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Quality Control in Frozen Vegetables

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I. INTRODUCTION

Freezing is an effective mean of preservation that maintains the quality of foods almost to fresh product. Although freezing is one of the easiest and least time-consuming methods, it is not as economical as canning; but it retains more nutrients in the food if properly done. Most vegetables retain their natural color, flavor, and texture better when frozen than if other methods of food preservation are used. Natural enzymes in foods cause changes in the above parameters, and freezing delays this activity, though it does not stop it. Thus, to prevent further enzyme activity, vegetables need to be blanched in boiling water or steamed for a brief period of time before freezing. However, nutrient loss occurs during blanching, and these losses are greater than those from enzymatic activity if vegetables are not blanched. An alternative method is the addition of antioxidants, such as ascorbic acid. Freezing does not destroy spoilage organisms, such as bacteria, molds, and yeasts; it merely retards their growth temporarily. Once the food is thawed, microorganisms may continue to grow. On the other hand, the blanching process can destroy several microorganisms, especially the mesophiles. During the storage of frozen vegetables, moisture evaporation can render them dry and tough, with the development of off-flavors. To solve this problem, two options are available: provide high relative humidity throughout the storage period; and/or use moisture vapor-proof or resistant packaging.

Although freezing has the disadvantage of the initial investment for equipment for the food industry, the beneficial effects of the use of frozen vegetables in terms of their quality attributes will be higher. This chapter focuses on the physical, structural, nutritional, and sensorial changes during the freezing and frozen storage processes.

II. IMPORTANCE OF FROZEN VEGETABLES IN THE FOOD INDUSTRY

Among the "mild" or "new" technologies of minimal processing in foods, industrial freezing is undoubtedly the most satisfactory method of preserving quality during longer storage periods (1). Vegetables were found to be more palatable and have better color when frozen than when canned, while dehydrated vegetables were shown to be as good or better than the canned. In terms of energy use, cost, and product quality, freezing requires the shortest processing time. Although more energy is required to process and store vegetables by freezing than by canning or dehydration, the overall cost, including packaging and cost of equipment, for preservation by freezing can be kept as low or lower than the cost for other methods of preservation.

The depletion of the ozone layer in the atmosphere caused by the use of chlorofluorocarbons is a leading concern for the global environment. This, together with high cost and high energy consumption, opens new challenges to the scientists and engineers of food freezing equipment, in terms of improved finished product quality, reduced processing costs, improved safety and environmental factors, and most importantly, consumer acceptance.

In order to achieve the desired freezing results, many factors are involved in the freezing process that determine final product quality, such as freezing methods, product ice crystallization, freezer burn, freezing rate, packaging, and moisture losses (2).

As nearly as Quick Frozen Foods International can determine, frozen food consumption in 13 European countries reached 11.1 million tons in the year 2000. Total retail sales of frozen foods in the U.S. reached more than $25 billion in 1999, up over one billion dollars from 1998 (USDA-NAAS Agricultural Statistics 1999). In 1999, manufacturers' food service sales of frozen foods in the U.S. totaled $40.6 billion. Thus the consumption of frozen vegetables has increased by 20% during the last 20 years (3).

III. PROCESSING OF FROZEN VEGETABLES

The freezing process is dependent on the freezing rate, the heat transfer coefficient, and the amount of heat removed from the food product. The freezing process time depends on the freezing rate, the amount of heat removed, the packaging and freezing methods used, the initial and final temperature desired, the thickness, and the food ingredients. The International Institute of Refrigeration (IIF) defines the freezing rate as the difference between the initial and final temperature of the product divided by the freezing time (4). The amount of heat to be removed and the cooling rate depend on the food structure and chemical composition. The freezing systems used affect ice crystal formation; large ice crystals induce product damage, which could be reduced with increased freezing rate. Several numerical mathematical models have been reported that consider assumptions including the irregular shape, the chemical composition, the heat transfer coefficient, and the type of freezing media used (5,6). Industries generally accept the target temperature of $-18^{\circ}C$ ($0^{\circ}F$) at the thermal center of the product for an efficient freezing process.

Several operations are needed during freezing that vary with the types of vegetables and the methods used, but general preparation procedures are summarized in Fig. 1, including postharvest preparation, blanching, freezing, and storage. Woodroof (7) reported general guidelines for harvesting, handling, and storing vegetables before commercial processing. To get an optimum quality after thawing, proper selection and control of raw material, cultivar, and maturity stage are very important factors. Thus vegetables should be harvested when they reach the peak of quality. During processing, vegetables should be handled promptly to avoid mechanical damage. During sorting and grading, insect-infected vegetables are removed, and during washing, dust, dirt, and insects are removed as well. In several cases, additional operations are needed, such as peeling, trimming, and cutting.

The most important step for enzyme inactivation is blanching. These enzymes cause the formation of off-flavors and discoloration during storage at freezing temperatures. An additional effect of blanching is the reduction of the number of microorganisms. There are several tests that can be used to assure that the blanching process has been adequately performed, the most

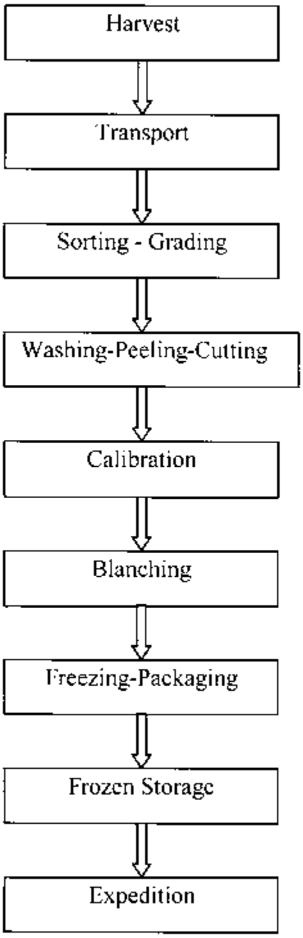

Figure 1 General flow diagram for processing of frozen vegetables.

commonly used being peroxidase, catalase, lipoxygenase, and polyphenoloxidase. A high correlation has been established between development of off-flavors during freezing storage and remaining peroxidase and lipoxygenase activities, suggesting the imperative use of blanching to inactivate these enzymes in frozen vegetables for a better final quality (8). However, there are some reports that several vegetables, such as tomatoes, green peppers, celery, and mushrooms, can be frozen for up to 12 months at $-18^{\circ}C$ without previous blanching and with no quality deterioration (9,10).

Classically, the peroxidase level activity has been used to monitor quality changes in frozen vegetables, since increases in peroxidase are thought to indicate changes in flavor, color, and texture in vegetables. Thus measurement of peroxidase is often performed prior to blanching as a reference for determining the effectiveness of the blanching process (11), for which a 95% loss of enzyme activity following blanching is considered adequate (9). Still, several studies have established that residual lipoxygenase activity was closely related to off-flavor of leguminous vegetables (12,13), while residual peroxidase activity has little effect on quality of frozen vegetables (14,15). Increased peroxidase activity during frozen storage was found in peas blanched at 93–100°C for 1 min (16). Recently, it has been shown that although changes in total peroxidase activity may not predict flavor changes, the presence or absence of certain peroxidase isozymes may be useful in predicting off-flavor development in specific frozen corn genotypes (17).

There are a large number of published reports that reveal that the freezing rate is a key factor that preserves food products when physicochemical changes are studied. Quick freezing can be achieved by increasing temperature gradient between freezing media and food. Thus conventional mechanical freezing methods, such as forced air, are considered slower than liquefied gases such as nitrogen or carbon dioxide, which have low boiling points and freeze faster. These gases are commonly called "cryogenic gases," since their temperature range is cryogenic and the process is called cryogenic freezing. This type of freezing improves product quality and offers many advantages over mechanical freezing. It benefits include reduction in freezing time (extremely fast), reduction in moisture and flavor losses, reduction in ice crystal formation, minimum product cell damage, and high heat transfer. It is also a flexible and versatile system.

IV. PHYSICAL, STRUCTURAL, NUTRITIONAL, AND SENSORIAL CHANGES DURING FREEZING OF VEGETABLES

Processing operations destroy the cytoplasmatic structure, producing loss of turgor, weakness of cell wall, and some degree of cell separation. These changes have important effects on the texture of the vegetable, which is one of the most important quality factors of frozen vegetables from the consumer point of view. Quality frozen vegetables are directly correlated to pectin substances, firmness, texture, and histological structures.

The freezing temperature is the most critical factor affecting the cell structure in vegetables such as carrots (18). The blanched carrots reduced only 21% of their initial firmness, while in the raw samples this decrease was about 50%, the effect being due to the formation of a gel from the interaction between heat and pectic substances. In turn, a reduction in pectin extraction was observed (19). These results would confirm that damages occur in the middle lamella of the cells, the main damage being due to freezing rather than blanching. On the histological level, frozen raw samples showed physical changes, such as cell walls irregular in shape and separation among the cell layers, which were explained by the ice crystal effect. Contrarily, the cells of the blanched samples did not show tissue disruption.

As previously reported, freezing is an effective method of preservation, but comprehensive studies on physicochemical changes of foods during freezing and frozen storage have revealed that the freezing rate influences the quality of frozen and thawed vegetables. Thus cryogenic freezing could cause internal stress buildup leading to cracking or shattering that is critical and reversible in frozen materials (20). This mechanical damage is mainly due to both contraction and expansion of the volumetric changes associated with the water–ice transition (21). Physical properties, such as porosity and density, may also be affected by an ultrahigh freezing rate. Porosity indicates the amount of void space inside the vegetable, and a larger void space increases the possibility of internal stress. Density is usually proportional to the moisture content and inversely proportional to porosity; thus the greater the density, the higher the probabilities that stress will occur.

Water makes up over 90% of the weight of most produce and is held within the cell walls to give support, structure, and texture to the vegetable. Actually, the freezing of vegetables consists of freezing the water contained in the plant cell. When the water freezes, it expands, and the ice crystals cause the cell walls to rupture. Freezing as quickly as possible can control the structural changes (cell wall disruption, internal stress, cracking, etc.). In rapid freezing, a large number of small ice crystal are formed, and less cell wall rupture can be expected by comparison with the formation of large ice crystals.

The size of the ice crystals affecting cell walls is related to the final quality after thawing. When a product is thawed, it is much softer than the raw product before frozen storage. The most typical example is tomato, which after being frozen and thawed turns liquid. The same can be concluded for celery and lettuce, which are not usually frozen. Textural changes due to freezing are not as apparent in products that are cooked before eating, since cooking also softens cell walls.

In frozen peppers, the maximum firmness was attributed to the activity of pectin-methylesterase (PME). Peppers blanched at 69°C showed increases in firmness, since PME was activated, generating free carboxylic acid groups that could cross-link with divalent cations. On the other hand, peppers blanched at 96°C showed inactivation of PME (22). Thus, for better texture attributes of this commodity, a decrease in temperature and an increase in time should be taken into account. In this sense, the use of calcium in combination with a low-temperature blanch is usually performed to maintain firmness during vegetable processing (23), through stimulation of the PME present in the cell walls by low-temperature blanching (24). The effects of this pretreatment on vegetables have been reported for canning (25), drying (26), and freezing (27).

The health benefits of vegetables are well recognized by nutritionists, but usually intakes are below recommendations. There are published reports linking fruit and vegetable intakes with a reduced risk of chronic diseases, such as cardiovascular disease and cancer (28). Among the nutrients, vitamins are essentials for human nutrition, and those acting as antioxidants deserve special attention. Vitamins C, Vitamin A, and its precursor β-carotene are considered the main agents responsible for the protective effects because of their antioxidant and antiradical properties. Vegetables are estimated to provide 30% of the vitamin C and 20% of the vitamin A (as carotenes). The expansion of the frozen food industry has meant that most food that can be frozen is available for consumption throughout the year. This is especially important for vegetables that are dense in the essential nutrients such as vitamins. Obviously, we must give consideration to the fact that the vitamin C content varies according to other factors such as cultivation, processing, and storage conditions. Since vitamin C has a high solubility in water and a high sensitivity to heat, its content gives a good indicator of the quality and freshness of the frozen product (29). Since vitamin C is vulnerable to chemical and enzymatic oxidation, it is an appropriate marker for monitoring quality change during transportation, processing, and storage (30). During the freezing process, water-soluble substances are lost, especially during blanching (31). Thus in broccoli half of the vitamin C was lost after a blanching time of 60 s (?) before freezing in a fluid bed tunnel (32). Similarly, in fiddlehead greens, losses of vitamin C ranged from 30 to 38% as a result of freezing (33), and losses were also attributed to the blanching process. However, losses of vitamin C during the canning process are much higher (47–57%), since vitamin loss is partly dependent upon heating time and temperature.

In a comparative study of the vitamin C content of fresh and frozen vegetables (peas, beans, broccoli, carrots, and spinach), the author concluded that the vitamin C level in the commercial quick-frozen product is equal to or better than that in the fresh produce market and much better than that in the supermarket stored at fresh or ambient temperature. Also, the loss of ascorbic acid from all these vegetables is most probably dominated by enzyme-induced oxidation. The variation in the rate of loss demonstrates the differing vulnerabilities of the different vegetables, such as surface area and mechanical damage, and their differing enzyme activities (30).

Carotenes are precursors of vitamin A, which is considered an essential nutrient for maintaining human health, but carotenes are susceptible to oxidation. The degradation of carotenes is associated with the development of off-flavors (34). Steam blanching is thought to result in little or no loss in β-carotene content (35). Similarly, the carotene retention was relatively high in frozen fiddlehead, since provitamin compounds are not very water-soluble (33). In a comparative study of carotene retention in carrots, broccoli, and spinach, the mean carotene content of the three vegetables decreased with time after thawing, but no differences were found for extended thawing time (36). This author also concludes that frozen and thawed vegetables exposed to home environmental conditions for 4 hours before cooking may not lose much carotene, whereas dehydration of vegetables may adversely affect carotene content.

V. CHANGES DURING STORAGE OF FROZEN VEGETABLES

Most vegetables will maintain high quality for 12 to 18 months at -18°C. However, it is well known that during frozen storage the number of ice crystals will be reduced, while their size will increase. These changes are affected by fluctuations in storage temperature, which in turn can cause the migration of water vapor from the product to the surface of the container. The increase of ice crystals during prolonged frozen storage induces drip loss. Also, physical and chemical changes can be expected, which were recently summarized (37). Since at frozen storage temperatures, no microorganism proliferation can be expected, the loss of quality is mainly due to physical, chemical, and sensorial changes of higher magnitude than those detected during the freezing process.

The main physical changes of vegetable products during frozen storage are due to recrystallization and sublimation phenomena related to the ice crystals' stabilization inside the product and on the outside surface. Both phenomena are thought to be controlled by temperature. The recrystallization rate decreases at low temperatures, with no ice crystal growth at lower temperatures than -20°C. The ice sublimation occurs in unwrapped vegetable products during temperature fluctuations during frozen storage, which causes product dehydration and accelerates the oxidative changes on the product surface area (38).

With respect to chemical changes, these are a consequence of the residual enzymatic action that produces loss of nutrients and color, and the occurrence of off-flavors. In terms of loss of nutrients, only small changes in carbohydrates may occur during frozen storage, as biochemical processes are delayed at freezing temperatures, but a reduction in water-soluble carbohydrates may occur as a result of water loss during thawing. In several vegetables, such as fiddlehead greens (33) and sweet potatoes (39), the nutritional parameters did not change throughout frozen storage. Minerals (Ca, K, Mg, and P) remained unchanged during 10 months of frozen storage, while sugars (fructose, glucose, and sucrose) showed increases during 9 months of storage, mainly due to starch being converted to sugars by reactivation of the enzymes involved.

Several vegetables, such as spinach, contain high concentrations of galactolipids and phospholipids among their fat-soluble components, which are used as substrates for lipid-acyl hydrolases such as galactolipases and phospholipases. The highly active thermal stability of these enzymes should be taken into account and the enzymes used as indicator enzymes for determining the quality deterioration during frozen storage (40). In this vegetable, after 10 months of frozen storage 80% of the total folacin activity was retained with proper blanching and freezing processes (41).

The main factor determining the shelf life of frozen vegetables in prolonged storage is effective blanching, but several vegetables do not need blanching for optimum quality, as has been reported before. Unblanched vegetables, such as onions and leeks, were more acceptable after 15 months of storage than blanched samples (10), the lower quality being due mainly to loss of volatile oils during the blanching process.

In terms of the acceptability of vegetables, one of the most important quality factors is texture. Texture has even been associated as a criterion for the selection of raw materials. During frozen storage of asparagus an increase of the maximum force during cutting is produced, mainly owing to increased fiber content that affects the fibrous attributes by a lignification process either enzymatically or otherwise (42). The enzymatic lignification has been attributed to residual peroxidase activity after blanching at the basal and medium zones of the asparagus, but not in the apical ones. During the freezing (with Freon-12 immersion) and frozen storage of peas, changes in texture properties have been reported. Thus freezing at a higher rate resulted in smaller ice crystals and less structural damage. In terms of chewiness, increased values during storage were observed due to the dehydration effects (43). Moisture loss by evaporation of water on the surface area of a product produces freezer burn, a grainy brownish spot where the tissues become dry and tough. This surface freeze-dried area is very likely to develop off flavors. Moisture-proof wrap is used to prevent freezer burn.

In a recent study of carrots (44), pronounced differences in textural quality were found between the freezing method and frozen storage. Thus decreasing the temperature from $-30^{\circ}C$ to $-70^{\circ}C$ resulted in increasing maximum firmness, with no differences after 1 and 5 months of frozen storage.

With respect to color, frozen vegetables show alterations in natural pigments, such as chlorophyll, anthocyanins, and carotenoids, or enzymatic browning. Chlorophylls *a* and *b* have been shown to be the main compounds responsible for the green color of vegetables (45). Degradation of chlorophylls has been studied because their bright green color is usually more pleasing to the consumer than the brownish color of pheophytin *a* and *b*, which is a chemical conversion (46). Since chlorophyll in green tissues may depend on the nature of its association with lipoproteins of the chloroplast, the lipid peroxidation, as a consequence of being frozen, will be increased by the lipoxygenase action (47). Thus chlorophylls *a* and *b* were slightly degraded (about 16%) in frozen spinach, but small amounts of pheophytins *a* and *b* were detected, because the spinach had been blanched.

Anthocyanins are hydrosoluble pigments responsible for the red color of some vegetables. Under several conditions, they may be destroyed as a consequence of polyphenol enzymatic oxidation. The final result of this oxidation is the occurrence of enzymatic browning in frozen vegetables such as cauliflower, potato, and mushroom. This reaction is catalyzed by the enzyme polyphenoloxidase in the presence of oxygen and the production of quinines, which in turn can oxidize other substrates like ascorbic acid and anthocyanins. The most convenient parameter for monitoring enzymatic browning is related to CIE Lab. L*, a*, and b* coordinates represent the color space, in which L* indicates lightness, and a* and b* are the chromaticity coordinates. These parameters are expressed as positive or negative values. In the color space, +a is the red direction and −a is the green direction. Similarly, +b is the yellow direction and −b is the blue direction. In this sense, the enzymatic browning in potatoes has been correlated with decreases in parameter b* (39).

The high or low acceptance of a specific frozen vegetable depends on its sensory attributes. Aroma and flavor together with color and texture are the most important. The lack of flavor and the absence of aroma are mainly due to the action of oxygen in the air on frozen product, producing rancid oxidative flavors. This can be solved with adequate wrapping material that does not permit air to pass into the vegetable, or by removing as much air as possible from the freezer bag or container before freezing.

VI. CONCLUSION

Freezing is a common process for long-term preservation of vegetables and is one of the best methods available in the food industry. Freezing retains the quality of vegetables near their fresh state, but interest has grown concerning the quality and shelf life of frozen vegetables. Consumption of frozen vegetables has increased by 20% during the last 20 years. However, during frozen storage, physical, chemical, and nutritional changes usually occur. To minimize these effects, blanching has been used traditionally in vegetable processing to slow quality deterioration caused by enzyme activity. Some benefits of blanching prior to freezing are color stability, reduced vitamin losses, texture improvement, and removal of undesirable substances.

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