8 Fruit Freezing

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CONTENTS

8.1 INTRODUCTION

Most fruits have limited harvest periods. In order to have extended availability, some form of storage and preservation is needed. A variety of preservation systems exist, each of which results in an extended shelf life. Freezing provides a significantly extended shelf life and has been successfully employed for the long-term preservation of many fruits. In this chapter, we will discuss the application of freezing preservation to fruits. In order to do so, it is necessary to first discuss the freezing preservation process briefly and to consider the special problems of preservation that are presented by fruits.

8.2 THE FREEZING PROCESS

Freezing involves the use of low temperatures. In general, reactions take place at slower rates as temperature is reduced. One of the more common temperature dependences of rate is expressed by the Arrhenius equation:

$$\log K = \text{const} - E^A/RT$$

where K is the reaction rate, E^A is the activation energy, R is the gas constant, and T is the absolute temperature. Based on this equation, the reduction in rate can be quantified through the activation energy. All other things being equal, therefore, storage at a low temperature would give an extended storage life, and the lower the temperature the better. All other things are not equal, however. The Arrhenius expression describes the temperature dependence of reaction rates when the mechanism of the reaction does not significantly change. It also describes single reaction rates and does not necessarily describe the temperature dependence of a series of reactions that have different individual temperature dependences. Furthermore, the Arrhenius expression does not describe reaction rates where the direction of the equilibrium changes, for example, phase change, where the favored form is temperature-dependent. For all of these reasons, it is necessary to examine the effect of temperature change in rather more detail.

8.2.1 The Influence of Temperature Change

As temperature is lowered, many processes will slow. In tissue systems, there may be changes in membrane and organelle properties that produce altered metabolic pathways. Should this happen, the mere act of chilling can produce product quality loss, known as chilling damage (Lyons, 1973; Wilson, 1987), If chilling damage is not a problem, refrigeration close to the freezing point can lead to a significant extension of shelf life. Freezing and the freezing point are the next sources of complications to the simplified "lower temperatures give longer storage" picture. Why should this be? Freezing implies phase change. The aqueous component of the tissue separates into at least two phases, one of which is ice. Because some of the water has separated out as ice, the remaining liquid phase has to have increased solute concentrations. The presence of ice and the increase in solute concentration can have significant effects upon the state of the tissue that is being frozen (Brown, 1979; Reid, 1983). Let us therefore follow a freezing process in some detail, from this particular viewpoint.

8.2.2 The Freezing Profile

In order to freeze, heat must be removed from the product. Figure 8.1 shows a typical freezing profile for a point close to the surface of a product. In region A, the temperature is falling but is still above the freezing point. At the surface, as cooling progresses, the temperature will reach the freezing point. Due to difficulty in seeding ice, freezing does not immediately initiate. The

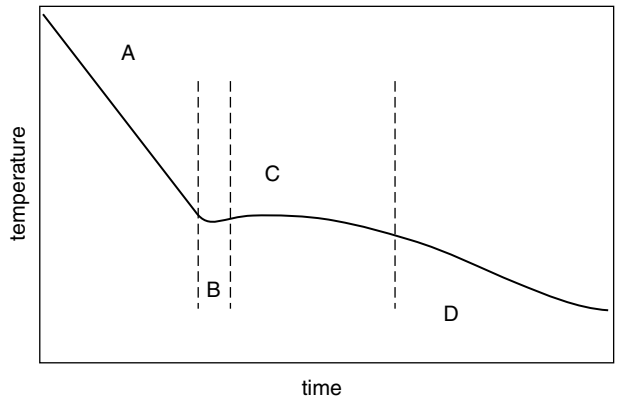

FIGURE 8.1 Schematic cooling curve. See text for an explanation of segments.

temperature continues to fall. At some point, seeding (or nucleation) initiates freezing, and the temperature rises to close to the freezing point. This is region B in the plot. Closer to the center of the product, this undercooled region is not seen, and freezing initiates at the freezing point. As heat continues to be removed, the temperature now falls more slowly. The reason for the slower fall, given that the rate of heat removal is unchanged, is that heat is released by the phase change from water to ice. This heat, termed latent heat, is additional to the sensible heat loss that accompanies temperature change. This region of slower temperature change due to the heat release of ice formation is region C in the plot. As the process continues, the rate of ice formation decreases, the contribution of latent heat decreases, and the temperature begins to fall more rapidly. This is region D. Many workers, e.g., Persson and Lohndahl (1993), have labelled these regions as follows: region A — prefreezing, regions B and C — freezing, region D — reduction to storage temperature.

8.2.3 The Freezing Process Described by Phase Diagram

Another view of this freezing process can be obtained through the use of a simplified phase diagram. If we assume that in the initial freezing process only ice will separate out, we can utilize the schematic binary phase diagram of Figure 8.2 to help describe the process. The product composition

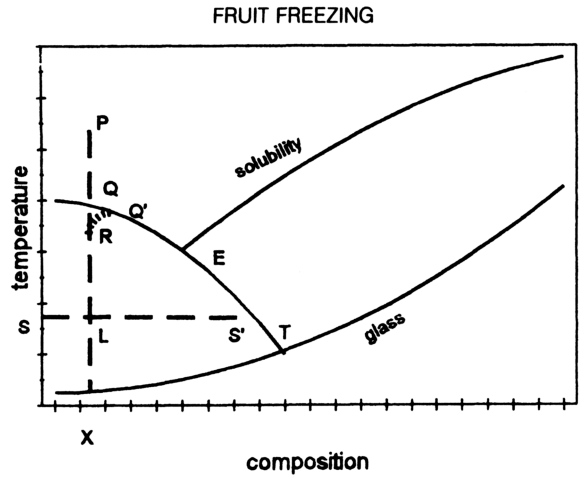

FIGURE 8.2 Schematic phase diagram for a binary system. See text for an explanation of labels.

is assumed to be represented by X. Initially, as the product is cooled, the composition stays unchanged. Segment PQ represents this initial cooling and corresponds to region A of Figure 8.1. Region B, the period of undercooling prior to the initiation of crystallization, is represented by the short section QR that lies below the liquidus curve (the liquidus curve shows the concentration dependence of the melting point, indicating the one temperature at which a solution of a *given* composition and ice can coexist in equilibrium). When freezing initiates, the system separates into two phases: (1) ice, represented by the left axis (i.e., 100% water) and (2) a more concentrated solution, where the concentration is defined by the liquidus coordinate for that temperature. This is represented by the short curve from R to Q′, where Q′ is a port on the liquidus curve QT. The curved segment of the liquidus from Q′ to S illustrates the change in concentration of the nonice matrix as we move through region C. The segment of the liquidus from S to T is region D, where the rate of ice formation has reduced. A useful property of a phase diagram of this type is that it allows for the estimation of the amount of ice at any temperature. For example, the line S′ S at temperature T_1 crosses the lute PX at point L. For our system of overall composition X, at temperature T_1, the ratio of the amount of ice to the amount of solution of composition represented by point S is simply S/LS′. The overall composition is still X. This diagram shows that, as the temperature decreases, the amount of ice increases, and the composition of the unfrozen phase increases. At some temperature and liquid phase composition, a second phase may start to separate out, yielding what is termed a eutectic mix. This would happen at point E, where the solubility curve of the crystallized material intersects the liquidus. Solute crystallization does not always take place, due to kinetic constraints (Franks, 1982). Should this prove to be the case, the unfrozen phase continues to cool until it crosses a kinetic threshold and becomes effectively solid (in a glassy state). Since this glassy phase is produced by the freeze-concentration process just described, it is often referred to as the glassy state of the maximally freeze-concentrated matrix. The temperature of transformation to this glassy matrix can be measured and has some significance for frozen storage stability because it has been suggested that, once the unfrozen matrix enters the glassy state, the rate of change in storage will significantly reduce (Levine and Slade, 1989; Slade and Levine, 1991). The relevance of this in producing freezing is discussed briefly in Reid (1990). Current research in my laboratory seeks to establish this critical temperature for many frozen products, including fruits.

8.2.4 Freezing in Tissue Systems

Up to this point, the discussion has been of freezing in a uniform system. Consider now the freezing process as it might occur in plant tissue. In addition to the complexities introduced by the formation of ice as temperature is lowered, an additional complexity is introduced. In plant tissues there are cells with cell walls. In other words, there are at least two distinct environmental situations. There are cell interiors that are individual, separate entities, and there are the extracellular spaces in between that exist in a connected network. This additional state, "inside or outside," interacts with the phase state of the aqueous system. The interaction depends upon the properties of the cell wall boundaries. If the cell wall and cell membranes are intact and in functional form, they provide a barrier that is permeable only to certain small molecules, including water. If this barrier is somehow damaged, molecular movements through the barrier become much easier. Damage to the barrier can result from a variety of causes. In processing, the most common cause of damage is heat treatment, such as might be applied in blanching. If the barrier is intact, it will allow the process of osmosis (or selective water transfer) to occur between the cell contents and the external environment of the cell. This assumes particular relevance if the external environment is changing due to ice formation. A damaged barrier does not support osmotic processes. The process of osmosis is the passage of solvent through a barrier permeable to solvent but not to solute, in such an amount as to tend to equalize the concentration of the solutions on either side of the barrier.

8.2.4.1 Freezing in the Presence of Cells

Let us look at the freezing process again, taking into account the presence of cells. The first cooling, A, is the same. Once we reach regions B and C, the presence of cells changes the detailed picture. Ice forms external to cells, in general, because even if some ice growth initiates within a cell, it can only reach another cell by growing into the external matrix between cells. If ice is in the external matrix and the cell wall barrier is intact and effective, ice does not penetrate into the cell. Because water can permeate through the membrane, an osmotic process will occur. Water will leave the cell, forming additional extracellular ice and, at the same time, increasing the concentration of the internal cell contents in the direction of the concentration of the external unfrozen matrix. As the temperature falls and the external unfrozen matrix concentration increases as described by the liquidus line in the phase diagram, the concentration of the internal medium will tend to increase in the same manner. The maximum rate at which water can leave the cell is important to the effectiveness of this process, as this governs the maximum rate at which the concentration of the internal medium can increase. If water cannot be exported sufficiently rapidly, the internal contents will be more dilute than required for equilibrium (described by a coordinate point below the liquidus). The contents are therefore undercooled by an amount described by the difference between the liquidus temperature coordinate for the actual internal solution composition and the actual internal temperature. If the undercooling exceeds a threshold value characteristic of the particular tissue, internal seeding of ice and consequent ice growth may occur. Once ice forms within the cell, the concentrations of the internal and external unfrozen matrices match, and there is no longer an osmotic driving force for water transfer. The system-dependent variation in cross-barrier water transport rates of the osmotic process accounts, in part, for the differences between fast freezing and slow freezing. In fast freezing, there is insufficient time to remove the water from the cell through osmosis. The cell contents undercool and seed, and ice forms within the cell. In slow freezing, there is enough time to remove the appropriate amount of water from the cell. The concentration of the cell contents increases sufficiently rapidly to prevent the cell contents from being significantly undercooled. Ice does not form within the cell. Note that, if any change should occur on freezing that would prevent this water from returning to the cell on thawing, then the water will become a source of drip loss. It may be for this reason that drip loss is often more marked in slowly frozen fruits. Fast freezing and slow freezing are therefore operational definitions, and the threshold freezing rate separating fast freezing from slow freezing will be system dependent.

8.2.5 The Freezing Process and Freezing Damage

8.2.5.1 Osmotic Damage

When heat is removed rapidly, ice forms rapidly. These ice crystals tend to be small. Because the ice grows rapidly, the concentration of the external unfrozen matrix rises rapidly. Osmotic transfer of water is limited: the cells freeze internally, and little water translocates. In slow cooling, the ice forms slowly, external to the cells, and there is sufficient time for a large amount of osmotic transfer of water from the cells. This results in cell shrinkage that can damage the membranes (Meryman, 1971; Steponkus, 1984). A considerable amount of water translocates. Due to cell wall damage consequent upon the freezing process, this water does not return to the cells on thawing but, rather, becomes drip loss.

8.2.5.2 Solute-Induced Damage

In addition to this cell shrinkage mechanism for damage, primarily linked to the extensive cellular dehydration accompanying slow freezing, there are other mechanisms of damage. The high-solute concentrations of the unfrozen matrix, in particular the high salt concentrations, can cause damage to many polymeric cell components and may kill the cell (Mazur, 1977). To prevent this, some

form of solution-based protection might be needed (Meryman et al., 1977). A typical method for reducing salt concentration-induced damage is to add sugars to the aqueous phase that is undergoing "freeze-concentration." Note that these sugars must actually be incorporated into the solution that is freezing. It is not enough to add the sugar to the overall system. The concentration effect is present whether freezing is fast or slow.

8.2.5.3 Structural Damage

In fast freezing, additional to the concentration effect, the formation of ice within the cell may cause damage to the delicate organelle and membrane structures of the cell. As one consequence, enzyme systems may be dislocated. This may result in uncontrolled enzyme action, leading to a variety of effects, including the production of off-flavors. Prevention of such enzyme-mediated damage can be achieved by utilizing blanching, a prefreezing heat treatment that denatures the enzymes and, hence, terminates their catalytic activity; however, it has to be remembered that blanching, because it is a heat treatment, will influence the semipermeable properties of the cell membrane and also destroy cell turgor. Cell turgor is an important component of the eating quality of many fruits. It is produced by the internal pressure of the cell contents. Lack of turgor is perceived as softness and lack of crispness and juiciness. Where turgor is an important product characteristic, blanching may not be an acceptable procedure, and other steps may be necessary to control enzymically initiated degradative processes. Blanching is not the only cause of reduced turgor. If cells become leaky or lose some of their contents, turgor is reduced or destroyed, and the texture of the fruit becomes much softer (Brown, 1977; Mohr, 1971). A loss of turgor caused by freezing is particularly evident in fruits such as strawberry (Szczesniak and Smith, 1969). Loss of turgor due to processing procedures is of most relevance to fruits that are customarily eaten raw, rather than fruits that are customarily cooked. Cooking, a more severe thermal treatment than blanching, destroys turgor so that the retention of turgor through earlier processing procedures is not necessary.

Familiarity with the molecular picture of the freezing process is necessary if we are to appreciate the sources of the freezing damage that results in a reduction in consumer-perceived quality in comparison to the fresh raw product. Through an awareness of the mechanisms of damage it is possible to identify whether careful design and control of the freezing processes applied to the product might avoid or minimize some of the quality degradation.

8.3 INDUSTRIAL FREEZING METHODS

8.3.1 Freezers

It is now appropriate to consider the industrial freezing processes that are applied to fruit products. In order to remove heat, the product must be brought into contact with a cold medium. This can be cold air, in a blast freezer, cryogenic liquids or gases in a cryogenic freezer, or cold surfaces in a plate freezer. The heat transfer mechanism in cold air is through convection. This can be assisted by blowing the air over the product. Cryogenic gases are similarly blown past the product and, due to their lower temperature, result in more rapid heat transfer. Cryogenic liquids have a higher thermal density and remove heat more rapidly due to an improved heat transfer capability. Heat transfer to a cold surface tends to be by conduction, and its effectiveness depends on the quality of the thermal contact. Reid (1991) discusses briefly the many types of commercial freezers that exist and that can be utilized in the freezing of plant tissues. This discussion includes consideration of the methods by which large quantities of the product can be exposed to freezing conditions, utilizing both batch and continuous methods. A more extensive discussion of freezers is given by Persson and Londahl (1993). The choice of appropriate freezer is, in part, governed by the product size and, in part, by the required freezing rate. Small fruits, which need to be frozen rapidly, might be frozen in a low-temperature, high air velocity blast freezer or in a cryogenic freezer to produce

an individually quick frozen (IQF) product. Fruits packed in large cans or drums, on the other hand, will not freeze quickly due to heat transfer limitations and so are usually frozen in a cold room with a high-capacity cooling unit and reasonable air circulation. Note that it is poor practice to freeze such product in a cold storage room. A separate room should be set aside for product freezing. Retail packs of approximately rectangular brick shape are often frozen in plate (i.e., conduction) freezers. This method is reasonably successful, provided that the package is well filled. Air spaces within the package will slow down heat removal significantly.

8.3.2 Prefreezing Handling and Preparation

Prior to entering the freezer, the fruit must be prepared appropriately. Methods of preparation are specific to the individual fruit, but there are some common factors that can be identified. The preparation begins at harvest. Poor handling at this stage can irreversibly degrade final product quality. Methods of harvesting are discussed in several major textbooks, for example, Woodroof and Luh (1975) and Tressler et al. (1968). Acceptable harvesting methods are designed to minimize mechanical damage to the fruit. After harvest, cleaning will be required. The method of cleaning is fruit specific. Sorting and trimming will also be required to remove undesirable materials. Many fruits are peeled, or they may be sliced. A variety of specially designed pieces of equipment exists for these tasks. It is often necessary to remove field heat rapidly prior to these process steps, especially for highly perishable fruits, if unacceptable damage is to be avoided. The processor has the responsibility of delivering the fruit to the freezing equipment at as high a quality level as is practical.

8.4 FREEZING METHODS FOR SPECIFIC FRUITS

In this section, details of the processing procedures for selected fruits are given. The information summarized in this section comes from a variety of sources, including Woodroof and Luh (1975), Tressler et al. (1968), and TRRF (1993).

8.4.1 Apple

Not all varieties of apple result in an acceptable product when frozen, whether the end use is for the bakery trade or for other purposes; however, some cultivars of apple are suitable for freezing. These are sorted, washed, peeled, cored, and sliced. The sliced fruit is treated to minimize enzymatic browning. This can be achieved by application of antioxidant solutions, including some proprietary treatments. One common treatment is salt brining, soaking slices in a 1% salt solution in order to remove intercellular air. Ascorbic acid solutions can also be used, but these tend to be expensive. A surface blanch, using steam or boiling water, can also be employed, though it results in a softened slice that may not be suited for some uses. The treated slices in a ratio of five parts fruit to one part dry sugar are frozen in large 30- to 50-lb containers in a blast freezer below –10°F. Some apples may be frozen using a dehydrofreezing process where about 50% of the water is removed from the apple slices by standard drying equipment prior to freezing the slices.

8.4.2 Apricot

Though some apricots are frozen whole for later processing, the major proportion of apricots are usually frozen as peeled apricot halves. This enhances the tendency for browning and, therefore, requires steps to be taken to minimize browning. The apricots are peeled, halved and pitted, and dipped in ascorbic acid solution to minimize browning, or blanched for a short time to inactivate the enzymes. The halves are packed in sugar or sugar syrup prior to freezing at a 3:1 or 4:1 ratio of fruit to sugar. Air blast freezers are adequate. It is best to freeze the apricots on trays or on a

belt prior to packing into barrels or 30-lb containers. This helps minimize discoloration. Storage should be below 0°F. For good retention of ascorbic acid, storage should be at –20°F.

8.4.3 Avocado

Avocados present a challenge to the commercial freezer due to their high oil content that readily becomes rancid, and also because of a very active oxidative browning system. Pureed avocado is a successful product. Preservation life is enhanced by lowering the pH of the puree to below 4.5 through the addition of lemon juice, lime juice, and salt. Packaging under nitrogen also enhances shelf life. Vacuum packaging has also been employed. Any reasonably rapid freezing method can be employed. Storage should be around 0°F for a reasonable shelf life.

8.4.4 Berries

Many varieties of berries are frozen. Berries can be frozen in syrup or as individual berries. As individual berries, they may be tray frozen or IQF frozen on a belt in an air blast or cryogenic freezer. Individually frozen berries will be discussed after bulk methods for freezing for retail or the processing trade.

Red raspberries for retail are packed in an approximately 50% syrup, in the proportion of six parts berry to four parts syrup, and 10- and 16-oz containers are used. Any reasonably rapid freezing method may be employed.

Black raspberries are used for further processing and are packed in 30-lb containers or larger. In order to successfully freeze berries in a large container, the following procedures have been shown to be necessary (*TRRF Commodity Storage Handbook,* 1993).

1. The temperature of the fruit should not exceed 60°F at the time of filling.
2. The containers should be moved to the freezer as quickly as possible.
3. The temperature on entering the freezer should be below 70°F.
4. Freezer conditions (air temperature < –15°F and airflow velocity high) should allow for the center of the container to reach a temperature of 32°F or less within 48 h.
5. Freezing should be continued until the center temperature is 0°F. This should take no more than 4 to 5 d.
6. Storage should be below 0°F.

Reasons for these recommendations were discussed previously in the text.

Blackberries, boysenberries, loganberries, and others are frozen utilizing the same procedures as have been described for raspberries. Blueberries are frozen in 20-lb containers, with steps being takers to minimize or eliminate air in the package.

8.4.5 Cherry

The major portion of cherries frozen are tart cherries, though some sweet cherries are also frozen. The procedures for freezing are essentially the same. Tart cherries are harvested when bright red, sweet cherries when mature. The cherries are held and transported in ice-cold water, which reduces losses due to crushing and bruising and makes the fruit firmer for pitting. Fruits are size graded, pitted, packed with sugar in large cans, and frozen in a blast freezer.

8.4.6 Coconut

Shredded coconut can be frozen without any particular preparation. The rate of freezing is not critical so long as cooling is sufficiently rapid to minimize microbiological contamination. Storage, in large containers, is at 0°F.

8.4.7 Cranberry

Cranberries are frozen at 0°F using conventional techniques. The majority of the frozen crop is used for processing.

8.4.8 Dates

Fresh dates may be frozen. The use of a good moisture-proof and vapor-proof wrapping is recommended to prevent moisture loss during freezing or storage.

8.4.9 Figs

Figs can be frozen as whole fruit in heavy syrup or as sliced fruit as four parts fruit to one part water. Standard freezing methods are employed. Storage temperatures should be below 0°F.

8.4.10 Mango

Mango is frozen as slices in syrup. The syrup contains ascorbic acid to inhibit polyphenol oxidase-induced browning. In addition, mango puree is a significant frozen product. Purees can be single or double strength. Storage should be at or below 0°F. Browning can be a significant problem at higher storage temperatures due to nonenzymic browning.

8.4.11 Melon

Melon is frozen when the texture is firm enough to allow for cutting of cubes or balls that retain their integrity. If too ripe, a very mushy product will result because fully thawed melon loses considerable texture. Melon is usually frozen in syrup.

8.4.12 Papaya

Papaya puree is prepared from ripe papaya. Steamed fruit can be sliced and crushed, and the pulp can be separated from the skin. The acidified pulp is passed through a heat exchanger to inactivate enzymes before cooling and freezing to –10°F.

8.4.13 Peach

In general, freestone peaches are used for freezing. Yellow fleshed varieties are preferred for better texture and lower susceptibility to oxidative browning. Fruit for freezing is usually harvested while still firm and then ripened under control. The peaches are pitted, peeled, and sliced prior to freezing. The usual pack is in syrup (one part syrup to five parts peach) containing around 250 ppm ascorbic acid to help protect against browning. Freezing is usually in packages; 32- to 40-lb packs are common. Larger barrels are also available. Freezing methods are, in general, as described for other bulk frozen fruit products. Some lQF slices are frozen for special markets. Storage should be at temperatures below 0°F if extended shelf life is required. The limiting change is the browning.

8.4.14 Pineapple

Pineapple for freezing is prepared in the same way as pineapple for canning. Rectangular chunks are filled in syrup into cans or bulk containers and frozen. The cans are frozen in a blast tunnel, the bulk containers in a blast freezer. The Smooth Cayenne variety should be frozen. The Red Spanish variety has a tendency to develop off-flavors on freezing.

8.4.15 Plum

A small volume of purple plums and prunes are frozen for institutional markets and for further processing. The fruit is halved, pitted, and packed in syrup in barrels. Freezing is by standard methods. Storage is at or below 0°F.

8.4.16 Rhubarb

Rhubarb freezes easily and requires no special treatment, though a short blanch can extend the storage life significantly. Rhubarb can be frozen with or without sugar. Stalks are trimmed to fit the package. Storage life at 0°F is at least 6 months.

8.4.17 Strawberry

Not all varieties of strawberry freeze well. The selection of varieties for freezing should be made in conjunction with agricultural advisors familiar with the production state. Strawberries are frozen in several forms, depending on the final end use. Most strawberries are frozen as a raw material for use in further processing. Depending on the final product, different freezing procedures might be appropriate. For use in jam manufacture or ice cream, strawberries are packed in syrup and frozen. This can be in 30-lb tins or 50-gal barrels. The strawberries may be sliced and sugared for this process. The procedures described under berries are appropriate. Because strawberries are even more fragile than many other berries, it is recommended that the critical times be shorter. For example, a core temperature of 15°F should be reached in no more than 24 to 36 h. Storage should be at 0°F or below for a reasonable shelf life. Flavor and color are lost rapidly if the storage temperature is too high.

Prefreezing treatments may be applied to strawberries to stabilize the integrity of the tissues. Suutarinen et al. (2000) studied the effects of various calcium chloride or sucrose prefreezing treatments on the textural integrity and drip loss in frozen strawberries. These authors examined $CaCl_2$ concentration of the dipping solution (1, 5.5, or 10 g/l), dipping time (0.25, 7.625, or 15 min) and solution temperature (25, 37.5, or 50°C) and found the greatest firmness resulted from the combination of 5.5 g/l $CaCl_2$ applied for 7.625 min at 37.5°C. Crystallized sucrose was compared to dips in water–sucrose solutions (350 and 700 g sucrose/l) and dipping times of 1 and 15 min were utilized. Sucrose prefreezing treatments also resulted in greater cellular integrity, with those strawberries sprinkled with crystalline sucrose having the highest firmness.

IQF methods are used to produce frozen whole strawberries for both institutional and retail trade. Freezing utilizes air blast, liquid nitrogen, or carbon dioxide belt freezers. Storage of IQF fruit should be at a stable, low temperature to prevent clumping of the berries (due to moisture migration) and loss of the lQF character.

8.4.18 Tomato

Whole tomatoes are not an item of frozen commerce. They lose turgor and, hence, texture on freezing and are no longer suited to the uses common for fresh tomatoes. Chopped or pureed whole tomatoes can be frozen and stored for 6 to 9 months at 0°F for use in further processing. Other tomato products such as purees, sauces, and pastes can readily be frozen. They are commonly employed as ingredients in other frozen products. Freezing provides an advantage of color stability compared to other storage methods.

8.5 EFFECTS OF FREEZING ON NUTRITIONAL COMPONENTS

Consumers are becoming increasingly aware of the importance of nutritional components in their diets, and the potential for fruit and vegetables in particular, to provide beneficial health effects.

Fruits are a relatively significant source of various antioxidant compounds, including the polyphenolics, carotenoids, and vitamins. Preservation of fruit by freezing, and the effect of this process on various antioxidant components, have been the subject of many recent investigations. A select group of publications on this topic will be highlighted in this section.

Asami et al. (2003b) evaluated the effects of storage at refrigeration and frozen temperatures on the concentration of total phenolics in clingstone peaches. Maturity stage III peaches of the Ross variety were peeled, pitted, sliced, and frozen at –12°C for a period of 3 months. There appeared to be a statistically significant increase ($P < 0.05$) in total phenolic content following freezing, and this higher content was retained after 2 and 3 months of frozen storage. It was postulated that the freezing process may have resulted in cellular disruption and more facilitated extraction of phenolics.

The effect of freezing and frozen storage on raspberry phytochemicals and volatiles was the subject of two manuscripts by de Ancos and colleagues (de Ancos et al., 2000a, 2000b). These authors compared two early-season and two late-season raspberry cultivars and found differential effects of freezing. In the early-season cultivars, freezing resulted in increased anthocyanin content, while in the late-season cultivars, which initially had higher concentrations of anthocyanins, freezing caused an overall reduction. The authors suggested that the preservation of anthocyanins during freezing depends on the pH of the fruit, organic acid content, sugar concentration, initial anthocyanin concentration, and initial cyaniding-3-glucoside content. They did not find a relationship between polyphenol oxidase activity and anthocyanin content.

De Ancos and colleagues (2000b) also found that freezing had a slight effect on ellagic acid, vitamin C, and total phenolics, depending on the raspberry cultivar. Free radical scavenging capacity was decreased as a result of the freezing process, anywhere from 4 to 26%, again related to cultivar. Frozen storage of raspberries at –20°C for a 1-year period did not appear to affect total phenolics or free radical scavenging capacity, but did cause a decline in ellagic acid vitamin C. In another study of the effects of freezing on raspberry phenolics, ellagitannins, flavonoids, and antioxidant capacity (Mullen et al., 2002), these authors found that the antioxidant capacity of the fruit and vitamin C levels were not affected by freezing. The raspberry cultivar used in this study differed from those evaluated by de Ancos, however, and this may have affected the results.

Freezing preservation of fruit and vegetables is less destructive toward some antioxidant compounds, in particular total phenolics and ascorbic acid, than other means of preservation. One illustration of this is a recent publication (Asami et al., 2003a) in which Marionberries, strawberries, and corn were preserved using freezing, freeze-drying, and air-drying methods. The highest levels of both total phenolics and ascorbic acid (reduced form) were consistently found in the extractions of frozen samples, followed by those of freeze-dried and then air-dried samples. Freezing may cause some damage to cell structure, and application of a drying procedure following freezing, even though this is under vacuum at reduced temperatures, may result in even greater losses of beneficial nutrients. Air-drying at temperatures above 60°C may result in oxidative condensation or decomposition of thermolabile compounds, such as (+)catechin and ascorbic acid. Therefore, the presence of total phenolics and ascorbic acid in the air-dried products was lower than that in either frozen or freeze-dried products.

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