (2001) with permission from IEEE Press.

Laser	Wavelength	Average power range
Carbon dioxide	10.6 μm	Milliwatts to tens of kilowatts
Nd:YAG	1.06 μm	Milliwatts to hundreds of watts
Nd:glass	1.06 μm	Pulsed only
Cr:ruby	694.3 nm (vis)	Pulsed only
Helium-neon	632.8 nm (vis)	Microwatts to tens of milliwatts
Argon-ion	515.5 nm (vis) 488.0 nm (vis)	Milliwatts to tens of watts Milliwatts to watts
Krypton-fluoride	248.0 nm	Milliwatts to a hundred watts

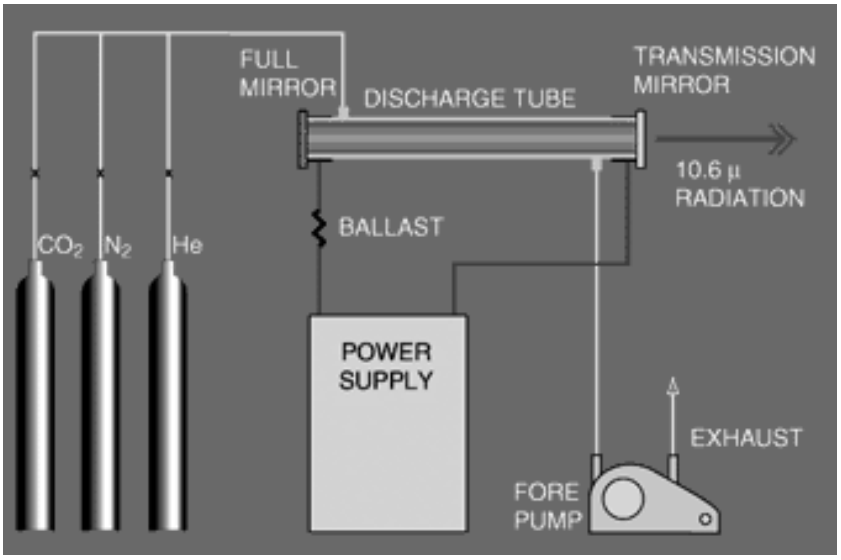

Figure 2.3. Schematic of typical commercial CO_2 laser. Reprinted from Whitehouse (1997) with permission from Laser Kinetics Inc.

CHAPTER 3

EFFECTS OF CARBON DIOXIDE (CO_2) LASER-ASSISTED SKIN PRETREATMENT ON SUGAR INFUSION PROCESS OF IQF (INDIVIDUALLY QUICK FROZEN) BLUEBERRIES

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3.1. Abstract

The feasibility of carbon dioxide (CO_2) laser perforation as a novel skin pretreatment for the stepwise sugar infusion of IQF (individually quick frozen) blueberries was investigated. The laser perforation parameters of interest were 1) perforation density (i.e., relative number of perforations per berry), and 2) perforation depth. The effects of the two parameters on infusion process characteristics were evaluated against a traditional mechanical pretreatment and control (untreated blueberries). IQF blueberries were subjected to varying degrees of laser perforation, followed by stepwise sugar infusion in a high fructose corn syrup (HFCS) solution to the final soluble solid content (°Brix) of 70. The two laser perforation parameters showed a significant effect ($p < 0.001$) on the rate of sample weight gain and the final fruit weight. The final fruit weight increased systematically with increasing perforation density and depth. The process duration (i.e., time to reach the target °Brix level) for the laser-treated samples was slightly shorter compared to the control ($p < 0.05$). An improvement on the physical attributes of the infused laser-treated blueberries was also noted; with increasing perforation density and depth, the size and volume of the infused fruit become substantially larger and the texture became less hardened. Laser perforation also greatly reduced shrinkage and wrinkling of the infused fruit, whereas the rupturing of the fruit was common among those mechanically treated. The effect of perforation depth was more prominent on the final process yield, solute gain, and physical characteristics of the infused blueberries than that of perforation density. The present results suggest that perforation with a CO_2 laser can be a viable pretreatment for the sugar infusion process of IQF blueberries, offering marked advantages over traditional mechanical treatment by improving final yield and final product characteristics.

3.2. Introduction

Lasers (acronym of *l*ight *a*mplification by *s*timulated *e*mission of *r*adiation) generate monochromatic, coherent and highly directional light beams that can be accurately collimated into small spots through focusing lenses, allowing site-specific, non-contact destruction without causing excessive damage to adjacent areas (Tanzi and others 2003; Ferraz and others 2007). Among the different types of lasers that are commercially available, carbon dioxide (CO_2) lasers are considered to be most suited for treating various biological materials for which water is the primary constituent, as the laser beams emitted at the operational wavelength of CO_2 lasers (i.e., 10.6 μm) are strongly absorbed by water (Bilanski and Ferraz 1991; Norris 1991; Etxeberria and others 2006; Ferraz and others 2007). The industrial use of CO_2 lasers, first introduced in 1971 for the cutting of plywood dye boards (Powell 1998), has revolutionized existing material processing practices (e.g., cutting, drilling, perforating, scoring) and has shown great commercial success in a wide range of industrial applications.

Although lasers offer superior process accuracy, reliability, environmental cleanliness, and safety, the food industry has not yet embraced this technology. An experimental application of CO_2 lasers to foodstuff was first reported by Bilanski and Ferraz (1991), who investigated the ablation rates of high moisture potato tissues subjected to CO_2 laser beams. In addition, a CO_2 laser etching of product identification on the surface of avocado, grapefruits (Sood and others 2009), and eggshells (Chen and others 2009a; Chen and others 2009b) was recently investigated. Although these studies showed promising results and highlighted the efficacy of CO_2 lasers for food processing, no other innovative applications of CO_2 lasers for food materials have appeared.

Osmotic treatment of food is based on immersing high-moisture materials in a hypertonic solution of soluble solids (e.g., sugars, salt). The difference in solute concentrations between the osmotic solution and tissue fluids initiates two simultaneous osmotic flows: 1) the influx of solutes from the external solution into the material, and 2) the outflow of water and other natural solutes present in the material

into the solution (Raoult-Wack 1994; Ferrando and Spiess 2001; Shi and Le Maguer 2003). The rate of the two-way osmotic mass transfer is dependent on many intrinsic and extrinsic factors (e.g., solute types, solute concentrations, immersion duration, process temperature, solution/food ratio, geometrical characteristics of food, the use of pressure and/or agitation in the system, etc.) and a wide range of compositional modifications of foodstuff can be achieved through the iteration of these factors (Raoult-Wack 1994). Osmotic dehydration (OD) and infusion are two types of osmotic treatment that have widely been used for fruits. Although they are similar in mechanism and are often interchangeably used (Shi and others 2009), the process goal and end product characteristics of the two are fundamentally different. Infusion focuses on the two counter-flows of water and solutes, with a primary objective of maximizing the impregnation of external solutes into the food and the final process yield. On the other hand, OD aims at maximizing the water removal from a product with minimal solute uptake (Kuntz 1995; Zhao and Xie 2004). Although infusion is a profitable process where expensive fruits can be infused with inexpensive solutes (e.g., sugar) to increase the fruit weight and final process yield (MacGregor 2005), the literature review indicated that there has been relatively little research on the infusion process. Nonetheless, methods to prepare good quality infused or candied fruits are often patented (e.g., Mochizuki and others 1971; Kahn and Eapen 1982; Phillips 2001).

The waxy outer skin structure of fruits such as cherries, blueberries, grapes, and tomatoes serves as the predominant physical resistance to osmotic treatment or other dehydration operations (Ponting and McBean 1970; Ponting 1973; Sunjka and Raghavan 2004). Various thermal (e.g., freezing and steam or hot water blanching) (Ponting and McBean 1970; Ponting 1973), chemical (e.g., dipping with ethyl esters of fatty acids) (Ponting and McBean 1970), physical (e.g., peeling, cutting of fruits into halves or quarters) (Sunjka and Raghavan 2004) pretreatment techniques have been utilized to facilitate the movement of water and solutes by altering the surface properties of the waxy skins. However, some of these methods may not be suitable for

infusion applications, especially when the preservation of original shape and appearance of fruits are needed for the final product.

Marking of microholes in fruits using a CO_2 laser can be a viable, advantageous skin pretreatment for infusion over the above traditional methods. Firstly, laser-induced spots are extremely small, serve as open passages for efficient mass transport, and can be created with minimal thermal damage and disruption to adjacent tissues and fruit structure. Secondly, because laser processing parameters can be flexibly controlled, materials with various shapes and compositions can be accommodated. Thirdly, and perhaps most importantly for the food industry, lasers offer non-contact processing with no equipment wear and tear, thereby reducing the chance of physical and microbiological contamination of materials that are typically associated with traditional cutting devices (Bilanski and Ferraz 1991; Ferraz and others 2007). One major shortcoming of the technology could be the substantial investment cost, but given that process efficiency can be significantly improved, the start-up costs could be successfully recovered within a short time (Powell 1998).

The aim of the present research was to investigate the efficacy of CO_2 laser perforation as a novel skin pretreatment for the sugar infusion process of blueberries. The influence of two laser perforation parameters (i.e., relative number of perforations per berry and perforation depth) on infusion characteristics was evaluated in terms of weight change, solid gain, water loss, and several physical and quality attributes of the finished product. A stepwise infusion process, which involves multiple baths containing an infusion solution of gradually increasing solute concentrations, was utilized in the present study. This practice allows an incremental solute uptake and minimizes the osmotic stress suffered by plant tissues, which can otherwise cause cellular structure collapse and subsequent reduction in the volume of finished products (Kahn and Eapen 1982).

3.3. Materials and Methods

3.3.1. Raw materials

Blueberries

US fancy (grade A) IQF blueberries of unspecified variety (Norpac Foods Inc., Lake Oswego, OR) were acquired in 20 lb (9.07 kg) cases from a local wholesale store. Because of the brief harvest season and shelf life of fresh blueberries, IQF blueberries were selected to ensure the availability of quality fruit in bulk regardless of the season. Frozen fruits have also been reported as favorable starting materials for osmotic treatment as alterations to their cellular structure induced by freezing and thawing enhances mass transfer (Yang and others 1987; Grabowski and others 2007) and favor solute impregnation (Saurel and others 1994). The blueberries were of the same production lot to ensure uniformity in terms of varietal characteristics and fruit quality. Because the structural integrity of small blueberries may be greatly disrupted by laser perforation, small berries were removed using a mesh hand sieve with ½" x ½" (1.27 cm x 1.27 cm) openings. The berries were further hand sorted to remove those with physical defects (i.e., crushed, decayed, scarred or wrinkled berries) and mixed to eliminate potential case-to-case variations. The sorted fruit was stored in cardboard boxes with polyethylene liners in a walk-in freezer (-18 °C) until use.

Osmotic solution

Commercial high fructose corn syrup (HFCS 42, ca. 70 °Brix, ADM, Decatur, IL) was selected as an active infusion agent due to its low cost, availability, and ease of use. HFCS contains low molecular weight carbohydrates that penetrate more easily into materials due to their small molecular size (Kuntz 1995), thereby favoring solute impregnation rather than dewatering (Zhao and Xie 2004). The syrup was stored in airtight containers at an elevated temperature (ca. 40 °C) until use to avoid evaporation and crystallization. Tap water was used to dilute the syrup to desired °Brix levels.

3.3.2. Carbon dioxide (CO_2) laser system

A 100 W CO_2 laser processing system (Firestar t100, Synrad Inc., Mukilteo, WA) located at Oregon State University Food Innovation Center (OSU-FIC, Portland, OR) was used in the present study. As depicted in Figure 3.1, the system consisted of a laser engine, a laser marking head equipped with a 200 mm focusing lens (FH series Flyer, Synrad Inc., Mukilteo, WA), an adjustable sample stand, and a computer interface with laser marking software (WinMark Pro, Synrad Inc., Mukilteo, WA). The CO_2 laser system was operated in a continuous wave mode (wavelength: 10.6 µm, frequency: 10 kHz). The properties, physics, instrumentation and safety of lasers are described elsewhere (e.g., Ozdemir and Sadikoglu 1998; Powell 1998; Ferraz and others 2007) and are thus beyond the scope of this report.

3.3.3. Raw material characterization

Initial soluble solid content (°Brix), initial moisture content, and average initial berry diameter and height were determined before day 0 (laser-perforation day). Prior to °Brix and moisture content determination, a representative sample of IQF blueberries were first thawed overnight at refrigeration temperature (ca. 4 °C) and then equilibrated to room temperature (ca. 20 – 22 ºC) for 4 hours in an airtight container. The moisture content of the thawed sample was determined gravimetrically by measuring the mass of a sample before and after drying overnight in a vacuum oven maintained at 70 °C. The °Brix of the thawed blueberries was determined using a refractometer (model RX-5000, Atago Co., Tokyo, Japan). The moisture content and °Brix were determined in triplicate. Average initial berry diameter and height were determined by measuring the longest chord and height of 100 randomly selected IQF blueberries (in mm with 0.01 mm sensitivity) using an electronic digital caliper (ProMax, Fred V. Fowler Co. Inc., Newton, MA). The average initial moisture content, °Brix, and initial fruit diameter and height were 86.71 ± 0.06 % (wet basis), 11.89 ± 0.12, 17.10 ± 1.26 mm and 11.32 ± 0.62 mm, respectively.

3.3.4. Skin pretreatment of IQF blueberries

Laser perforation of blueberries

In order to span a wide range of laser treatment conditions, combinations of three levels of perforation density (i.e., relative number of perforations per berry) and three levels of perforation depth were used. As shown in Figure 3.2, IQF blueberries were perforated in a grid pattern. Three grid sizes (G1: 5.0 mm x 5.0 mm, G2: 3.8 mm x 3.8 mm, G3: 2.5 mm x 2.5 mm) were selected based on the results of the preliminary study in order to yield a relatively different number of perforations per berry; the smaller the grid size was, the greater number of perforations were on the frozen blueberries. The three levels of depth investigated were D1: penetrating the surface of the berries, D2: penetrating through the middle section of the berries, and D3: penetrating through the berries. Perforation depth was controlled as a function of the firing duration of the laser beams, which directly correlates with the amount of energy consumed; the longer the firing duration, the more laser energy is applied to materials, resulting in deeper penetration. In order to find an appropriate firing duration to achieve three different perforation depths, thinly-sliced, halved, and whole blueberries of average diameter and height were perforated on white paper at varying firing durations until a slight burnt mark corresponding to the center of the fruit appeared on the paper (Figure 3.3). Using this method, three firing durations (i.e., 3 ms, 15 ms, and 42 ms) were established. Due to the spherical shape of blueberries, the thickest part of the blueberries was used to validate the three perforation depths. IQF blueberries perforated at these three firing duration were then cut latitudinally and observed under a microscope to visually verify each perforation depth (see Figure 3.2).

All laser marking parameters were controlled using the laser marking software. IQF blueberries (~100 g) were first loaded onto an aluminum tray (15 cm x 10.5 cm) in a single layer. The tray was then placed on the sample stand directly under the laser head and stabilized at 190 mm from the laser's output. This working distance between the sample surface and the laser head was based on the specified focal length for the 200 mm focusing lens used in the study, which produces a fixed beam size of 290 µm

(0.29 mm). This approximately corresponded to the size of the individual perforations on the blueberries. The laser beam travel velocity and power level were 381 mm (15.00 inch)/s and 100 % (100 W), respectively. Those were found to be the highest speed and power level to perforate the frozen blueberries without causing excessive burns or detrimental damage to the material. Approximately 100 g of IQF blueberries were perforated at all once, and the processing time per tray ranged from 3 s to 112 s depending on the perforation density and perforation depth (Table 3.1). The sample was transferred into a sugar infusion solution immediately after laser perforation. Great care was taken to minimize the air exposure of the frozen blueberries during the process.

Mechanical treatment

In order to simulate a typical mechanical treatment that is practiced in the industry, a latitudinal slit (~ 3mm deep) was made on individual IQF blueberries with a 3 mm blade (Figure 3.4). This was carried out in a walk-in freezer (-18 °C) and the scored blueberries were immediately transferred into a sugar infusion solution.

3.3.5. Sugar infusion of blueberries

A sample of 1000 g of pretreated (i.e., mechanically or by laser) and untreated (i.e., control) IQF blueberries were placed into a 1-gallon (3.79 L) plastic bucket containing 1500 g of HFCS solution (fruit: solution = 1: 1.5 (w/w)). This fruit: solution ratio was selected as it was found to be the lowest at which the blueberries could stay adequately immersed in the bucket. The °Brix of the solution was adjusted to be 5 degrees higher than the original °Brix of the IQF blueberries by diluting the HFCS syrup (ca. 70 °Brix) with tap water. The buckets were then covered with tight fitting lids to prevent evaporative losses, and the immersion was maintained for 24 ± 2 hours with no agitation at 50 °C in a temperature humidity chamber (model T21RS, TPS Inc., White Deer, PA) equipped with an environmental chamber controller (Tidal Engineering Corporation, Randolph, NJ). This fixed immersion time was relatively long in order to

ensure that the mass transfer equilibrium between the fruit and infusion solution was reached.

The blueberries were then carefully removed from contact with the spent solution by draining over a stainless steel strainer for 8 minutes. This practice was found to be sufficient to achieve the optimal separation of the fruit and the syrup in the preliminary testing. The strainer containing the blueberries was then placed on a tarred electronic balance (Model HF-3000, A&E Weighing Inc., Sun Jose, CA) to determine the weight of the blueberries with an accuracy of ± 0.01 g. Approximately 15 g of blueberries was sampled for °Brix and moisture content determination. After being blotted with a paper towel to remove adhering syrup and free water, the sampled blueberries were mashed in a disposable plastic cup until homogenized. A portion of the mashed sample was used for °Brix determination with a refractometer. The remaining sample was vacuum-dried at 70 °C overnight in a non-corrosive aluminum dish for moisture content determination.

The blueberries separated from the spent solution were placed into a new solution, which °Brix was adjusted to be 5 degrees higher than that of the berries. The immersion was again maintained in the new solution for 24 ± 2 hours in the chamber. This procedure was repeated every day until the °Brix of the blueberries reached 70 ± 0.5. The finished products were kept in airtight containers at ambient temperature for further analyses. The stepwise infusion experiment was repeated three times and all instrumental measurements were performed in duplicate.

3.3.6. Characterization of infusion process and final product

Change in fruit weight, solid gain and water loss

The weight change of blueberries was monitored as a function of time (days) throughout the infusion process. As the weight gain or reduction of the sample during osmotic treatment is derived from the removal of water and the uptake of solute(s), the evolution of weight change was also evaluated in terms of these two countercurrent flows. Solid gain (SG, g/g initial material) and water loss (WL, g/g initial material),

representing the total amount of solid absorbed by and water lost from the blueberries after being infused for a certain time, were calculated using the following equations (Pan and others 2003):

$$SG \text{ (wet basis)} = [M_t \times (1\text{-}MC_t) - M_0 \times (1\text{-}MC_0)]/M_0$$

$$WL \text{ (wet basis)} = [M_0 \times MC_0 - M_t \times MC_t]/M_0$$

where M and MC are the average wet weight of blueberries (g) and average moisture content of blueberries (g/g material), respectively. Subscripts t and 0 respectively denote the value at time t (day) and the initial value. Subtraction of WL from SG (SG-WL) at the same t gives the overall weight change (g/g initial material). The two mass transfers were assumed to be independent. Because of the non-selective nature of cell membrane, leaching of various soluble constituents of the material also takes place along with the outflow of water. This third mass flux may be significantly important for the final product composition, but is considered quantitatively negligible (Raoult-Wack 1994; Sunjka and Raghavan 2004). It was therefore disregarded for the SG and WL calculations.

Physical characteristics of final product

Because product shrinkage inevitably occurs during the osmotic treatment of food, it was of interest to assess whether laser perforation of the fruit would affect the extent of product shrinkage of the infused material. Product shrinkage also greatly influences physical and organoleptic attributes of the final product such as its texture and appearance, thereby potentially affecting consumer acceptability of the product. The following measurements were performed in order to determine the effects of varying laser perforation conditions on several key physical attributes of the infused blueberries. Prior to analyses, the infused blueberries were rinsed with tap water for a few seconds to remove the adhering syrup and blotted dry with paper towels.

***Final average diameter*:** The diameter of the final product was determined by measuring the longest chord of 100 randomly selected infused blueberries (in mm, with 0.01 mm sensitivity) using an electronic digital caliper (ProMax, Fred V. Fowler Co. Inc., Newton, MA). The mean value was then reported.

Average berry count: Approximately 100 g of the finished product was randomly sampled and the number of the individual infused blueberries was counted. This was repeated three times. The average berry count per given unit mass (i.e., 100 g) was reported.

***Degree of product shrinkage*:** The percent volume change of the blueberries after sugar infusion was quantified using the following equation (Singh and others 2007):

$$\% \text{ Shrinkage} = [1 - (V/V_0)] \times 100$$

where V is the final volume of 100 g of the infused blueberries and V_0 is the volume of 100 g of IQF blueberries that had been thawed. The volumes of blueberries were determined by placing a weighed mass of blueberries in a graduated cylinder (250 ml) containing a known volume of water at room temperature. The displaced volume (i.e., new volume minus the original volume of water) corresponded to the volume of the blueberries. Although the graduations on the cylinder were 2 ml apart, the level of the meniscus was estimated to the nearest 0.5 ml. When measuring the volume of uninfused blueberries, a weight was used to ensure the complete submersion of the fruit in water. Volume measurements were performed three times and the mean % shrinkage value was calculated.

***Textural evaluation of infused blueberries*:** To assess the impact of varying degrees of CO_2 laser perforation on the textual characteristics of the final product, the firmness of the infused blueberries was determined by the Instron Universal Testing Machine (model 5581, Instron Corp., Canton, MA) equipped with the Kramer Shear cell with

10 blades with the maximum cell load of 500 N. The standard stainless steel shear-compression square sample box with a base of equally spaced bars was filled with 50 ± 1 g of the infused blueberries in a single layer, and force was applied at a constant crosshead speed of 500 mm/min to fully compress the sample. The peak force (N) required for the blade to pass entirely through the sample was obtained and used as a measure of the fruit firmness. The test was repeated three times at room temperature, and the mean peak force value was reported.

3.3.7. Experiment design and statistical analysis

A 3 x 3 factorial design was used in this experiment for the laser-perforated blueberries, with two independent factors (i.e., perforation density and depth) with each having three levels. A two-way analysis of variance (ANOVA) was conducted in order to examine the simple effect of the two laser perforation parameters and any notable grid size/perforation depth interactions at a significance level of $p < 0.05$. A one-way ANOVA followed by Tukey's HSD (honestly significant difference) test was then utilized for post hoc examination of specific interactions and contrasts between the laser-perforated, mechanically treated, and control samples at a significance level of $p < 0.05$. All statistical analyses were conducted using TIBCO Spotfire S+ (TIBCO Software Inc., Palo Alto, CA).

3.4. Results and Discussion

3.4.1. Infusion characteristics of laser-treated blueberries

Figure 3.5 compares the evolution of fruit weight change for the laser-perforated blueberries against the mechanically treated sample and control as a function of infusion time (days). The data illustrate distinct behaviors of the samples subjected to varying degrees of laser perforation. A substantial weight loss occurred during the initial 24-hour period (from Day 0 to Day 1) for all samples. This is chiefly attributable to the rapid dewatering of materials that is known to take place during the initial stage of osmotic treatment (Raoult-Wack 1994) coupled with the loss of cellular exudate upon thawing of the fruit (Saurel and others 1994). The results of the two-way

ANOVA showed a significant effect of perforation depth ($p < 0.001$) and perforation density ($p < 0.001$) on the extent of initial weight loss, indicating that the greater the perforation depth and density, the greater the amount of weight lost by the fruit (Table 3.1). The results of the one-way ANOVA indicated that the weight loss for the mechanically treated sample was statistically comparable to the laser-perforated samples except for those with higher degrees of perforation (i.e., G2D3, G3D2, and G3D3). On the other hand, the smallest weight loss was observed for the control sample, followed by those with surface perforation (i.e., G1D1, G2D1, and G3D1). The weight difference between the sample with the least weight loss (control) and the sample with the greatest weight loss (G3D3) on Day 1 was nearly 40 g.

From Day 2 on, all laser-perforated and mechanically treated samples began to show a weight increase, reaching the target °Brix level of 70 within 18 to 21 days (Figure 3.5). As previously seen for Day 1weight, the two laser perforation parameters showed a significant effect ($p < 0.001$, for both parameters) on the weight gain patterns of blueberry samples. For each perforation density, the rate of weight gain and the final weight were always the highest for the sample perforated at the greatest depth (D3), followed by the intermediate depth (D2) and the shallowest depth (D1) (Figure 3.5). Similarly, for each perforation depth, the highest perforation density (G3) showed the highest rate of weight gain and the highest final weight, followed by the middle (G2) and the lowest density (G1). A visual examination of the data implies, however, that the impact of perforation density on the final fruit weight was not as prominent as that of perforation depth (see Figure 3.5 and Table 3.1). In contrast, no weight gain was observed for the untreated (control) blueberries during the course of sugar infusion; the sample continued to show a gradual weight loss even after the initial weight loss period. The mean final weight for the untreated blueberries was 895.83 g, the lowest among all treatments, followed by the sample with the lowest dose of laser perforation (D1G1).

On the contrary, the final weight of those with higher degrees of laser perforation (i.e., greater number of perforations and deeper depth) reached over 1000

g, with G3D3 showing the highest mean final weight of 1112.18 g, followed by G2D3 (1080.89 g) and G3D2 (1065.33 g). The % yield increase of the laser-perforated samples compared to the final weight of the untreated fruit ranged from 3.9 % (G1D1) to 24.2 % (G3D3), with only two laser-treated samples (G1D1 and G2D1) showing % yield increases less than those mechanically treated (Table 3.1). In fact, the weight curve for the samples with surface perforation (D1) tended to flatten out as opposed to those perforated at D2 and D3, which exhibited continuous weight gain until the end of the infusion process. This implies that for those perforated at D2 and D3, sample concentration was achieved through promoted solute gain, whereas for the control and D1 samples product concentration took place mainly by cellular water transport with less solute gain. These results suggest that laser perforation above D2 and D3 can be an effective pretreatment to promote solute gain, thereby increasing the final process yield of infused blueberries. This is of practical importance from an industrial point of view, as the increase in the process yield directly translates into increased profits.

The curves for water loss (WL) and solid gain (SG) (Figure 3.6) revealed that the extent of SG increased with an increase in perforation density and depth, whereas the extent of WL, irrespective of the treatment type or the degree of laser perforation, was virtually identical (see Figure 3.6b). This further confirms the ability of laser perforation to promote solute gain, and that the significant increase in the final yield of the laser-treated samples was solely a result of enhanced solute gain by the fruit.

Perforation depth and density had a significant effect on the length of the infusion process ($p < 0.001$ and $p < 0.05$, respectively), indicating that the time required to reach the target °Brix level became slightly shorter as the two parameters were increased. However, statistical significance was only found between the sample with the highest degree of laser perforation (G3D3, 18.33 days) and the control (20.67 days) (see Table 3.1).

3.4.2. Physical properties of laser-treated infused blueberries

Because shrinkage of fruits and vegetables associated with dehydration may not be non-isotropic (Yang and others 2001; Yadollahinia and Jahangiri 2009), the degree of product shrinkage was quantified using several different indices. The two-way ANOVA performed on the data of the final berry diameter and final berry count per 100 g of blueberries showed that there was a significant effect of perforation depth ($p < 0.001$) and perforation density ($p < 0.001$); the final diameter of the infused blueberries tended to become greater with increasing perforation depth and perforation density (Figure 3.7a). This implies that latitudinal product shrinkage was alleviated by the use of deeper perforations and higher perforation densities. The mean final diameter of the samples perforated at the lowest depth (D1) was statistically comparable to that of the control sample, indicating surface perforation of the fruit was not effective in preventing shrinkage in diameter. Despite the statistical significance indicated by the results of the two-way ANOVA, it appears that the impact of perforation density on the final diameter was not as prominent as that of perforation depth (see Figure 3.7a). This agrees with the patterns that were observed earlier for the final product weight of the laser-treated samples.

Similarly, the effect of perforation depth was more evident than that of the perforation density for the final berry count (Figure 3.7b). The final berry count tended to become smaller with an increase in perforation depth at each perforation density, indicating that the blueberries were larger and heavier. However, perforation density often did not produce a significant effect at a given perforation depth.

The determination of percent volume shrinkage (Figure 3.7c) indicated that the fruit experienced shrinkage ranging from 11 % to 17 % by volume after infusion. The two-way ANOVA showed a significant effect of perforation depth ($p < 0.001$) but no effect of perforation density ($p > 0.05$), indicating that the use of deeper perforations, but not higher perforation densities, significantly alleviated the volume shrinkage of the fruit. This result was also confirmed by a visual inspection of the finished product (Figure 3.8), which showed a substantial difference in appearance among those

perforated at varying perforation depths. The fruit perforated at D2 and D3 remained fairly intact in shape and showed minimal shrinkage or wrinkling, which closely resembled the appearance of the IQF blueberries. However, those with surface perforations (D1) and the control sample were wrinkled, and the proportion of ruptured and shrunken fruit was considerably higher compared to those perforated at D2 and D3. Product shrinkage caused by osmotic treatment is mainly attributable to three reasons: 1) significant osmotic stress created within the material as the dehydration progresses, 2) subsequent formation of a porous structure due to the removal of water from the cellular structure, accompanied by less solute uptake (Yao and Le Maguer 1996; Viberg and others 1998), and 3) the water loss during osmotic treatment also causes the separation of cell walls from cell membranes, which induces the flux of fruit liquid through cell walls and eventual structural collapse (Rastogi and others 2000). It is therefore assumed that the good final quality of the laser-treated blueberries was achieved by the increased solute impregnation provoked by moderate and high doses (D2 and D3) of laser perforations. The void area created as a result of water loss was then effectively refilled with the solute, thereby contributing to the increased final weight and reduced volume loss of the fruit.

Extremely small-sized perforations on the fruit structure may further explain the good quality of the laser-perforated infused samples. Ruptured berries were common among the mechanically treated blueberries (Figure 3.9). This may be attributable to the invasive nature of mechanical treatment, which could have caused a detrimental effect on the fruit's integrity, leading to the disruption of cellular structure after the prolonged infusion period.

Skin treatment prior to the infusion also impacted the textural characteristics of the finished product as previously reported (Taiwo and others 2003). The peak force (N) required to compress the infused blueberries was significantly higher for the control sample than that required for all the pretreated samples, indicating that the use of pretreatment yielded infused products with softer textures. The samples with greater degrees of perforation tended to be easier to compress, and therefore had softer

textures. The effects of perforation density and depth on the textural characteristics were statistically significant (p <0.001 for both parameters), although the impact of the perforation density appeared to be less prominent. This pattern reasonably correlates with those previously seen for the final diameter and product shrinkage results, as the shrinkage of osmotically treated plant tissues is a well-known contributor to product hardening. This result, however, differs from those reported in a study by Taiwo and others (2003), in which the highest firmness was associated with the highest SG in osmotically dehydrated strawberries. This discrepancy may be explained by the hygroscopic property of fructose, which acts as an excellent humectant (Davis 1995; MacGregor 2005). In the present study, the final moisture content of the infused blueberries that showed a high SG tended to be higher compared to those with low SG levels (data not shown). This implies the potential of HFCS exhibiting its high water-retaining capability in the infused blueberries.

3.5. Conclusions

The results of the present study demonstrate that CO_2 laser perforation could be a viable skin pretreatment for the sugar infusion of IQF blueberries. The final process yield of the laser-perforated blueberries was significantly higher than the untreated samples (up to 24 %). The increase in perforation density and depth showed a significant positive effect on the final product yield of the infused blueberries. The two laser perforation parameters also showed a significant impact on product shrinkage and final product quality. Increasing perforation density and depth contributed to producing infused blueberries with significantly larger diameters, a softer texture, and reduced surface wrinkling and volume loss (17 % volume shrinkage for the control sample vs. 11-14 % volume shrinkage for the laser-perforated samples). Of the two perforation parameters investigated, perforation depth consistently showed more pronounced effects on the measured attributes than perforation density. Compared to intermediate (D2) and full penetration (D3) of the fruit, surface perforation (D1) was

found to be somewhat ineffective in producing a significant improvement on weight gain and physical attributes of the final product.

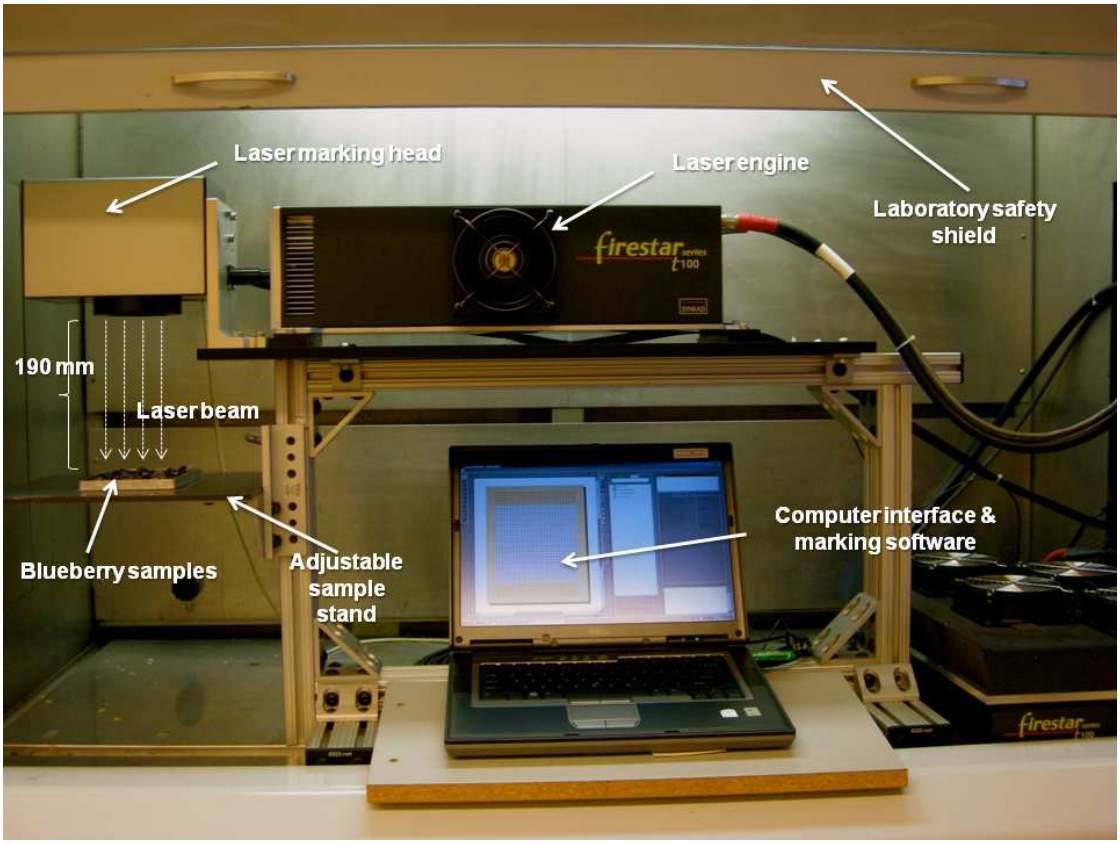

Figure 3.1. A 100 W carbon dioxide (CO_2) laser processing system (Firestar t100, Synrad Inc., Mukilteo, WA).

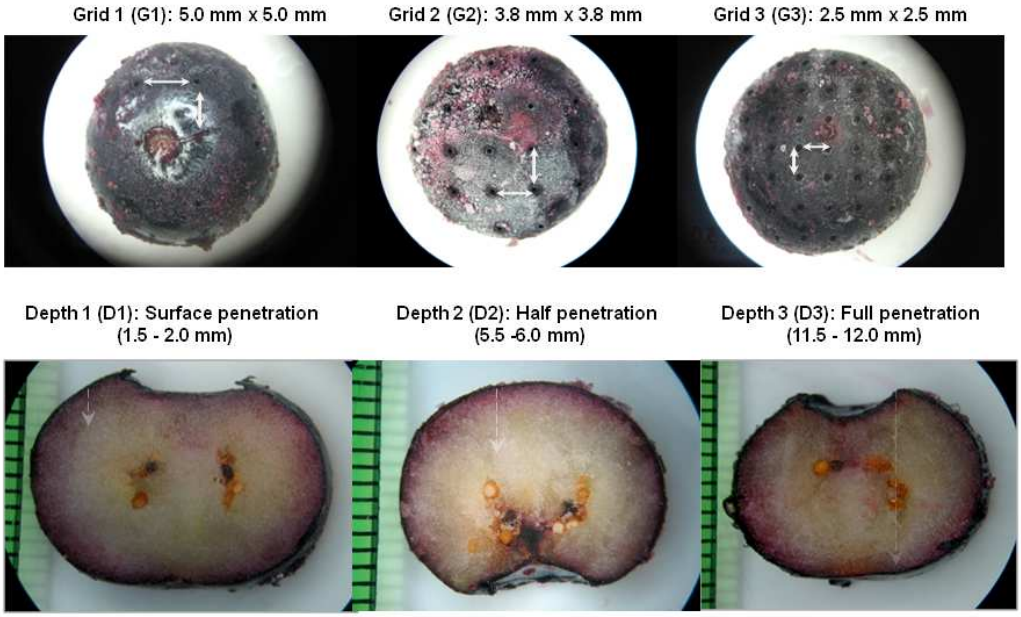

Figure 3.2. IQF (Individual quick frozen) blueberries after laser perforation. Combinations of three different levels grid sizes (G1, G2, G3) and three levels of perforation depths (D1, D2, D3) were used in the study. Arrows and lines were added for visualization of the laser marks. Images were captured using a digital camera mounted on a microscope (x 10 magnification, ACCU-SCOPE Inc., Commack, NY)

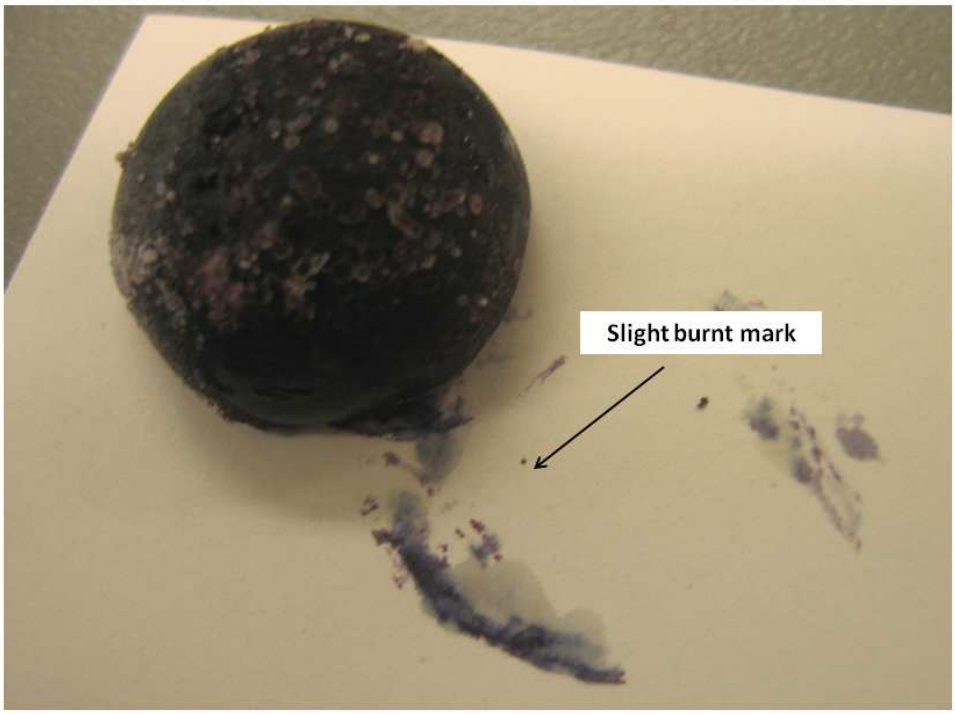

Figure 3.3. Validation of perforation depth. The fruit was considered perforated at desired depths when a perforation corresponding to the thickest part of the fruit produced a slight burned mark on white paper at each firing duration (see text).

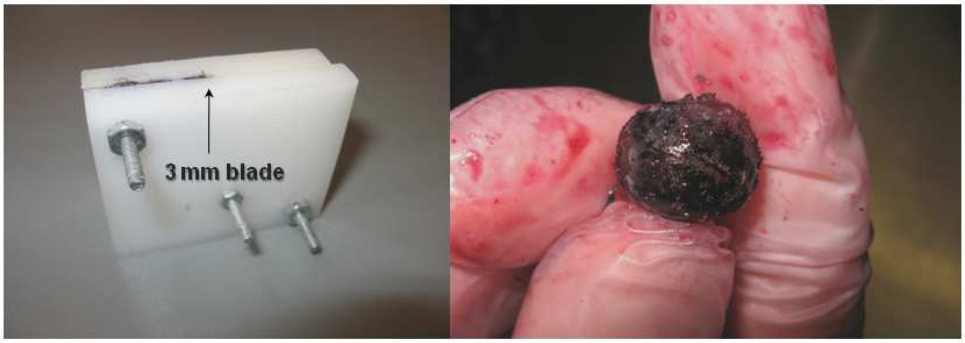

Figure 3.4. Device used for mechanical treatment of IQF blueberries (left) and mechanically treated blueberry (right).

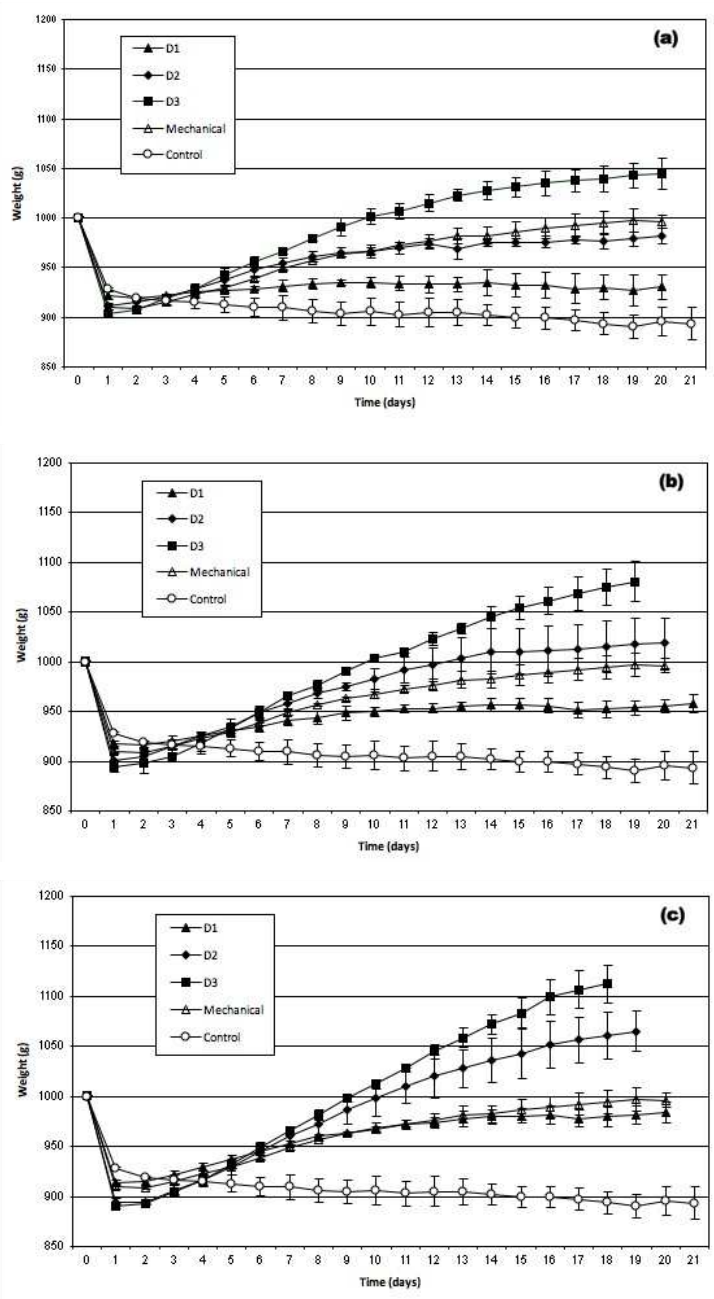

Figure 3.5. Weight change of laser-perforated blueberry samples compared to mechanically treated and untreated samples at given perforation density. (a) G1 (5.0 mm x 5.0 mm), (b) G2 (3.8 mm x 3.8 mm), (c) G3 (2.5 mm x 2.5 mm). The samples were subjected to the stepwise infusion (5 °Brix increments/day) to the final °Brix of 70 at 50 ºC. The error bars indicate standard deviations (n=3).

Table 3.1. Summary of laser processing time, mean Day 1 and final weight, and infusion duration of laser-perforated, mechanically treated and control samples.

Laser perforation		**Processing time per tray[1] (s)**	**Weight change**			**Infusion duration (day)**
Grid size	**Perforation depth**		**Day 1 (g)**	**Final (g)**	**% Final yield[2]**	
G1	D1	3	921.81^{ab} (2.14)	930.63^{ab} (7.32)	3.89 %	20.67^{a} (0.33)
	D2	11	911.88^{bc} (1.32)	982.40^{cd} (4.51)	9.67 %	20.00^{a} (0)
	D3	28	903.75^{cd} (1.96)	1042.70^{ef} (6.99)	16.40 %	19.67^{ab} (0.33)
G2	D1	4	917.41^{abc} (1.48)	955.58^{bc} (3.51)	6.67 %	20.67^{a} (0.33)
	D2	18	901.31^{cd} (3.85)	1018.93^{de} (14.57)	13.74 %	20.00^{a} (0)
	D3	48	894.35^{df} (3.36)	1080.89^{fg} (11.45)	20.65 %	19.33^{ab} (0.33)
G3	D1	9	913.99^{bc} (1.48)	984.06^{cd} (6.19)	9.85 %	20.00^{a} (0)
	D2	41	894.71^{df} (2.14)	1065.33^{f} (11.89)	20.02 %	19.33^{ab} (0.33)
	D3	112	890.43^{f} (1.43)	1112.18^{g} (10.96)	24.15 %	18.33^{b} (0.33)
Mechanical treatment			910.07^{c} (1.31)	977.22^{cd} (6.89)	9.08 %	19.67^{ab} (0.33)
Untreated (control)			927.75^{a} (0.91)	895.83^{a} (8.18)	–	20.67^{a} (0.33)

[1]: Each tray contained approximately 100g of IQF blueberries. [2]: Compared to the final weight of the untreated sample. Numbers in parenthesis are standard errors (n=3). Common superscript letters within the same column indicate no significant difference by Tukey's HSD test followed by the one-way ANOVA ($p < 0.05$).

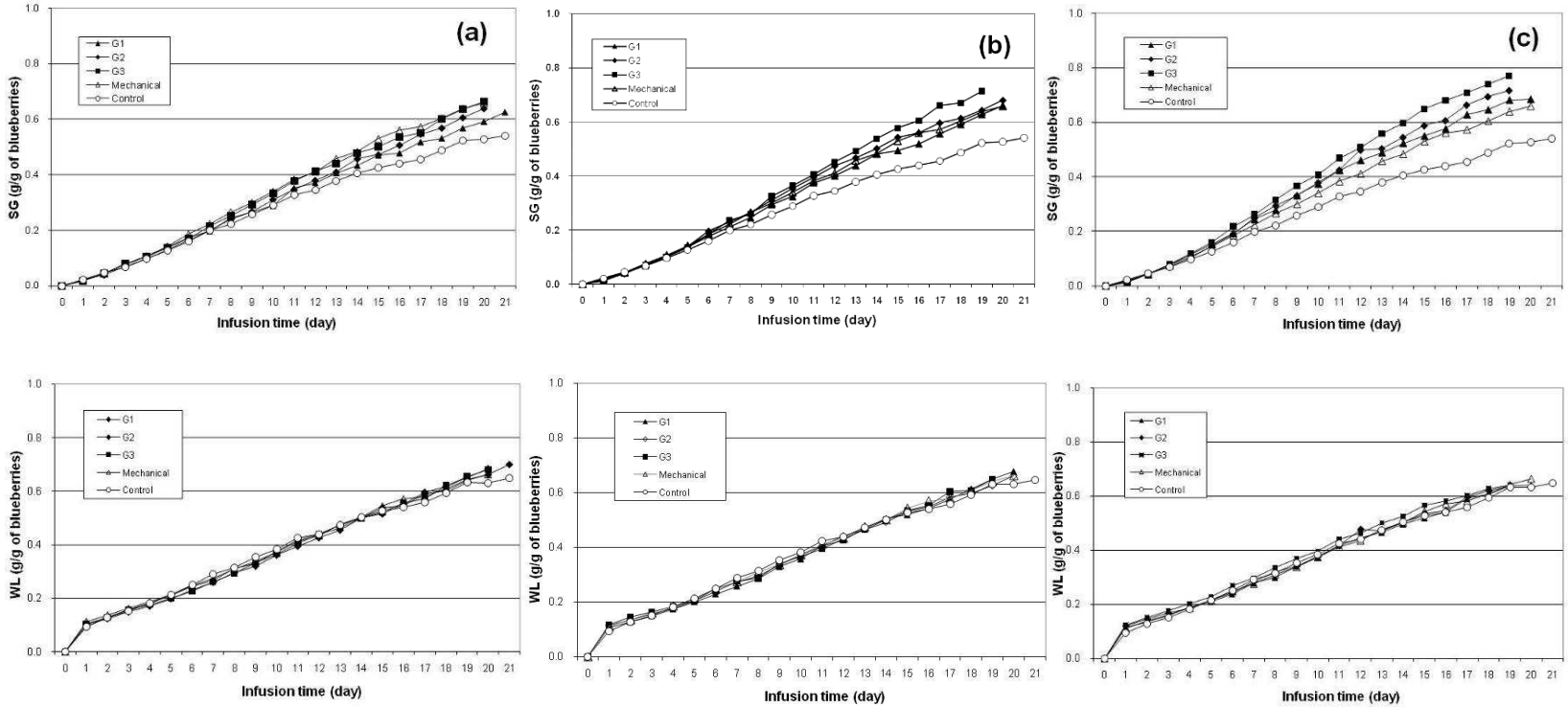

Figure 3.6. Extent of water loss (WL, top row) and solid gain (SG, bottom row) from laser treated, mechanically treated and untreated blueberries during the stepwise infusion. Each column shows the effect of different perforation depths at given grid size (left (a): G1, middle (b):G2, left (c):G3).

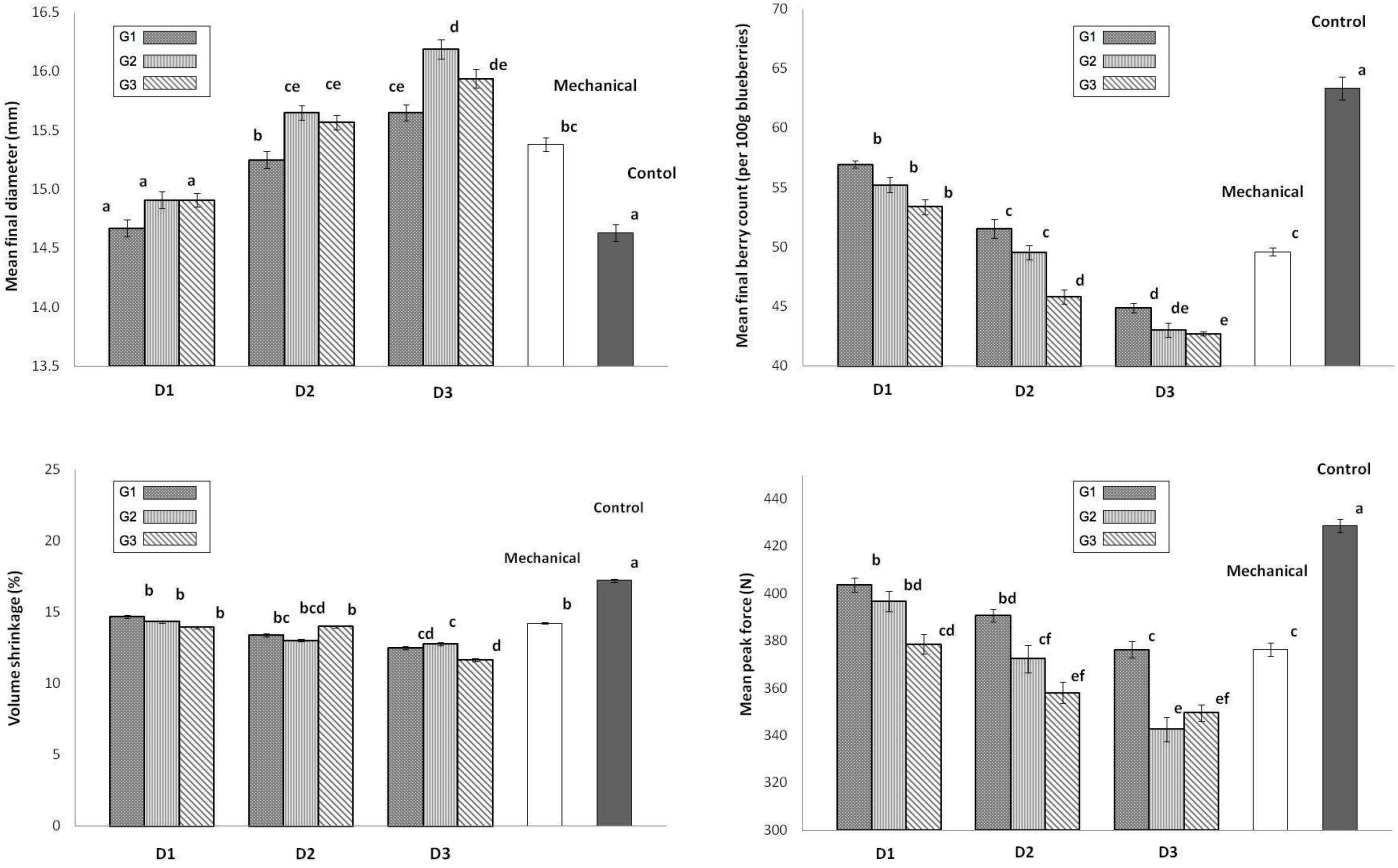

Figure 3.7. Physical characterization of infused blueberries. Mean final diameter (n=100, upper left) final berry count per unit mass (i.e., 100 g) (n=9, upper right), % volume shrinkage (n=9, bottom left), d) peak force (N) required for blueberries sample compression by the Kramer Shear Press (n=9, bottom right). Error bars indicate standard errors. Common subscripts letters within each graph indicate no significant difference by Tukey's HSD test followed by the one-way ANOVA ($p < 0.05$).

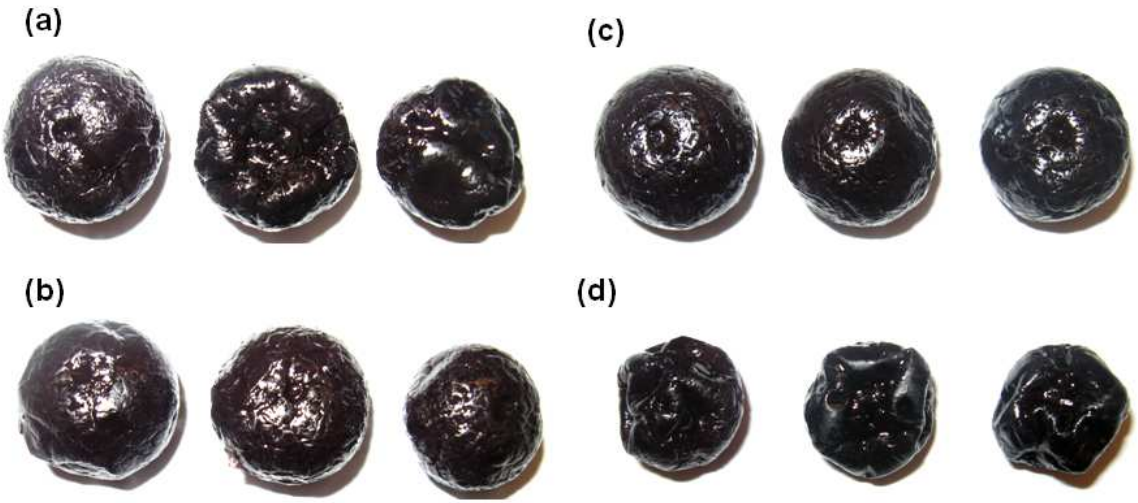

Figure 3.8. Appearance of infused blueberries perforated at G3 (highest perforation density). (a)D1, (b) D2, and (c)D3, and (d) untreated (control) samples.

Figure 3.9. Mechanically treated blueberries at the end of infusion process. Arrows indicate ruptured berries.

CHAPTER 4

EFFECTS OF CARBON DIOIXIDE (CO_2) LASER-ASSISTED SKIN PRETREATMENT ON SUGAR INFUSION PROCESS OF IQF (INDIVIDUALLY QUICK FROZEN) BLUEBERRIES II: WITH HIGHER SOLUTION CONCENTRATIONS

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4.1. Abstract

The performance of carbon dioxide (CO_2) laser-assisted skin pretreatment in the stepwise sugar infusion of IQF (individually quick frozen) blueberries with varying osmotic solution concentrations was investigated. This novel approach was previously found to bring about significant improvement on the final yield while alleviating texture hardening, shrinkage, and rupture of fruit infused at low concentration increments (5 °Brix/day). In the present study, IQF blueberries were first perforated with a CO_2 laser at varying degrees of perforation density and depth, and then infused to a final °Brix of 70 with a high fructose corn syrup (HFCS) solution using three different concentration increments (10, 20, and 30 °Brix/day). For each concentration studied, the final process yield of the fruit increased systematically with increases in perforation density and depth, with the highest perforation depth showing the highest weight gain. An evaluation of the physical properties of the infused fruit indicated that those perforated at higher perforation densities and depths were less prone to product wrinkling and breakage due to enhanced solute impregnation. Taken together, the previous findings and the present results highlight the two main benefits of CO_2 laser-assisted skin pretreatment: 1) the promotion of solute impregnation during sugar infusion and subsequent increases in the final process yield, and 2) the preservation of the fruit's original appearance and structure in the infused product. Moderate to high doses of laser perforation allowed the use of higher solution concentrations, which markedly shortened the process time without adversely affecting the final process yield and final product quality.

4.2. Introduction

Based on immersing a high-moisture material in a concentrated solution of substances that exhibit an osmotic pressure (e.g., sugars and salts), osmotic treatment is a non-thermal dehydration method that has been utilized for food materials of both plant and animal origins (Raoult-Wack 1994; Ferrando and Spiess 2001). The concentration gradient between the osmotic solution and the intercellular fluid causes two countercurrent flows: 1) the outflow of water from the material into the solution, and 2) the influx of solute from the solution into the material (Kaymak Ertekin and Cakaloz 1996a; Ferrando and Spiess 2001; Shi and Le Maguer 2003; Marani and others 2007). As a result, dewatering and compositional modification of the product can be attained simultaneously (Raoult-Wack 1994).

There are two primary categories of osmotic treatment of food: osmotic dehydration (OD) and infusion. The fundamental difference of the two lies in their applications and final product characteristics. The primary focus of OD is to achieve rapid dewatering of the material while limiting the solute uptake. It is generally used to prepare intermediate moisture (IM) foods, or as a pre-dewatering step to reduce energy consumption and damage to heat-sensitive substances during subsequent drying operations (Ponting 1973; Jayaraman and Das Gupta 1992; Grabowski and others 2007). In contrast, infusion, often referred to as “candying”, aims at maximizing the incorporation of external solutes into the food with moderate water removal, thereby maximizing the final product yield (Raoult-Wack 1994; Kuntz 1995; Shi and others 2009). The rate of osmotic treatment and the final product quality are largely influenced by many process parameters (e.g., type of osmotic solutions, solute concentration and other physical properties of solutions, process temperature, immersion duration, solution/food ratio, geometry of food materials, the use of agitation or pressure). While the influence of these factors on OD have been extensively studied, the literature addressing ways to improve the process efficiency and the final yield for infusion are relatively sparse, and methods to prepare good-quality infused fruits are often protected by patents (e.g., Mochizuki and others 1971;

Kahn and Eapen 1982; Phillips, 2001). This is presumably because infusion is an attractive process from an economic viewpoint, as fruits can be impregnated with inexpensive solutes (e.g., sugars) to achieve considerable increase in product weight and final yield (MacGregor 2005).

Because the unique skin structure of fruits such as cherries, blueberries, grapes, and tomatoes greatly hinder osmotic mass transport (Ponting 1973; Azoubel and Murr 2002), various physical, chemical, and thermal skin treatments have traditionally been applied prior to osmotic treatment in order to facilitate the movement of water and soluble solids. However, some of these methods may not be ideal in the current market due to potential consumer aversions to using chemicals in food products (Sunjka and Raghavan 2004). In addition, in some applications where the retention of the original product's character (i.e., size and shape) is desired, cutting or punctuating of the material is unacceptable.

In recognition of these potential disadvantages of existing pretreatment methods, the previous experiment (Chapter 3) investigated the possible utilization of carbon dioxide (CO_2) lasers as a novel skin pretreatment for the sugar infusion of IQF (individually quick frozen) blueberries. IQF blueberries were laser-perforated in a grid pattern using three predetermined levels of perforation density and depth, followed by the sugar infusion with a high fructose corn syrup (HFCS) solution using a steady concentration increase of 5 °Brix/day increments. The results showed that moderate and high doses of laser perforation offered a significant improvement on the final product yield, producing infused blueberries with reduced fruit shrinkage, texture hardening, and rupture. However, because of the small osmotic gradient employed in the previous experiment, the process duration was long (i.e., 18 - 21 days). In principle, the use of higher solution concentrations shortens the time for the fruit to reach the target °Brix level, but it also creates a condition more favorable for dewatering rather than solute incorporation. The likelihood of product rupture and shrinkage can also increase due to the increased osmotic gradient. Furthermore, increasing solution viscosity could result in decreased solute diffusivity into the

material (Pan and others 2003). Based on the previous finding, it was hypothesized that laser perforation could potentially alleviate these drawbacks associated with using higher solution concentrations without adversely affecting the final fruit yield and final product quality.

The aim of this study was to investigate the efficacy of CO_2 laser perforation under the stepwise sugar infusion of IQF blueberries utilizing higher solution concentrations (i.e., 10, 20, 30 °Brix/day). The influence of laser perforation and depth was evaluated in terms of weight change, solid gain and water loss, as well as the quality and physical properties of the finished product.

4.3. Materials and methods

4.3.1. Raw materials

Blueberries

US fancy (grade A) IQF blueberries of unspecified variety (Norpac Foods Inc., Lake Oswego, OR) were acquired in 20 lb (9.07 kg) cases from a local wholesale store. The berries were of the same production lot in order to ensure uniformity in terms of varietal characteristics and fruit quality. As it was of concern that the structural integrity of small blueberries might be greatly disrupted by laser perforation, small berries were eliminated using a mesh hand sieve with ½" x ½" (1.27 cm x 1.27 cm) openings. The berries were further hand sorted to eliminate those with physical defects (i.e., crushed decayed, scarred or wrinkled berries), and thoroughly mixed to eliminate potential case-to-case variations. The sorted blueberries were then stored in cardboard boxes with polyethylene liners in a walk-in freezer (-18 °C) until use.

Osmotic solution

Commercial HFCS (HFCS 42, ca. 70 °Brix, ADM, Decatur, IL) was used as an active infusion agent for the present study. The syrup was stored in airtight containers at an elevated temperature (ca. 40 °C) until use to avoid evaporation and crystallization. Tap

water was used to dilute the syrup to desired °Brix levels (i.e., 10, 20, and 30 above the °Brix of blueberries).

4.3.2. Carbon dioxide (CO_2) laser system

A 100 W CO_2 laser processing system (Firestar t100, Synrad Inc., Mukilteo, WA) located at the Oregon State University Food Innovation Center Experiment Station (OSU-FIC, Portland, OR) was employed in the present study. The system consists of a laser engine, a laser marking head equipped with a 200 mm focusing lens (FH series Flyer, Synrad Inc., Mukilteo, WA), an adjustable sample stand, and a computer interface. The computer interface was equipped with laser marking software (WinMark Pro, Synrad Inc., Mukilteo, WA), which was used to control the laser perforation parameters. A schematic of the laser system and the features of laser processing were presented in the previous chapter (Figure 3.1). The CO_2 laser system was operated in a continuous wave mode (wavelength: 10.6 µm, frequency: 100 kHz).

4.3.3. Raw material characterization

Initial soluble solid content (°Brix), initial moisture content, and average initial berry diameter and height were determined prior to day 0 (laser-perforation day). Prior to °Brix and moisture content determination, a representative sample of IQF blueberries was first thawed overnight at refrigeration temperature (ca. 4 °C) and then equilibrated to room temperature (ca. 20 - 22 ºC) for 4 hours in an airtight container. The moisture content of the thawed berries was determined gravimetrically by measuring the mass of a sample before and after drying overnight in a vacuum oven maintained at 70 °C. The °Brix of the thawed sample was determined using a refractometer (model RX-5000, Atago Co., Tokyo, Japan). The moisture content and °Brix were determined in triplicate. Average initial berry diameter and height were determined by measuring the longest chord and the height of 100 randomly selected IQF blueberries (in mm with 0.01 mm sensitivity) using an electronic digital caliper (ProMax, Fred V. Fowler Co., Inc., Newton, MA). The average initial moisture content, °Brix, and initial fruit

diameter and height were 85.20 ± 0.27 % (wet basis), 12.52 ± 0.2, 15.81 ± 1.09 mm, and 11.21 ± 0.76 mm, respectively.

4.3.4. Laser perforation of IQF blueberries

In the previous study (Chapter 3), a total of 9 combinations of varying perforation density (i.e., grid size, G1: 5.0 mm x 5.0 mm, G2: 3.8 mm x 3.8 mm, D3: 2.5 mm x 2.5 mm) and perforation depth (D1: penetrating the fruit surface, D2: penetrating through the middle section of the fruit, and D3: penetrating through the fruit) was used to span a wide range of laser perforation conditions. The present study utilized 5 out of the 9 possible perforation density/depth combinations to assess the impact of the two laser perforation parameters (see Table 4.1). Because the IQF blueberries used in the present study were smaller than those employed in the previous experiment (average diameter: 15.81 ± 1.09 mm vs. 17.10 ± 1.26 mm), the firing duration of the laser beam, which governs the depth of perforation, was adjusted to 12 ms for D2 (as opposed to 15 ms in the previous study) to ensure the adequate penetration of the laser beam to the middle section of the fruit. The same method used to validate the penetration depth in the previous experiment was again used: thinly-sliced, half-pieced, and whole average-sized blueberries on white paper were perforated at the three established firing durations (see text in Chapter 3 and Figure 3.3). It was assumed that adequate, but not excessive, penetration was achieved when the laser perforations at the thickest part of the blueberry left a faint burnt mark on the paper. The depth of perforations was further verified by inspecting a latitudinal slice of the perforated blueberries under a microscope (see Figure 3.2).

Prior to laser treatment, IQF blueberries were first loaded onto an aluminum tray (15 cm x 10.5 cm). The tray was placed on the sample stand located directly under the laser head and stabilized at 190 mm from the laser's output. This working distance between the sample surface and the laser head was based on the focal length specified for the 200 mm focusing lens used in the study, which was to produce a fixed beam size of 290 µm (0.29 mm). This approximately corresponds to the size of

individual perforations on the blueberries. The laser beam travel velocity and the power level were 381 mm (15 inch)/s and 100 % (100 W), respectively. Approximately 100g of IQF blueberries were loaded on a tray and perforated all at once, and the processing time for the 5 perforation density/depth combinations per tray ranged from 4 s to 112 s as reported previously (Table 3.1). The sample was then transferred into a sugar infusion solution immediately after laser perforation to minimize the air exposure of the frozen blueberries throughout the process.

4.3.5. Sugar infusion of blueberries

A sample of 1000 g of laser pretreated and untreated (i.e., control) IQF blueberries were placed into a 1-gallon (3.79 L) plastic bucket containing 1500 g HFCS solution. The solution was prepared by diluting the straight HFCS with tap water to be 10, 20 and 30 °Brix higher than the original °Brix of the IQF blueberries. The fruit: solution ratio of 1:1.5 (w/w) was used as it was found to be the lowest ratio in order for the fruit to remain adequately immersed over the course of sugar infusion. The buckets were then covered with tight fitting lids to prevent evaporative losses, and placed in a temperature humidity chamber (model T21RS, TPS Inc., White Deer, PA) equipped with an environmental chamber controller (Tidal Engineering Corporation, Randolph, NJ) at 50 °C for 24 ± 2 hours. No agitation of the system was provided during the experiment.

The blueberries were then separated from the solution by draining over a stainless steel strainer for 8 minutes. The strainer containing the fruit was then placed on a tarred electronic balance (Model HF-3000, A&E Weighing Inc., San Jose, CA) to determine the weight of the blueberries with an accuracy of ± 0.01 g. Approximately 15 g of blueberries was sampled for °Brix and moisture content determination. After being blotted with a paper towel to remove adhering syrup and free water, the sampled blueberries were mashed in a disposable plastic cup until homogenized. A portion of the mashed sample was used for °Brix determination with a refractometer. The

remaining sample was vacuum-dried at 70 °C overnight in a non-corrosive aluminum dish for moisture content determination.

The blueberries were placed into a new solution with °Brix adjusted to be 10, 20 and 30 ºBrix higher than that of the berries. Immersion was again maintained at 50 ºC for 24 ± 2 hours in the chamber. This procedure was repeated until a final °Brix of 70 ± 0.5 was reached. The finished products were kept in airtight containers at ambient temperature overnight for further analyses. The infusion experiments were repeated three times, and all instrumental measurements were performed in duplicate.

4.3.6. Characterization of infusion process and final product

Change in fruit weight, solid gain and water loss

The weight change of blueberries was monitored as a function of time (days) throughout the infusion process. Because the weight change of the material during osmotic treatment is a result of the additive effect of the water loss and solute pickup by the material, the evolution of weight change was also assessed in terms of these two component transfers. Solid gain (SG, g/g initial material) and water loss (WL, g/g initial material), representing the total amount of solid absorbed by and water lost from the blueberries after being infused for a certain time respectively, were calculated using the following equations (Pan and others 2003):

$$SG\ (\text{wet basis}) = [M_t \times (1\text{-}MC_t) - M_0 \times (1\text{-}MC_0)]/\ M_0$$

$$WL\ (\text{wet basis}) = [M_0 \times MC_0 - M_t \times MC_t]/M_0$$

where M and MC are the average wet weight of blueberries (g) and average moisture content of blueberries (g/g initial material) on wet basis. Subscripts t and 0 indicate the value at time t (day) and the initial value, respectively. Subtraction of WL from SG (SG-WL) at the same t gives the overall weight change (g/g initial material). The osmotic solute and water transfers were assumed to be independent. The third osmotic flow, the leaching of the fruit's original soluble constituents due to the partially selective nature of cellular membrane, is considered quantitatively insignificant (Lerici

and others 1985; Raoult-Wack 1994), and thus not considered for the WL and SG calculations.

Physical characteristics of final product

The following measurements were taken in order to evaluate the influence of varying laser perforation conditions and solution concentrations on the physical properties of the infused product. Prior to analyses, the samples were rinsed with tap water for a few seconds to remove the syrup adhering to the surface of the berries and blotted dry with paper towels.

***Final average diameter*:** The diameter of the final product was determined by measuring the longest chord of 100 randomly selected infused blueberries (in mm, with 0.01 mm sensitivity) using an electronic digital caliper (ProMax, Fred V. Fowler Co. Inc., Newton, MA). The mean value was then reported.

***Berry count*:** Approximately 100 g of the finished product was randomly sampled and the number of individual infused blueberries was counted. This was repeated three times. The average berry count per given unit mass (i.e., 100 g) was reported.

***Bulk density*:** Bulk density is an important indicator of bulk storage size of the product. The weight of a 400-ml volumetric flask filled with infused blueberries was taken and the weight of the blueberries per unit volume (i.e., 100 ml) was expressed as bulk density. Care was taken to pack the flask with the sample in a consistent manner, since the way of filling can affect the measurement considerably (Sahin and Sumnu 2006). Bulk density measurement was performed in triplicate and the average value was reported.

4.3.7. Statistical analysis

A one-way ANOVA followed by Tukey's HSD (honestly significant difference) test was utilized for post hoc examination of specific interactions and contrasts between the laser-perforated and control samples at a significance level at $p < 0.05$. All statistical analyses were conducted using TIBCO Spotfire S+ (TIBCO Software Inc., Palo Alto, CA).

4.4. Results and discussion

4.4.1. Infusion characteristics of laser-treated blueberries

Figure 4.1 depicts the variations in fruit weight change of the laser-perforated and untreated (i.e., control) samples infused with HFCS solutions at 10, 20 and 30 ºBrix increments/day. The previous result (infusion at 5 °Brix/day increments, Chapter 3) is also presented in the same figure for comparison despite the size difference in the raw material. As observed previously, a considerable decrease in fruit weight was again noted for all treatments during the first 24 hours (between Day 0 and 1). This is attributable to the rapid dewatering of materials that takes place during the initial stage of osmotic treatment (Raoult-Wack 1994), combined with the loss of cellular exudate upon thawing of the fruit (Saurel and others 1994). The increase in solution concentrations resulted in a higher osmotic gradient between the external solution and the internal cellular fluid, and hence, lower Day 1 weights for each treatment condition (Table 4.2). However, no systematic effects of perforation density and depth on Day 1 weights were found as opposed to the previous study. This can be explained by the fact that the use of higher solution concentrations accelerated the initial dewatering, which could have caused solute impregnation to take place before the end of the first 24-hour period.

The evolution of fruit weight change at 10 °Brix/day increments (Figure 4.1b) was fairly identical to that observed at 5 °Brix/day increments (Figure 4.1). For all laser-treated samples, the magnitude of weight gain increased with increasing perforation density and depth at these two solution concentrations. As expected, the

control sample at 10 °Brix/day increments showed a significantly more weight loss than the control at 5 °Brix/day increments due to the higher osmotic gradient. In the previous study, perforation depth was found to have more impact on fruit weight gain than perforation density. This was also true at 10 °Brix/day increments (Figure 4.1a and b, see G2D1: G2D2: G2D3 vs. G1D3: G2D3: G3D3). As opposed to D2 and D3 samples, the weight change curve for those with surface penetration (i.e., G2D1) at 10 °Brix/day increments flattened after Day 1, yielding an average final weight of 924.62 g, which was only 10 g more than Day 1 weight (Table 4.2). G2D1 sample showed quite similar behaviors when infused at 5 °Brix/day increments (Figure 4.1a). This result confirms the ineffectiveness of surface perforation (D1) in producing enhanced solute impregnation, thereby producing no significant weight gain after the initial dewatering period.

As a result of using a higher solution concentration, the length of infusion was significantly shortened by approximately 7 days (Figure 4.1a and 4.1b) compared to the infusion with 5 °Brix/day increments. Surprisingly, the final fruit yield was slightly higher for those infused at 10 °Brix/day increments except for those with surface perforations (G2D1) and the control. This was not initially expected, since less solute gain was supposed to occur due to the increased osmotic force, which typically favors sample dewatering over solute impregnation. One potential explanation for the discrepancy is the difference in berry size, and possible differences in variety or maturity of the raw materials used in the two experiments. This may have caused the fruit to respond differently to the laser perforation and/or the osmotic solution.

The geometry of materials is indeed one of the well-recognized factors that impact the rate of mass transfer, and the literature has often reported the effect of berry size on drying characteristics of blueberries under conventional dehydration conditions. For example, MacGregor (2005) observed that the air drying time for larger IQF wild blueberries was much longer compared to the time required for smaller berries, and the larger berries exhibited a higher mass-losing rate than the smaller ones. Shi and others (2008b) reported that the drying rate decreased with a

decrease in blueberry diameter from 13 mm to 11 mm under infrared radiation heating, although the drying rate remained similar for berries with diameter between 13 mm and 16 mm. Since it was not possible to obtain information regarding the identity of the raw materials used in the present study, this anomalous behavior of the blueberries can only be verified by repeating the experiment using the identical material.

A comparison of the fruit weight change at 20 °Brix/day and 30 °Brix/day increments (Figure 4.1c and 4.1d) versus that at 10 °Brix/day increments presents a somewhat different picture. Although the order of the laser perforation density/depth combinations in relation to the final process yield of the infused blueberries remained the same as the 10 °Brix-samples, the infusion duration (i.e., the number of days required to reach the target °Brix) was further shortened and the final fruit yield decreased. This follows the general principle of osmotic infusion or candying process: increasing solution concentrations promotes sample concentration by water transport with lesser solute gain, leading to reduced process yield (Barat and others 2002). It may also be noted that the length of the infusion duration did not differ considerably between 20 °Brix- and 30 °Brix-samples (9 days vs. 8 days) compared to 10 °Brix-samples vs. 20 °Brix-samples (13 days vs. 9 days). This is because the straight HFCS syrup (ca. 70 °Brix) was continuously used after the °Brix of blueberries reached certain levels (i.e., over 40 °Brix for 30-Brix samples and 50 °Brix for 20-Brix samples, respectively) until the target °Brix level (70 ± 0.5) was attained. This practice gradually diminished the concentration gradient between the fruit and the solution, which considerably slowed infusion towards the end of the process.

It is also noteworthy that G2D2, which produced the final process yield that is statistically comparable to that of G1D3 at 5 °Brix/day and 10 °Brix/day increments, didn’t exhibit weight gain from Day 1 weight at 20 °Brix/day and 30 °Brix/day increments (Table 4.2). On the contrary, all D3 samples (G1D3, G2D3, and G3D3) still showed a considerable weight gain after Day 1. As shown by % final yield increase (in comparison with the control, see Table 4.1), the effect of laser perforation,

especially at D3, in promoting fruit weight gain after Day 1 became more apparent with increasing solution concentrations. These results suggest that laser perforation can be a powerful tool to accelerate the sugar infusion process, which tends to be much longer than osmotic dehydration (Zhao and Xie 2004), by allowing the use of higher solution concentrations with moderate fruit weight gain.

An evaluation of the sample weight gain in terms of WL and SG (Figure 4.2) further revealed characteristic mass transfer behaviors provoked by each laser perforation/density combination. In the previous experiment, weight gain for the laser-treated samples was derived solely from the enhanced SG, as the degree of WL was virtually identical across the treatments, irrespective of the difference in perforation depth and density (Figure 3.6). In the present study, however, slight variations in WL were observed among different levels of perforation density and depth at each solution concentration. In general, the control and G2D1 samples showed smaller SG (Figure 2a, b and c) and greater WL (Figure 4.2 d,e, and f), resulting in greater weight loss of the fruit. On the contrary, those that exhibited much greater SG (e.g., G2D3, D3D3) showed smaller WL, yielding much greater overall weight gain. This clearly implies the ability of laser perforation, especially at D3 (full penetration), to encourage greater solute impregnation with less water loss. Greater fruit weight recovery was therefore attained after the initial dewatering period.

4.4.2. Physical properties of laser-treated blueberries

Physical properties of osmotically treated materials are largely influenced by product volume change, as well as the extent of water loss and solid gain (Shi and Le Maguer 2003). As previously seen in the stepwise infusion at 5 ºBrix/day increments, notable effects of the two laser perforation parameters on the physical characteristics of the final product were again observed at each concentration investigated in the present study.

Although statistical significance was not always reached, the average final berry counts showed a consistent decrease with increasing perforation depth and

density (Figure 4.3a), indicating that the deeper the penetration and the larger the number of perforations per berry, the larger the size of the infused blueberries. At each solution concentration, untreated blueberries (control) showed the highest berry count (thus smaller and lighter berries), indicating a positive effect of laser perforation in increasing the size of the infused product. Increasing solution concentrations contributed to an increase in the average final berry count, indicating a negative effect of using higher solution concentrations on the size of the berries (Figure 4.3a). These trends were generally true for the final berry diameter (Figure 4.3b), thereby confirming the influence of the two laser perforation parameters and solution concentrations on the size of finished product.

Higher values in bulk density are attributable to a lower degree of product shrinkage and higher solid gain by osmotically treated materials (Kim and Toledo 1987; Kaymak Ertekin and Cakaloz 1996b). As seen for the final berry count and final berry diameter, a clear tendency of lowering bulk density values was seen with increasing solution concentrations (Figure 4.3c). At each solution concentration, average bulk density values tended to increase with increasing perforation density and depth, with the control sample having the lowest average bulk density value. This result is in line with the final product yield values, as low sample shrinkage would be expected for those exhibiting a high final yield as a result of the promoted solute impregnation by laser perforation. The reduced shrinkage in the laser-perforated infused berries was also evident from their larger diameter.

A visual examination of the final product (Figure 4.4) further confirmed the above results. It was apparent that the absence of laser perforation (control, Figure 4.4a) resulted in considerable berry shrinkage and wrinkling. A large proportion of the untreated blueberries infused at 30 ºBrix/day increments was found ruptured and collapsed (picture not shown). This is clearly a result of the increased concentration gradients. Product shrinkage was also prevalent for those with surface perforations (G2D1, Figure 4.4b), but notably reduced for G2D2 (Figure 4.4c). The berries with the largest penetration depth (D3, Figure 4.4d, e, f) maintained intact fruit shape and

appearance with minimal shrinkage even when infused using the highest concentration increment investigated (i.e., 30 ^{o}Brix). It should also be pointed out that the effect of laser perforation depth appeared to be more prominent than that of perforation density for the results of the physical characterizations and visual examination of the final product. This is in agreement with the previous observations at 5 °Brix/day increments (Chapter 3).

4.5. Conclusions

In addition to the previous findings, the results of the present investigation highlight two important properties of the laser-assisted skin pretreatment for the sugar infusion of blueberries. First of all, perforations with a CO_2 laser, especially when the fruit is fully penetrated (D3), produced a marked increase in the final fruit weight at higher solution concentrations. This implies that laser perforation considerably accelerates the infusion process without sacrificing the final process yield. Secondly, as a result of the enhanced solute impregnation provoked by laser perforations, the laser-treated samples were considerably larger and showed reduced product shrinkage. Compared to the untreated sample or those with surface penetration (D1), complete penetration of the fruit by laser produced a final product with its original round fruit shape, minimal wrinkling, and no disruption of fruit integrity. The magnitude of fruit weight gain and the size of the infused fruit became significantly smaller with increasing solution concentrations, but laser perforation evidently alleviated negative impacts that could have been caused by the increasing osmotic gradient. Of the two laser perforation parameters investigated, perforation depth was again found to have more significant impacts on fruit weight gain and measured physical attributes. Surface perforation was ineffective in producing a significant final yield increase and preventing fruit shrinkage.

Based on the previous and present findings, it can be concluded that the laser-induced microholes in the fruit serve a dual-purpose during the course of stepwise sugar infusion. They serve as spots where the osmotic pressure induced by an

increased concentration gradient can be actively dissipated, thereby preventing fruit shrinkage and collapse. The laser-induced perforations also provide open pathways through which effective solute impregnation can be attained. As a result, solute gain by the fruit is enhanced and the degree of fruit shrinkage and breakage is remarkably reduced. Full penetration of the fruit was especially effective in the previous and present experiments, presumably because it efficiently brought the core of the berry in contact with the osmotic solution.

Table 4.1 Combinations of perforation grid size (i.e., perforation density) and perforation depth used in the present and previous study (Chapter 3). The shaded combinations are those examined in the present experiment.

Grid Size / **Depth**	Grid 1 (5.0 mm x 5.0 mm)	Grid 2 (3.8 mm x 3.8 mm)	Grid 3 (2.5 mm x 2.5 mm)
Depth 1 (surface penetration)	G1D1	G2D1	G3D1
Depth 2 (penetration through middle section)	G1D2	G2D2	G3D2
Depth 3 (penetration through the fruit height)	G1D3	G2D3	G3D3

Table 4.2. Effects of perforation density and depth on fruit weight change and infusion duration at various solution concentration increments/day.

Parameter		10 ºBrix				20 ºBrix				30 ºBrix			
Density	Depth	Weight change			# of days to reach final Brix^{NS}	Weight change			# of days to reach final Brix^{NS}	Weight change			# of days to reach final Brix **
		Day 1^{NS}	Final***	% final yield		Day 1^{NS}	Final***	% final yield		Day 1***	Final***	% final yield	
G2	D1	914.73 (3.97)	924.62 (5.31)	12.99%	13.33 (0.33)	889.95 (3.43)	771.66 (9.56)	11.97%	9.67 (0.33)	857.71^{a} (5.11)	702.66 (4.89)	13.52%	8.00^{ab} (0)
	D2	916.18 (0.92)	1040.00^{a} (17.74)	27.09%	13.00 (0)	881.09 (2.82)	868.90 (6.81)	26.08%	9.67 (0.33)	869.32^{ad} (2.87)	837.78 (1.19)	35.35%	7.67^{ab} (0.33)
	D3	917.33 (5.67)	1110.34^{b} (9.89)	35.69%	13.00 (0)	886.58 (6.24)	988.62^{a} (12.07)	43.44%	9.33 (0.33)	874.74^{ac} (5.00)	972.78 (12.33)	57.16%	7.67^{ab} (0.33)
G1	D3	916.35 (11.30)	1056.34^{abc} (18.93)	29.08%	13.00 (0)	899.50 (1.86)	955.90^{a} (4.15)	38.70%	9.33 (0.33)	894.12^{b} (3.72)	932.78 (11.34)	50.70%	8.00^{ab} (0)
G3	D3	904.13 (4.03)	1123.00^{c} 6.64)	37.23%	13.00 (0)	888.09 (13.82)	1053.68 (6.00)	52.89%	8.67 (0.67)	879.69^{bc} (1.58)	1023.41 (4.92)	65.34%	7.00^{b} (0)
Control		918.17 (2.28)	818.30 (6.38)	-	13.33 (0.33)	885.23 (0.28)	689.19 (11.01)	-	9.67 (0.33)	848.14^{d} (3.01)	618.96 (0.21)	-	8.67^{a} (0.33)

Numbers in parenthesis are standard errors (n=3). Common superscript letters within the same column indicate no significant difference by Tukey's HSD test (NS: no statistical difference, *$p < 0.05$, **$p < 0.01$, ***$p < 0.001$).

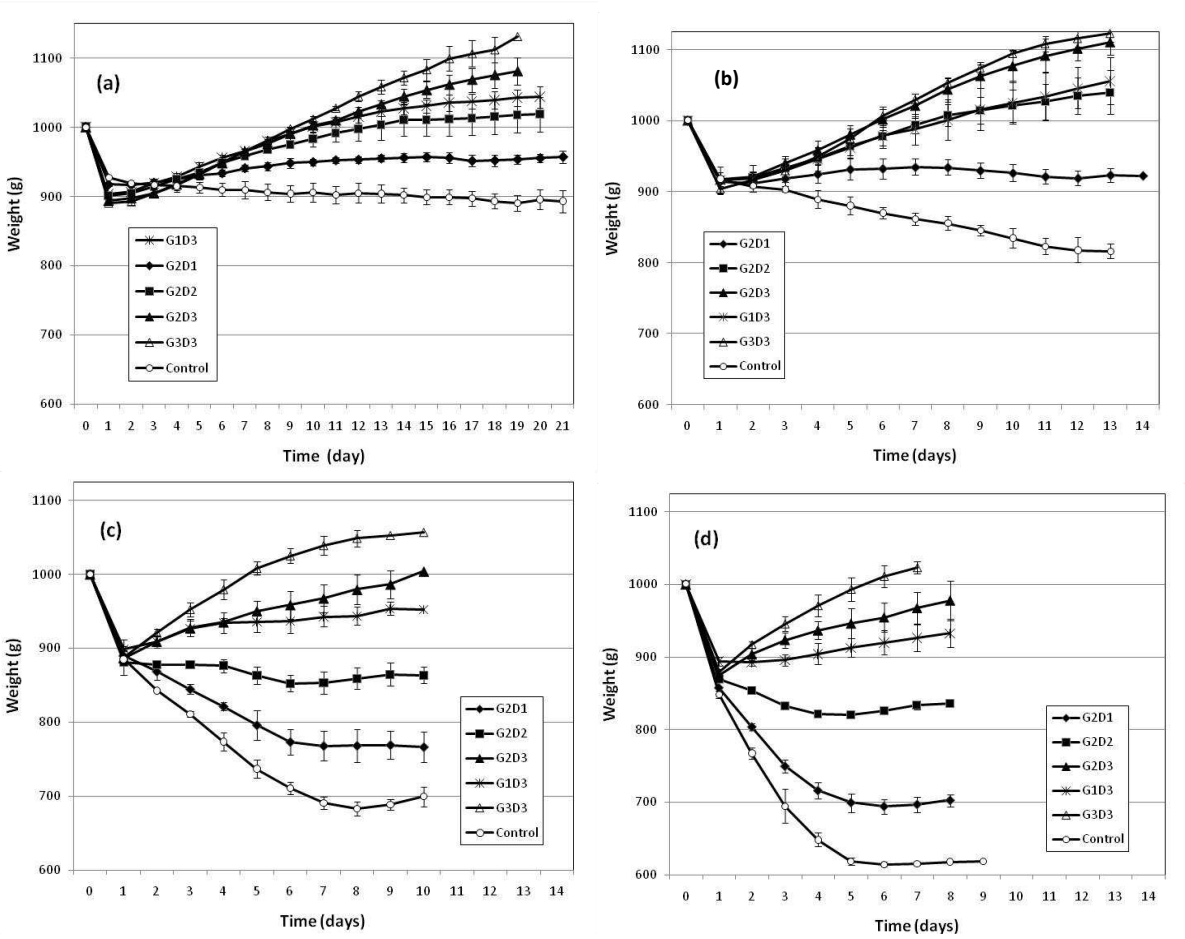

Figure 4.1. Changes in blueberry weight during the stepwise infusion with varying solution concentration increments/day. a) 5 °Brix (adopted from Chapter 3), b) 10 °Brix, c) 20 °Brix, and d) 30 °Brix. Error bars indicate standard deviations (n=3).
Note: the horizontal axis scale of (a) is different from the the other three graphs due to the difference in the infusion duration.

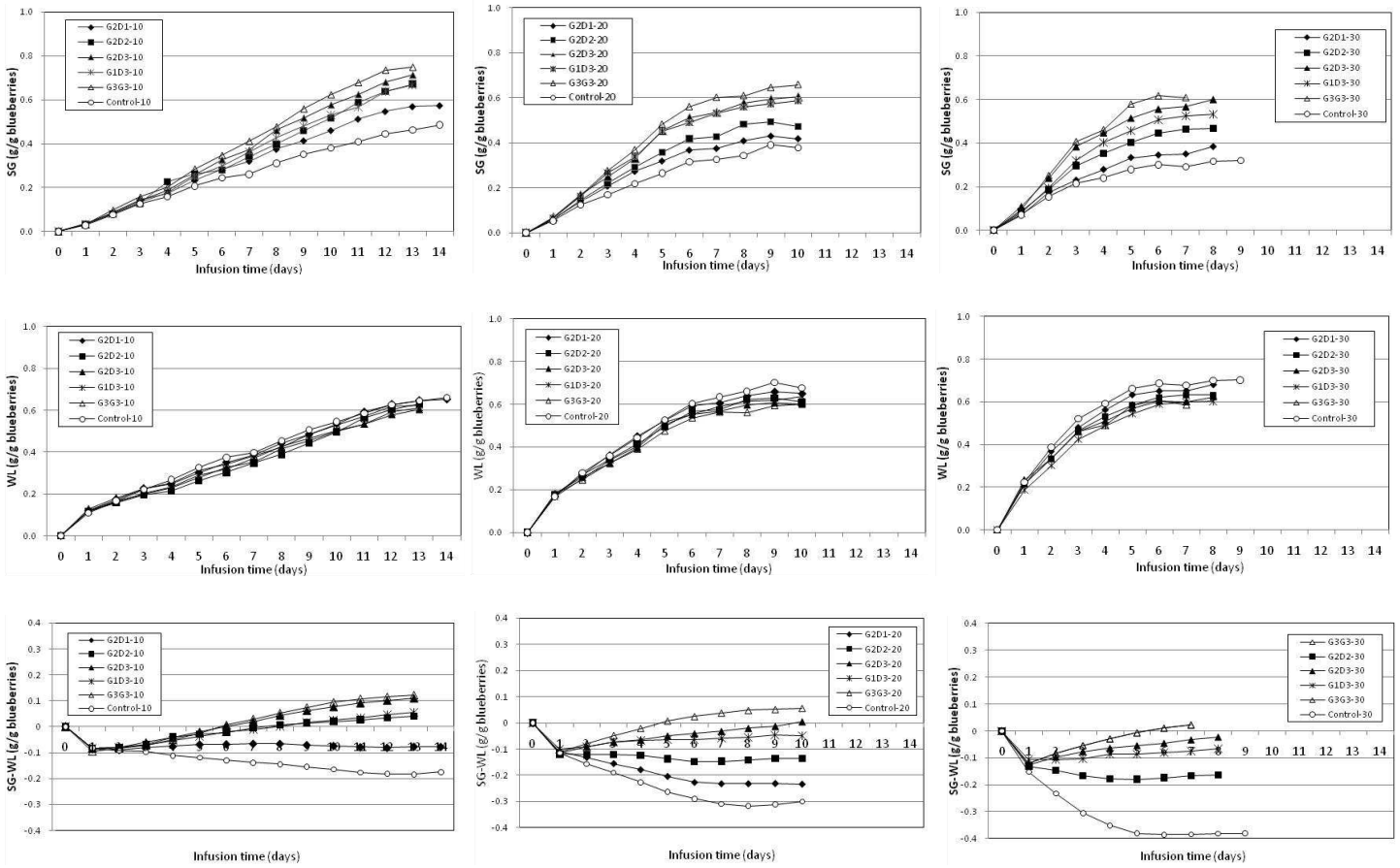

Figure 4.2. Extent of water loss (WL, top row), solid gain (SG, middle row) and total weight change (WL-SG, bottom row) of laser perforated blueberries during the stepwise infusion with varying solution concentration increments/day. Each column shows the effect of HFCS solution concentration (left: 10° Brix, middle: 20 °Brix, right: 30 °Brix).

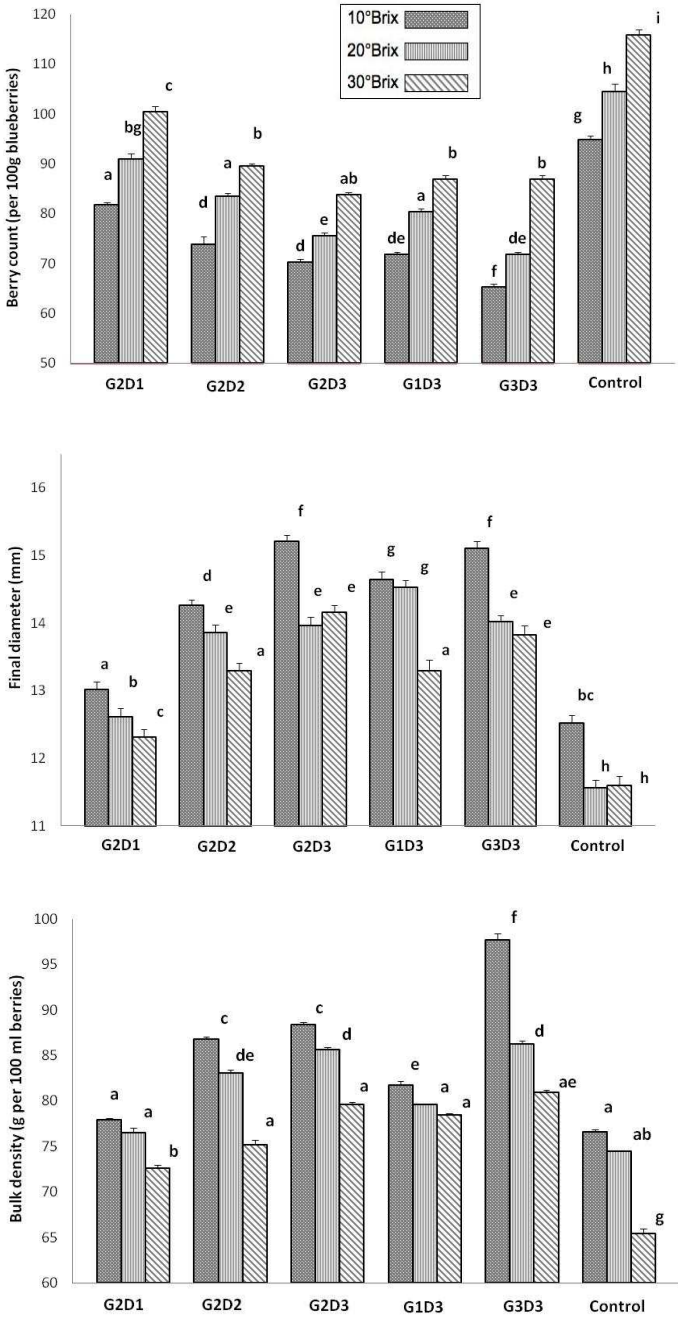

Figure 4.3. Physical characterization of blueberries infused with varying HFCS solution concentration increments/day. (a) average final berry count per unit mass (top, n = 100), (b) average final berry diameter (middle, n = 3), and (c) average berry bulk density (bottom, n = 3). Error bars indicate standard errors. Common letters within the same graph indicate no significant difference by Tukey's HSD test followed by the one-way ANOVA ($p < 0.05$).

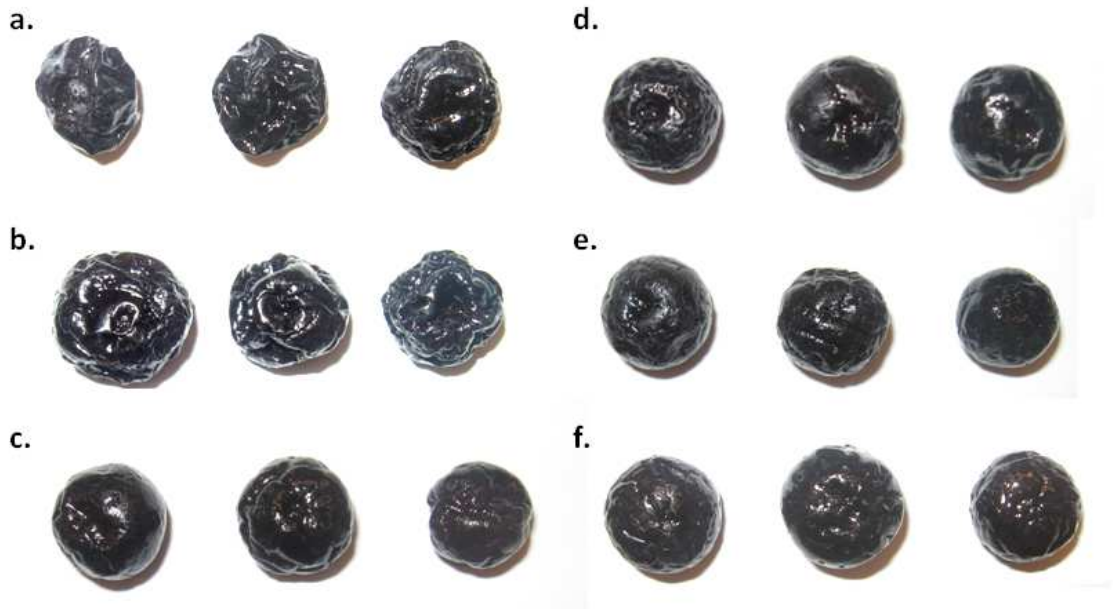

Figure 4.4. Appearance of the final product after the stepwise infusion with a HFCS solution at 30 °Brix increments/day. a) Control, b) G2D1, c) G2D2, d) G1D3, e) G2D3, and f) G3D3.

CHAPTER 5

GENERAL CONCLUSIONS AND FUTURE STUDIES

Although restricted to one commodity, the findings in the present research show that CO_2 laser perforation can be a viable skin pretreatment for the sugar infusion of blueberries. The first experiment (Chapter 3), investigated the effect of various perforation density/depth combinations on the stepwise sugar infusion using low concentration increments (5 °Brix/day). A notable promotion of solute gain was observed for the laser-treated blueberries, especially for those that received moderate to high doses of laser perforation. As a result, a significant improvement on the process yield (ranging from 3% to 24% compared to the untreated fruit) was achieved, and product shrinkage and volume loss were markedly reduced. Although a moderate process yield was attained, a considerable portion of the mechanically treated fruit was ruptured at the end of the infusion process due to the invasive nature of the treatment. In contrast, the fruit with moderate and high doses of laser perforation maintained its original shape and appearance without excessive wrinkling and texture hardening. The second experiment (Chapter 4), evaluated CO_2 laser-assisted skin pretreatment under the stepwise infusion utilizing higher solution concentration increments (10, 20 and 30 °Brix/day). The results further highlighted the efficacy of this novel pretreatment method. Although the effect of surface penetration (D1) and intermediate penetration (D2) on promoting solute gain diminished with increased solution concentrations, a full penetration of the fruit (D3) effectively provoked solute gain. Consequently, considerable fruit weight recovery after the initial dewatering period was attained, and reduced shrinkage and maintenance of original fruit appearance were observed in the final product. The use of higher solution concentrations markedly shortened the time required for the fruit to reach the target soluble solid content (70 °Brix), but only those subjected to full laser penetration showed intermediate weight gain when infused with higher solution concentrations. It is assumed that laser treatment allowed the formation of microholes that were minimally invasive to the cellular structure of the fruit, serving a dual purpose during the infusion process; the laser-induced

perforations served as pathways for solute incorporation from the osmotic solution, while alleviating the buildup of pressure within the material due to increased osmotic gradient, a major culprit of cellular rupture and collapse during osmotic treatment. Laser perforation's ability to enhance process yield and final product quality with shortened process time would make this novel approach an appealing alternative to traditional skin pretreatment techniques.

In the present research, IQF blueberries were chosen as a raw material, as the use of fresh blueberries was restricted by their short harvest season and shelf life. Some advantages and drawbacks of using prefrozen materials for osmotic treatment have been noted in the literature; it is reported that prefrozen materials offer enhanced rates of water removal and solute uptake, but the use of prefrozen materials may cause a considerable leaching of cell constituents during the process and subsequent alteration in color and texture (Taiwo and others 2003). However, Saurel and others (1994) observed no significant difference in the behavior of fresh and frozen apple tissues with respect to solute uptake. No literature addressing the difference of fresh and frozen blueberries in terms of their response to osmotic treatment was found. It may therefore be of interest to conduct a study using fresh and prefrozen materials to compare the responses of the two to laser perforation and subsequent osmotic treatment. In addition, because infusion operations at lower temperatures would lead to considerable energy savings, it may be of practical interest to examine the effect of laser perforation on infusion process characteristics at ambient temperatures rather than slightly elevated temperatures (ca. 50 °C), which were used in the present work as they were the temperatures frequently used in published studies of osmotic treatment of fruits.

In the present research, the perforation of IQF blueberries was achieved as a result of instantaneous thermal ablation by energy-intensive laser beams penetrating the internal structure of the fruit. Previous research investigating the utility of laser processing for various food products (e.g., Choi and Li 2006; Etxeberria and others 2006; Chen and others 2009a; Chen and others 2009b) were accompanied by

morphological studies that provided preliminary information on laser-induced structural changes. However, because the application of laser beams was limited to food surfaces in these studies, there is presently a lack of scientific knowledge regarding the effect of laser beams on the internal structure of food materials. The microscopic analysis of laser-perforated fruits with appropriate instrumentation (e.g., scanning electric microscopy (SEM)) will provide valuable information regarding laser beam-food material interactions, laser-induced structural and compositional changes, and the degree of cellular damages at a microstructural level.

This research was conducted in a laboratory setting using a small-scale 100 W CO_2 laser processing system to study the efficacy and potential use of this novel approach. In actual industrial settings, CO_2 lasers above 1 kW of power coupled with various automations are commonly used in the material processing industry, which allow increased processing speed and efficiency. This would cause the initial investment costs to be substantially higher (Bell 2006). The advantages of improved final yield and quality of the infused product must therefore be critically weighed in view of high investment costs and the increased operating expenses associated with the implementation of laser technology. In order to implement this technology in real commercial settings, one of the next research steps should be dedicated to a conceptual study assuming a commercial production size operation in order to undertake an economic evaluation of the complete process. This will be crucial in addressing the advantages of the technology more clearly.

Furthermore, questions may be raised as to the effect of laser perforation on sensory properties of infused products. Because the tissue damage induced by lasers is thermal in nature, a notable burnt smell was detected from the IQF blueberry samples immediately after they were subjected to laser perforation. Informal taste tests suggested the burnt note of the fruit slowly vanished as the infusion process continued, and at the end of the process it was virtually non-existent. This is presumably because of the high degree of solute impregnation attained over the course of a relatively long infusion period. Unfortunately, we were unable to conduct a formal sensory

evaluation, as the application of laser beams to edible food materials has not been approved in the United States. To date, no scientific literature is available regarding substances formed through the interaction of laser beams and foodstuffs that are potentially harmful to human consumption. Because the volume of the laser-perforated portion accounts for only a small percentage of the total fruit volume in the specific application investigated in this research, it may be reasonable to assume that the amount of substance that could potentially be generated by lasers would be minimal. Nevertheless, the safety aspect is of crucial importance for the commercial adoption of any technology, and future investigation is therefore needed to address this critical issue.

In conclusion, the results of this thesis research demonstrates the promising efficacy of the CO_2 laser-aided perforation process as a novel skin pretreatment for the sugar infusion of frozen blueberries. From a broader perspective, the results may be encouraging to food processors, scientists, and engineers to pursue other potential applications of laser technology for food processing.

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APPENDICES

APPENDIX A

TWO-WAY ANOVA (ANALYSIS OF VARIANCE) SUMMARY TABLES CHAPTER 3 SUPPREMENT

This appendix contains the two-way ANOVA (analysis of variance) tables for the experimental data (i.e., Day 1 weight and final weight of the blueberries) presented in Chapter 3. All statistical analyses were carried out using TIBCO Spotfire S+ (TIBCO Software Inc., Palo Alto, CA) at a significance level of $p < 0.05$.

Table A.1. Effects of three levels of grid size (i.e., perforation density) and perforation depth on the mean Day 1 weight of blueberries.

Source of Variation	**df**	**Sum of square (SS)**	**Mean square (MS)**	**F-values**	**p-values**
Grid size(G)	2	751.727	375.863	23.77489	<0.001
Perforation depth (D)	2	2204.214	1102.107	69.71278	<0.001
G x D interaction	4	71.388	17.847	1.12889	0.3741403
Residuals	18	284.567	15.809		

Table A.2. Estimated marginal means for Day 1 weight of blueberries (g).

Grid size / Depth	**G1**	**G2**	**G3**	**Marginal row totals**
D1	921.81	917.41	913.99	917.74
D2	911.88	901.31	894.71	902.63
D3	903.75	894.35	890.43	896.18
Marginal column totals	912.48	904.36	899.71	2716.55 (Grand totals)

Table A.3. Effects of three levels of grid size (i.e., perforation density) and perforation depth on the mean final weight of blueberries.

Source of Variation	**df**	**Sum of square (SS)**	**Mean square (MS)**	**F-values**	**p-values**
Grid size(G)	2	211911.40	10595.70	40.8259	<0.001
Perforation depth (D)	2	66923.97	33461.99	128.9311	<0.001
G x D interaction	4	726.11	181.53	0.6994	0.6023301
Residuals	18	4671.61	256.53		

Table A.4. Estimated marginal means for final weight of blueberries (g).

Grid size / Depth	**G1**	**G2**	**G3**	**Marginal row totals**
D1	930.63	955.58	984.06	969.82
D2	982.40	1018.93	1065.33	1022.22
D3	1042.70	1080.89	1112.18	1078.59
Marginal column totals	1012.55	1018.47	1053.86	1053.86 (Grand total)

APPENDIX B

CALCULATINON OF ENERGY COMSUMED BY CARBON DIOXIDE (CO_2) LASER PERFORATION

The energy consumption for laser processing can be calculated using the following equation.

$$E_s = P_d \cdot V_s$$

where E_s is the energy (J) consumed by laser perforation, P_d is the density of laser power (W/mm), and V_s is the speed of laser processing (mm/sec).The amount of energy consumed by laser perforation can therefore be calculated as follows:

Energy (J) = laser power level (W) x firing duration (s)
x perforation density (per unit mass) x sample mass

Table B.1 shows the experimental conditions used in the study outlined in Chapter 3. Table B.2 summarizes the amount of energy consumed for treating 1000 g of IQF blueberries using each perforation density: perforation depth combination used in the study. A sample calculation is also shown.

Table B.1. Summary of the experimental conditions used in the study outlined in Chapter 3.

Power level	100 W (100 %)
Laser firing duration[1]	3 ms (D1), 15 ms (D2), 42 ms (D3)
Average # of perforation per berry[2]	8 (G1), 18 (G2), 38 (G3)
Average weight of IQF blueberries	1.65 g/berry
Mass of sample per batch	1000 g

[1] Correlates to perforation depth; 2 governed by the three different grid size (see Chapter 3)
*1 millisecond (ms) = 0.001 second

Table B.2. The amount of energy consumed by perforating IQF blueberries by CO_2 laser (in the study outlined in Chapter 3, per 1000 g sample).

Depth \ Density	**G1** (8 holes)	**G2** (18 holes)	**G3** (38 holes)
D1 (3 ms)	1455 J	3273 J	6909 J
D2 (15 ms)	7273 J	16364 J	24546 J
D3 (42 ms)	20364 J	45818 J	103636 J

Example calculation:

G1D1: 100 (W, J/s) x 0.003 (s) x 8 (holes/1.65 g berry) x 1000 g (sample/batch) ≈ 1455 J