



# Impact of Processing Factors on Quality of Frozen Vegetables and Fruits

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## Abstract

In this paper I review the production of frozen vegetables and fruits from a chain perspective. I argue that the final quality of the frozen product still can be improved via (a) optimization of the complete existing production chain towards quality, and/or (b) introduction of some promising novel processing technology. For this optimization, knowledge is required how all processing steps impact the final quality. Hence, first I review physicochemical and biochemical processes underlying the final quality, such as water holding capacity, ice crystal growth and mechanical damage. Subsequently, I review how each individual processing step impacts the final quality via these fundamental physicochemical and biochemical processes. In this review of processing steps, I also review the potential of novel processing technologies. The results of our literature review are summarized via a causal network, linking processing steps, fundamental physicochemical and biochemical processes, and their correlation with final product quality. I conclude that there is room for optimization of the current production chains via matching processing times with time scales of the fundamental physicochemical and biochemical processes. Regarding novel processing technology, it is concluded in general that they are difficult to implement in the context of existing production chains. I do see the potential for novel processing technology combined with process intensification, incorporating the blanching pretreatment—but which involves quite a change of the production chain.

**Keywords** Freezing · Cellular tissue · Food quality · Causal network

## Introduction

Freezing is a widely used long-term preservation method for foods, where they retain attributes associated with freshness much better than other conventional preservation methods like canning and drying [1]. But especially the texture of cellular foods, like meat, vegetables and fruits, can be strongly impacted by the freezing process. Above all, vegetables often require blanching prior to freezing to prevent enzymatic browning. Blanching already impacts the vegetable texture. Fruits are seldom blanched, but due to their relative softness they are more severely impacted by freezing than vegetables. Via research projects with industry I have learned that significant improvements to the textural quality of fruits and vegetables can still be made. This is also indicated by the wealth of recent studies on the application

of novel processing to improve the freezing process, like ultrasound and high-pressure freezing. There are several review papers on these novel technologies [2–6], but most of these papers focus on freezing as a single unit operation, without considering it as part of the complete frozen food production chain. An exception is the review paper, where novel technological developments in both blanching and freezing unit operations on vegetables are discussed [7].

Via this review I like to show that improvement of frozen vegetables and fruits can be obtained via (1) optimization of the total production chain of frozen foods and (2) introduction of some promising novel processing into the production chain, combined with process intensification. Literature shows there is very little study towards the optimization of the production chain. Only, a limited number of studies investigate the interaction between blanching and freezing steps [7, 8]. The usefulness of novel technology is often evaluated on the basis of the reduction of energy usage or food quality. As food losses and waste have much more impact on sustainability than energy usage [9], I will focus on the improvement of food quality, and in particular to the textural quality.

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Still, there is not sufficient knowledge on how freezing impacts on the matrix of tissue-based food materials like vegetables, fruits, and meat, via the freeze concentration and the mechanical stress imparted by the growing ice crystals [10]. For example, one of the major impacts of freezing on vegetables and fruits is the drip loss occurring after thawing. This drip loss occurs due to changes in water holding capacity of the food imparted by freezing. These changes and their physical causes are hardly discussed in the literature, with a few early exceptions discussing freezing of starch-rich foods [11], and meat [12–15].

Hence, before discussing effects of the different unit operations on the final quality of the frozen vegetables and fruits, I discuss the physics and (bio)chemistry of water holding and ice formation in plant tissue, using insights from the fields of cryopreservation of tissue [16–19], and freezing tolerance in plants [20–24]. As freezing and thawing imparts dehydration and subsequent rehydration of the tissue, one can expect many similarities with drying and rehydration of plant tissue [25–27].

Subsequently, I discuss the production chain of both vegetables and fruits, and the novel technologies, which can be applied in these chains. I have evaluated how each unit operation in the processing chain impacts physicochemical factors of relevance to the final quality of frozen fruits and vegetables. This evaluation is summarized in a so-called causal network linking processing factors via physicochemical factors to final product quality factors. Finally, I discuss modifications of the production chain for improved final product quality.

## Physics and Chemistry During Freezing of Plant Tissue

Here, we discuss the physics and (bio)chemistry of water holding and ice formation in plant tissue. For the latter insights will also be obtained from the field of cryopreservation of tissue [16–19], and freezing tolerance in plants [20–24]. As freezing and thawing impart dehydration and subsequent rehydration of the tissue, one can expect many similarities with drying and rehydration of plant tissue [25–27].

### Steps in the Freezing Process

#### Supercooling and Nucleation

Freezing can only happen if the food material is below freezing point, i.e., it has to be supercooled. The freezing does not happen immediately, because first ice crystals have to be nucleated. A cluster of liquid water molecules has to adapt to the ice crystal structure, and only a cluster of sufficient size can outgrow to an ice crystal. A cluster

smaller than the so-called critical nucleus size will remelt again. The nucleation process is a balance between two opposing energy contributions: (a) the energy gain via the formation of the ice crystal structure and (b) the energy cost of forming an interface between the nucleated ice crystal and the unfrozen liquid phase. Only at the so-called critical nucleus size the energy gain is larger than the energy cost of forming the interface. It is said that the nucleation process has to overcome the energy barrier imposed by the surface energy. Via classical nucleation theory [28] one can calculate the critical nucleus size and the change of forming a nucleus, that is larger than the critical size and will outgrow. The change of nucleation depends largely on the amount of supercooling, the difference between freezing point and the actual temperature of the unfrozen phase. For pure water without any impurities, nucleation will happen only at  $T = -40$  °C. If foreign material is present in the solution, having asperities or hydrophobic properties, ice can nucleate at much smaller degrees of supercooling due to the lowering of the energy cost of forming an interface.

It was commonly assumed that food is full of foreign material, that ice will form quite instantly, already at several degrees of supercooling, as stated in the Recommendation of the International Institute of Refrigeration [29]. However, scientific literature shows that significant supercooling occasionally can occur. Some vegetables like fresh garlic and shallots show a high capacity for supercooling [29, 30]. Few studies have reported a moderate supercooling of other vegetables like broccoli, cauliflower [30], strawberries [31], tomatoes [32], and potato slices [33]. Also in gel-like food products supercooling is observed like soy tofu [34], agar gels [35], tylose [36], agar/maltodextrin gels [37] and rice gels [38]. The amount of supercooling will determine the nucleation rate (the number of ice crystals formed per unit of time). Supercooling is well observed in recordings of product temperature at low heat transfer rates, such that the heat release during nucleation and further ice crystal growth cannot be cooled away fast enough, leading to temperature rise after nucleation [38].

The homogeneous nucleation temperature of pure water is 40 K lower than its freezing point. Surprisingly, in aerosols with solutes added the difference between freezing point and nucleation temperature remains 40 K [39]. The nucleation temperature is independent on the type of solute, but only on the water activity, similar to the freezing point (as follows from Clausius-Clapeyron [40, 41]). It is also assumed that the nucleation rate is a function of the water activity.

Heterogeneous nucleation can also occur in aerosols, if organic solutes are present in the crystalline state immersed in the aerosol for example [42]. Dicarboxylic acids are such solutes which are non-volatile, and have low solubility. Also biopolymers, especially proteins, are thought to promote heterogeneous nucleation in food [43–46]. Also, for

heterogeneous nucleation it holds that the nucleation temperature depends only on water activity. Consequently, there is a fixed difference between equilibrium freezing point and nucleation temperature [42, 46]. The heterogeneous nucleation temperature is always higher than the homogeneous nucleation temperature. Similar effects are observed during spray freezing of coffee [47].

The heterogeneous nucleation temperature does depend on the type of nucleation site (organic/inorganic crystal or biopolymer), and the (partial) wetting of the nucleation site. Importance of the interface on nucleation is shown in a recent study [48]. If air/water interface is sealed by oil, the nucleation of ice at the interface is highly suppressed. Even, the nucleation cannot be initiated via mechanical shocks or ultrasound. Also, nucleation can be suppressed by alcohols, which form an intricate structure at the interface due to their amphiphathic nature.

In the fields of cryopreservation of tissues [19] and freeze-drying of pharmaceuticals [49] the phenomenon of supercooling is much more acknowledged and observed. In these fields good control of ice morphology is demanded. Hence, there are serious research activities towards methods of controlling the ice nucleation event, which are based either on formulation or on process conditions. For the control of nucleation via formulation one can obtain much inspiration from organisms showing high cold tolerance [50]. Furthermore, food science can learn from this field how supercooling and ice nucleation depend on cell volume [51]. Nucleation is expected to occur earlier for tissues with smaller cells, due to the higher amount of cell surface (wall) area. Furthermore, at slow to moderate freezing rate ice nucleation is expected to happen in the extracellular space [52] (Fig. 1).

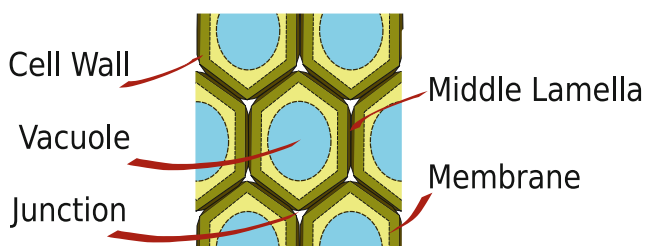


Fig. 1 Cellular structure of vegetables and fruits

## Crystal Growth

As the supercooled state, where ice crystals are nucleated, is not at equilibrium, ice crystals will grow to restore equilibrium. Solutes or biopolymers present in the unfrozen phase are excluded from the growing ice crystals. Hence, the growing ice crystals push the solute and polymers forward in front of the growing ice crystals, leading to gradients of solutes or density in the biopolymeric matrix. For growth of the ice crystals the liquid water has to diffuse through these concentrated boundary layers of solute or biopolymer [53, 54].

As stated above, the formation of ice releases energy (latent heat), and consequently the (local) temperature will increase and approach the equilibrium freezing point. This release of latent heat after nucleation is called recalescence [55]. If the freezing rate is sufficiently slow, the average temperature and solute/biopolymer concentration will follow closely the freezing line until the temperature of the cooling medium is reached. Food is commonly frozen at temperatures around  $-18\text{ }^{\circ}\text{C}$ , which is the common storage temperature for frozen food. The changes in the state of the unfrozen phase during the freezing operation is illustrated in Fig. 2. Here we have used the phase diagram of sucrose, which is a good model system for fruits rich in sugar. Observe that initially the temperature drops below the freezing line, where the unfrozen liquid enters the supercooled state. At a sufficient degree of supercooling ice crystals are nucleated (event 1), and the temperature will rise due to recalescence. Simultaneously, the mass fraction of water in the unfrozen phase decreases due to the freeze concentration effect. After a brief moment, the state of the food will commonly follow

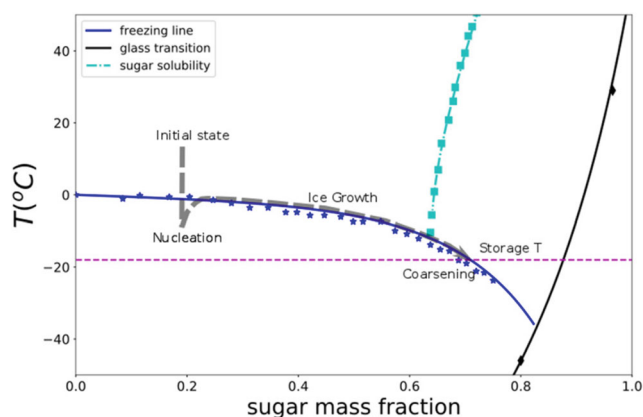


Fig. 2 Different steps in freezing process as depicted in the supplemented state diagram of sucrose, showing the freezing line, sucrose solubility, and glass transition line. Sucrose is viewed as model system for fruit. Path taken by state of the system during freezing is shown by the dashed gray line

the equilibrium freezing line, until the outside temperature of cooling medium is reached (here  $-18\text{ }^{\circ}\text{C}$ ).

Depending on the process conditions and the food material properties, the ice crystal growth rate is either determined by the heat transfer or by the diffusion rate. The resulting ice crystal size is often the resultant of the interaction between ice crystal growth and the diffusion of the excludes solutes and/or biopolymers, as we have discussed earlier [53, 54]. At slow freezing rates the ice crystal size is independent of the number of initial nuclei, but depends only on the freezing rate, and initial solute concentration [54]. Only at quite fast freezing rates, where the state of the food remains significantly below the equilibrium freezing line, ice crystal size can depend on the number of initial nuclei.

### Coarsening

The freezing operation is commonly stopped if a minimal product temperature is reached. The frozen food is transferred to storage facilities, where temperatures around  $-18\text{ }^{\circ}\text{C}$  are maintained. As one can observe in Fig. 2, this storage temperature is likely to be above the glass transition temperature of the food matrix. This means that moisture still has sufficient mobility to diffuse through the unfrozen phase, and allow changes in the morphology of the frozen phase. Consequently, the physical process of ice coarsening (or Ostwald ripening [56–58]) can still proceed. The coarsening leads to further growth of the largest ice crystals, at the expense of smaller ice crystals.

Temperature fluctuations around the storage temperature lead to ice crystal melting and regrowth [59, 60], which is assumed to be a different mechanism than coarsening via Ostwald ripening. Hydrocolloids are assumed to have a large impact on this melting/regrowth mechanism, as shown for ice creams [59]. One can assume that cell wall material in frozen fruits and vegetables act in a similar way [61]. Hydrocolloids are thought to have a stabilizing effect on the ice crystal distribution, thus limiting the coarsening via temperature fluctuations. The hypothesis behind the stabilizing effect of hydrocolloids is that they hinder the diffusion of solute towards/away from the interface of a melting/growing ice crystal [59]. However, in carrots it is found that ice crystals grow due to temperature fluctuations during storage [60].

### Interaction of Ice Formation with Plant Tissue

In the discussion of the interaction of ice formation with plant tissue, we follow the classification in damage as used by Reid [62]. He distinguishes (1) dehydration of the cell due to the location of ice nucleation, (2) solute damage induced by freeze concentration of the intracellular fluid,

and (3) mechanical damage via the stress imparted by the expanding ice phase. To understand the damage induced by dehydration and loss of turgor, it is important to have an understanding of water holding capacity of foods. This is first discussed below.

### Water Holding Capacity of Vegetables and Fruits

The water holding capacity of cellular tissue of plants like vegetables and fruits strongly depends on their structure, which is depicted in Fig. 1. Plant cells comprise of vacuole embedded in cytoplasm. Both vacuoles and cytoplasm are surrounded by lipid membranes, which are impermeable to most of the solutes, but they are permeable to water. The vacuole contains simple solutes like sugars, while the cytoplasm contains mainly biopolymers like proteins. In some vegetables like potatoes the cytoplasm is also rich in starch. The cell membrane is enveloped by the cell wall, which gives the plant tissue strength. The individual cells adhere to each other via the middle lamella, which is rich in pectin. There is little adherence in the three-way junctions, which often contains air and provides pathways for gas diffusion [26, 27, 63, 64].

Due to the solute impermeability of the vacuole membrane an osmotic pressure is generated, which attracts fluid from the extracellular space, the apoplast. The cell walls are viewed part of the apoplast, and connect to the vascular tissue—allowing for transport of water, nutrients and assimilates. The inflation of the vacuole leads to expansion of the cell, and stretching of the cell wall, which can be regarded as a biopolymer network. This deformation of the cell wall leads to mechanical stress, which will counteract the osmotic pressure. If the mechanical stress balances the osmotic pressure, the cell is at full turgor [26, 27, 63–65].

In a recent paper we have elucidated the physical theory behind the water holding of vegetables [65], which extends our earlier papers on Flory-Rehner theory [66]. In fresh vegetables water is held in three compartments: (a) in the intracellular space, both the vacuole and the cytoplasm, (b) the extracellular cell wall material, and (c) the capillary space, which can be filled with fluid after vacuum impregnation [67]. The water holding in the intracellular space critically depends on the integrity of the cell membranes, otherwise leading to the loss of osmotic pressure and turgor. The cell wall material (CWM) can be regarded as a hydrogel, containing hemicellulose and pectin, embedded with cellulose fibers [65]. The water holding of the CWM can theoretically be described by Flory-Rehner theory and its extensions. The theory describes the amount of water holding of the gel as function of its hydrophilicity (as indicated by the Flory-Huggins interaction parameter) and the cross-link density.

During food processing the cross-link density of CWM is often modulated, especially during blanching [64]. During conventional blanching the thermal solubilization of pectin via beta-degradation lowers the cross-link density, whereas during long-time-low-temperature blanching the cross-link density is increased via the activation of the PME enzyme, which de-esterifies pectin, and the subsequently cross-linking via calcium ions. As pectin is a polyelectrolyte, extensions of Flory-Rehner theory learns that its water holding is also influenced by ionic strength and pH of the fluid the CWM is immersed in [68, 69].

If the integrity of the cell membrane is lost, also the osmotic pressure and turgor pressure are lost. The stretched network of the CWM will relax back to its zero stress state, thereby absorbing a little water [65]. Due to the relaxing of the CWM the intracellular space will shrink in volume, which cannot be compensated by the increase of water holding of the relaxed CWM. The excess fluid will be located in the extracellular capillary space, which is enlarged compared with the full turgor state. Now the water in the intracellular space and the extracellular capillary space is only held by capillary forces, and consequently it can easily be pressed out by external forces, as occur during eating [65, 70] or it can drain easily via gravity, for example appearing as drip loss after thawing or slicing.

### Location of Nucleation

One of the important factors for the interaction of ice and the plant tissue is the location of nucleation with respect to the cell, which imparts the integrity of the cell membrane. In cryopreservation it is crucial that tissue survives the freezing operation, for which it is critical to control or even prevent intracellular ice formation [71]. If the size of the intracellular ice approaches that of the cell size, it will puncture the cell membrane of the vacuole. Consequently, the membrane loses its integrity, and solutes diffuse to the extracellular space. The osmotic pressure and turgor pressure are lost. The stretched cell wall material will return to its relaxed state, and will squeeze out liquid from the intracellular space. For foods like fruits it is important to maintain cell membrane integrity and turgor.

In plant tissue it is energetically favorable that ice nucleation happens in the extracellular space. The extracellular space is thought to have quite a number of heterogeneous nucleation sites [72], while intracellular ice formation often requires homogeneous nucleation [73]. The air/liquid interface in the junctions between cells (if filled with air) can be a preferred nucleation site [74]. Extracellular nucleation will indeed happen at sufficiently slow freezing rates. Extracellular ice growth extracts water from the cell. There will be only extracellular ice growth if the water extraction rate from the cell can keep up with the ice formation rate

[72]. Otherwise, the cell gets sufficiently supercooled to ice nucleation to happen. Thus, at relatively fast freezing rates both extracellular- and intracellular ice formation will happen. If the tissue is suddenly immersed in liquid nitrogen, the nucleation is mostly intracellular, because the temperature gets quickly below the homogeneous nucleation temperature (around  $-40\text{ }^{\circ}\text{C}$  [73]). However, sufficiently rigid cell wall can prevent intracellular ice nucleation, due to the development of negative pressures, which is a consequence of the deformation of the stiff cell wall [73].

If nucleation happens extracellular the cell membrane need not to lose its integrity. Growth of extracellular ice will draw water also from the intracellular space, which will freeze concentrate and shrink (and gets in the state known as cytorrhysis [72]). As the volume of the cell membrane cannot shrink, as it contains lipids only, the shrinkage of the cell can lead to buckling and damage of the cell membrane. Some of the invaginations of the cell membrane can bud off as endocytic vesicles, leading to reduction of the cell membrane area. Hence, upon thawing the melt water of extracellular ice returns to the cell (via osmosis), which will expand again. Due to the reduced area of the membrane due to endocytosis, it will burst just before it is fully hydrated [72].

### Freeze Concentration

The intracellular space and vacuoles also contain sugars, salts and possibly some acids [75]. Hence, freeze concentration will lead to increase of the ionic strength, and change in pH via the decrease of water activity. These altered conditions may lead to protein denaturation or permeabilization of the cell membrane. Freeze concentration also has influence on the biochemistry, as it increases the substrate concentration for enzymes [76]. During freezing of vegetables enzyme activity can lead to undesired browning due to loss of the integrity of the vacuole, via which substrates get into contact with membrane-bound enzymes like PPO, leading to discoloring [77, 78].

Consequently, many vegetables are blanched before freezing. Yet, blanching also imparts the textural quality of the vegetables due to (1) loss of membrane integrity via the enhanced temperature, (2) the solubilization of pectin, and (3) enhanced cross-linking of cell wall material with calcium made possible via the modification of pectin by the PME enzyme [79–82]. Hence, for the final textural quality of frozen vegetables the conditions for blanching and freezing should be well balanced.

Freeze concentration can also enhance oxidation processes [83], especially to the lipid cell membranes [72]. Furthermore, retrogradation of starch can happen in cooked products like par-fried potato products [84, 85]. During retrogradation recrystallization of amylose is enhanced. For

products like frozen rice gels it is shown that retrogradation leads to syneresis, which is released from the food after thawing as drip loss [86].

Note that the low product temperature slows down the diffusion and reaction kinetics, and thus counteracts the effect of freeze concentration. At temperatures of the frozen storage the slowed-down diffusion and reaction kinetics commonly overwhelms the effect of freeze concentration [87, 88]. But at temperatures just below freezing point, effects of freeze concentration can be considerable. Mind that, these conditions reoccur during thawing. Consequently, also the rate of thawing should be taken into account during the design of the frozen food production chain.

### Mechanical Stresses

As the density of ice is smaller than liquid water, the food will expand and its matrix will be subject to tensile stresses upon ice formation [89, 90]. Later if coolant temperatures are reached the stresses will be compressive as the density of ice increases with the lowering of temperature [91]. The simultaneous occurrence of compressive and tensile stresses make the food especially vulnerable to freeze cracking. Freeze cracking occurs particularly at quite high freezing rates as occur during cryogenic freezing. During freeze cracking cells will be ruptured straight through the cells.

During slower freezing rate the growth of adjacent ice crystals can lead to localization of stresses [92–94], which will rupture the food matrix at weak points. If the vegetable has been blanched the weak spots are in between cell walls, where pectin has been solubilized. This will lead to separation of cells. Also, in frozen living plants mechanical stresses are thought to be a major cause in freezing damage [72].

The growth of adjacent ice crystals towards each other compresses the cell wall material in between. We hold the hypotheses that due to the compression extra cross-links or hydrogen bonds will be made in the cell wall material, which will reduce its water holding capacity, but it will also hinder the swelling back to its original density. Reduction of the cell wall thickness after freezing has been observed in living plants [72]. This is also apparent in the structure of rehydrated vegetables which have been subject to slow freezing and subsequent (freeze) drying [70]. The compression of a starch matrix as in freezing (par-fried) potato products will probably enhance the retrogradation, which also lowers the water holding of the starch matrix [84, 85].

It is also claimed that freezing and frozen storage leads to breakdown of pectin (depolymerization). For papaya it is shown that multiple freeze/thaw cycles increases to amount of soluble pectin, which indicates indeed the breakdown of

pectin. This results in further weakening of the cell wall matrix, and lowers its water holding capacity [95]. For (non-blanching) apples also decreased cell adhesion after thawing is observed [96]. This has been explained due to the action of enzymes on the cell wall material, which have come into contact due to rupture of the cell membranes.

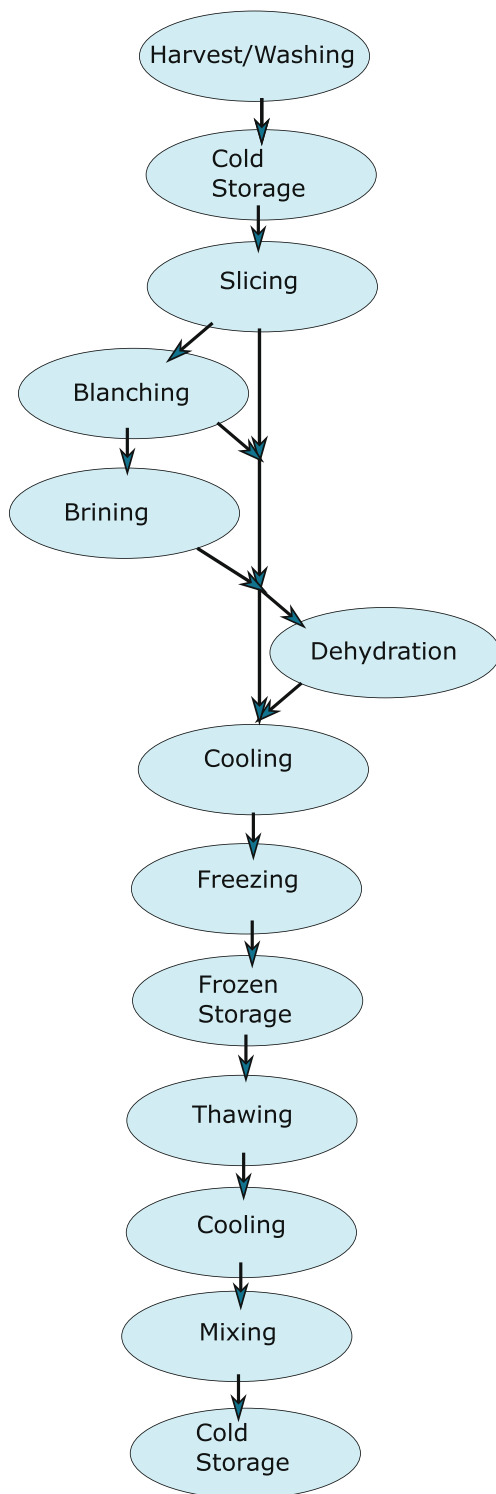
## Impact of Processing Steps in Production Chain

A typical production chain of frozen vegetables or fruits is shown in Fig. 3, which is line with production chains described in several patents [97–99] and textbooks [100]. The production chain is also consistent with the typical production chain for frozen fries as given by Scanlon [101], but I have not included par-frying explicitly, but it can be viewed as just another means for dehydration. The main difference between vegetable and fruit processing is that vegetables are commonly blanched, while it is absent for fruits. For the soft fruits it is important to retain the full turgor state, which will otherwise lead to detrimental loss of texture. Below, I discuss how each step in this production chain impacts the final quality, and the potential improvement of that, as offered by novel technology. Promising novel technologies are summarized in Tables 1 and 2.

### Cold Storage

After harvest fruits and vegetables are stored at low, non-freezing temperatures for buffering before further processing like freezing. Optimal long-term chilled storage conditions are found in literature [102]. In general fruits and vegetables are stored at low temperatures, provided that chilling injury or freezing injury is prevented [103]. Due to the applied temperatures and storage time, this cold storage will have little impact on the freezing quality. However, there is some potential in inducing *cold acclimation*, which is the physiological adaptation of plants to freezing conditions [10, 104–106]. This will be discussed below.

Many overwintering plants will show *cold acclimation*, if ambient temperature declines slowly below 5 °C [23, 107]. The physiological adaptations are targeted at the survival of the dehydrated cell after extracellular ice formation. The primary freezing injury to living tissue is the permeabilization of the cell membrane. The physiological adaptation comprises of (1) changes in lipid composition of membranes, making them less vulnerable to chilling injury, (2) increased accumulation of solutes in the vacuole, (3) synthesis of special proteins for protection of cell membrane, and modulation of the ice growth similar to antifreeze proteins, and (4) synthesis of anti-oxidants. Anti-oxidants are required because the freeze concentration of the



**Fig. 3** Process flow sheet for frozen vegetables and fruits. Prior to freezing the produce may either be blanched, brined and/or dehydrated (as in dehydrofreezing)

cell can promote oxidation reactions. Even, other proteins can be synthesized, that promote ice nucleation in the extracellular space [74].

The cold acclimation is thus primarily targeted at protection of the cell membrane, or prevention of the dehydration of the cell, via an increase of its osmotic pressure. In acclimated tissues, both the cell membrane and cell wall have become effective barriers for extracellular ice [20, 22]. Non-acclimated tissues often show intracellular ice growth, originating from extracellular ice via secondary nucleation. Membranes with chilling injury allow passage of ice from the extracellular space to the intracellular space. Intracellular ice formation is often lethal for living tissue.

Cold acclimation as a pretreatment to freezing has been investigated for carrots [10] and spinach [106], showing a significant decrease of freezing damage. Carrots have been stored at 0 °C to elicit cold acclimation. Cold acclimation of spinach leaves is elicited via changing the environmental temperature during growth. The experienced cold stress-induced cold acclimation.

However, if the acclimated vegetable is subject to blanching several protective effects provided by proteins or membrane composition will be eliminated, due to protein denaturation and thermal injury to the membrane [10]. Still, the amount of accumulated solutes in the vacuole will lead to a lowering of freezing point and decrease in amount and size of ice crystals.

Cold acclimation will be difficult for (sub)tropical produce. For these produces the cold storage temperature must also remain above a critical value, otherwise, chilling injury happens, leading to damage of the cell membrane, and loss of turgor [22].

### Slicing

Processed vegetables and fruits are often sliced or cut to reduce size for consumer convenience, or to enhance the heating rate of thermal processing like blanching, cooling or freezing. Slicing is often done if the product is still in the turgid state, because of its firmness. Hence, the plant is still metabolically active, and slicing will trigger biochemical defense mechanisms. Via slicing phenolic substrates, present in the vacuole, come into contact with enzymes leading to browning. Also the ripening biochemistry is accelerated, leading to faster softening of texture [108–110]. Also, slicing can enhance the loss of leaching of solute if further processing is performed in water (like blanching).

The negative effects of the activated biochemistry due to slicing can be stopped if the food is immediately blanched. For fruits blanching is often not done, and they can be frozen directly after slicing. As the freezing takes time, the sliced fruits can be dipped in water, to infuse it with anti-oxidants,  $\text{Ca}^{2+}$  and PME enzyme [111]. Anti-oxidants can retard the browning, and the  $\text{Ca}^{2+}$  and PME enzymes enhance the texture via cross-linking pectin. Furthermore,  $\text{Ca}^{2+}$  also retards the accelerated softening.

**Table 1** Critical factors related to drip loss

Process step	Input	Effect	Correlation with drip
Cold acclimation	Temperature/time	Amount solute	–
		AFP synthesis	–
		Anti-oxidants	0
Slicing	Size	Tissue rupture	+
		Blanching/freezing rate	–
PEF impregnation	Solute concentration	Amount of solute	–
		Antifreeze protein	–
Blanching	Temperature/time	Enzyme inactivation	0
	Size	Loss of turgor	+
	Heat transfer coefficient	Pectin solubilization	–
	Wet/dry medium	Solute leaching	+
Blanching	LTLT	Loss of turgor	+
		PME/Ca <sup>2+</sup> cross-linking	+/-
Dehydration	Temperature/time	Amount of solute	–
Freezing rate	Heat transfer coefficient	Ice crystal size	–
	Temperature	Amount of ice	–
Frozen storage	Temperature/time	Stress relaxation	–
		Pectin solubilization	–
	Temp. fluctuations	Ice crystal size	+
Thawing	Temperature/time	Stress relaxation	–
		Enzyme reactivation	0

Slicing plant-based products in the turgid state requires quite some energy, and consequently one sees the application of PEF (pulsed electric field) technology to puncture the cell membranes, leading to a reduction or loss of turgor pressure, and thus a reduction of the energy required for slicing [112, 113]. It is applied in practice to frozen potato products. Also, it is claimed that PEF before slicing can already provide (partial) inactivation of enzymes [114]. However, this claim is controversial as it is debated that the enzyme inactivation can just be imparted by the thermal effects of PEF [115].

## Blanching

For consideration of the blanching of vegetables on freezing, it is important to know the actual functionality of this pretreatment. Often, it is primarily intended to inactivate enzymes. For green vegetables it is important to inactivate lipid oxidase [116, 117]; otherwise, off-odours can develop due to lipid oxidation during freeze concentration. Also one desires to inactivate peroxidase, to reduce enzymatic browning [118, 119]. However, for

some vegetables like carrots it is questionable if blanching is required to inactivate enzymes, for they have limited impact on texture and browning [8]. Other studies state that a very quick treatment of dipping carrots in boiling water for 10–20 s is sufficient for inactivation enzymes responsible for lipid oxidation [10].

The temperature treatment during blanching will give undesired effects on the texture. First of all, the permeability of cell membranes is imparted, leading to loss of turgidity [120]. Especially for fruits, this is highly undesired, and consequently fruits are seldom blanched prior to freezing [121]. Furthermore, blanching at high temperatures,  $T > 80$  °C, will solubilize the pectin of the cell walls via the  $\beta$ -elimination process, leading to cell separation and weakening of the tissue [7]. Water holding properties of cell wall materials are imparted by the solubilization of pectin [64].

Common blanching processes involve the immersion of the vegetables in hot water or steam [7]. Blanching via immersion in hot water renders a good heat transfer, but it can also lead to leaching of solutes. Sliced products are of course extra vulnerable to leaching of solutes. The loss



**Table 2** Opportunities for novel technology

Processing step	Novel technology	Pro	Con	Refs
Cold storage	Cold acclimation	Freezing tolerance	Several effects lost after blanching	[206]
Pretreatments	PEF impregnation	Stress/freezing tolerance	Only for small sizes	[152, 154]
	Xlinking via Ca <sup>2+</sup>	Firmer texture	Must be blanched	[152, 207]
	PEF vacuum impregnation	Solute increase	Effective for porous food	[150, 154]
Blanching	MW blanching	Cell viability after freezing	Only applicable non-blanched	[150]
	Ohmic	Fast volumetric heating, in air	Non-uniform heating	[7]
	High pressure	Rapid, uniform heating	Immersion in liquid, leaching	[208]
	Infrared/HA	Firmer texture	Batch process	[138]
Dehydration/blanching	HA- RF blanching	Fast heating and drying	Only for sliced products	[140]
	Impingement blanching	Fast heating, no leaching	Less uniform than wet RF	[141, 142]
		high heat transfer/combined with peeling	Only efficient for small sizes	[124, 136, 137]
Dehydration	PEF-assisted dehydration	Retention of texture	Only for small sizes/partial viability	[209–211]
	Polyol OD	Higher osmotic pressure/health	Lower solubility	[145]
Freezing	Ultrasound for nucleation	Small ice crystals	Requires immersion in liquid	[173]
	Pressure shift freezing	Small ice crystals	Batch process	[174]
Thawing	Ohmic	Fast thawing	Requires immersion in liquid	[170, 200]

of solutes implies an increase of the freezing point, and therefore an increase of amount and size of ice crystals—which are both negative for freezing quality. Solute leaching is reduced via steam blanching [122]. Steam blanching is also a fast process, due to the efficient transfer of heat via the condensation of steam [123]. The use of superheated steam allows for temperatures below 100 °C [124, 125].

The impact of the thermal treatment during blanching on texture can be reduced via two strategies: (a) LTLT (low temperature long time) blanching or (b) HTST (high temperature short time) blanching [126–128]. During LTLT blanching the low temperature enhances the activity of the PME enzyme, which enhances the strength of the cell wall via mediating cross-links between pectins with  $\text{Ca}^{2+}$  [129]. Many vegetables already contain sufficient calcium in their cell wall material [126, 130], but it can be added to the blanching water, or infused via vacuum impregnation [131, 132]. The strengthened cell wall will have reduced water holding capacity but may resist better the compression induced by the growing ice crystals during freezing [8].

The HTST blanching strategy can be applied with technologies having a high heating rate. The texture degradation is reduced if the heating rate is significantly faster than the kinetics of the  $\beta$ -elimination of pectins [133]. A faster heating rate is often the target of novel blanching technologies like Ohmic heating [7], or radio-frequency or microwave heating [134, 135]. These are volumetric heating methods, which can heat foods up to 80 °C within one minute. The volumetric heating makes the heating rate quite independent of the size of the product. However, especially via microwave heating, there is often a large non-uniformity in temperature—making such a blanching technology hard to design and control. The HTST strategy can also be achieved by enhanced heat transfer coefficients as in jet impingement technology [124, 136, 137]. However, the enhanced heat transfer coefficient is only efficient if the size of the product is small enough that the heating rate is still determined by the external heat transfer coefficient, rather than the thermal conduction inside the product.

Good enzyme inactivation, while maintaining a firm texture, can be achieved with high-pressure blanching [138, 139]. However, high-pressure treatment is a batch operation, requiring specialized equipment, which is difficult to incorporate in the continuous production chain of frozen vegetables and fruits.

Another measure against solute leaching is the addition of solutes to the blanching water [8, 132]. This can even promote the diffusion of solutes into the vegetable if the solute concentration in the blanching water is higher than in the tissue. The addition of solutes will lower the food's initial freezing point [8]. But, their effect might not be very large, due to diffusion barriers imposed by the cell wall material.

Some dry blanching techniques allow for combining the process with dehydration, i.e., drying, with the purpose of increasing solute concentration, and thus lowering of the initial freezing point, and the ultimate improvement of the quality of frozen product. Examples of these dry blanching technologies are infrared/hot air blanching [140], and blanching via hot air and radio-frequency heating [141, 142]. Dehydration can only be performed at practical time scales for small (sliced) products. Also, one must be careful and prevent case hardening, the formation of a dense skin on the product, which leads to a significant lower appreciation of the texture by consumers, and limits possible rehydration after thawing.

## Dehydration

Potato products and some vegetables are air-dried after blanching to remove surface water to avoid clumping during freezing operation in the tunnel [97] or oil splashing during par-frying [101]. Dehydration can also be performed to improve the quality of frozen fruits and vegetables. The dehydration lowers the amount of water and increases thus the solute concentrations, and consequently it lowers the initial freezing point of the food—leading to smaller ice crystals and a smaller amount of ice formed. These combined processes of dehydration and freezing is known as dehydrofreezing [7, 52].

Although dehydrofreezing is already known for years, it has received little attention in the scientific literature. It has been argued that there is much room for improvement if the two processing steps are jointly optimized [52]. The dehydration step can be performed via conventional air drying [143] or via osmotic dehydration, but this process requires intact cell membranes [144]. This technology is then particularly applied to fruits, and to vegetables, which are nearly always blanched (destroying the integrity of the cell membrane). For vegetables, dehydration can conveniently be combined with blanching, as reviewed in the previous section.

To improve the quality of frozen vegetables or fruits the amount of water to be removed via dehydration should be in the order of 30–50% [52]. Next to improvement of texture, there is also a reduction of freezing time, which significantly reduces energy consumption [52].

Osmotic dehydration is performed via immersing food in an osmotic solution, containing a high concentration of solutes like sugars or salts. The process has some negative side effects like leaching of solutes from the food, and the increase of salt or sugar levels of the food [144], which can impair the sensorial and nutritional value of the food. The nutritional constraints of sugar or salt in osmotic solutions can be lifted via the use of sugar replacers with smaller molecular weight such as polyols [145]. Per mass of solute

they also offer higher osmotic pressure, i.e., a higher driving force for osmotic dehydration.

Furthermore, osmotic dehydration is a slow process [146] as (1) water has to pass through the cell membrane, which is the dominant resistance to mass transfer and (2) the dehydrated crust of the food with increased concentration of the solute from the osmotic solution has a decreased permeability. The temperature and solute concentration of the dehydration solution are limited because at high temperature or high osmotic pressure cell lysis will occur (also known as osmotic plasmolysis) [147, 148], leading to the loss of function of the membrane—becoming fully permeable. Generally, osmotic dehydration is performed at 30 °C, avoiding the loss of cell membrane integrity [52]. Furthermore, the recycling of the osmotic solution is a concern from a technological and hygienic point of view [144, 146].

Significant enhancement of osmotic dehydration is via the combination with vacuum impregnation [149, 150]. During this pretreatment the air in the intercellular space is removed and replaced by the osmotic solution. This pretreatment is especially advantageous for highly porous foods like apples. Recently, it is also applied to carrot and strawberries, where sugar impregnation is combined with  $\text{CaCl}_2$  and/or PME to promote cross-linking of pectin, which will increase the mechanical strength of the cell wall [151, 152].

Because osmotic dehydration is inherently a slow process, there has been a variety of research studies of improving the mass transfer rate via combining the dehydration with techniques like high pressure or pulsed electric fields (PEF) [146], with the purpose to increase (temporarily) the permeability of the cell membrane. The treatment should be mild enough, such that the resistance to mass transfer is lowered, but the loss of membrane permeability is reversible, such that full turgor can be restored after osmotic dehydration [5, 152].

Some studies concerning PEF-assisted osmotic dehydration have investigated whether the viability of the cells can still be retained after freezing. PEF is combined with vacuum impregnation of antifreeze agents and/or antifreeze proteins that are impregnated into the tissue, leading to enhanced cryoprotection of the tissue [153]. Retention of cell viability requires fast freezing rates as in cryogenic freezing, such that intracellular ice formation occurs. The small, round ice crystals will not puncture the cell membrane. However, this is achieved for few porous products, such as leafy vegetables (like spinach leaves) [154, 155], and fruits as strawberries [150] and apples [156]. However, the texture and drip loss is still comparable with a vacuum impregnation treatment without PEF [150].

If one tries to achieve retained cell viability via air dehydration, the drying must be done at very mild conditions

to prevent permeabilization of the cell membrane, which happens at temperatures above 40 degrees [143]. It is suggested to use vacuum-microwave drying performed at low temperatures [52].

## Freezing Operation

Commonly, industrially processed fruits and vegetables are frozen using air blast freezing in conveyor belt tunnels [100]. Air is forced by big fans over a mechanical refrigerator unit, and then over the belt with produce. The belt allows vertical airflow to pass through it. The air temperature is often set between  $-18$  and  $-40$  °C, and air velocities are in the order of 1 m/s. Heat transfer coefficients of  $10$ – $80$   $\text{W/m}^2$  K are commonly reached [157, 158], which are not as high as in fluidized bed freezing or impingement freezing [159]. Hence, there is definitely room for improvement of final product quality and texture. One can follow two strategies to improve freezing, aiming at either (1) the enhancement of the freezing rate or (2) the enhancement ice crystal nucleation [5].

Earlier I have discussed how the freezing rate impacts the ice crystal size, and thus the food texture [53]. The freezing rate is determined by several factors, namely the size of the food, the heat transfer coefficient of the coolant medium, and the freezer temperature, as indicated by Planck's equation [53]. Heat transfer rate can be improved via enhancement of airflow velocity, as in jet impingement freezing [160, 161] or in fluidized bed freezing [162], or by choosing another coolant medium like a liquid in immersion freezing, or a cryogenic liquid or gas from liquid nitrogen or  $\text{CO}_2$  freezing [163]. Via jets of airflow impinging the surface of foods one can achieve a local heat transfer coefficient of  $400$   $\text{W/m}^2$  K [164]. It must be noted that the increase of air velocity also promotes mass transfer, i.e., the evaporation of water from the food, which might not be desired.

Cryogenic freezing is used in practice for freezing quite vulnerable fruits and vegetables, such as berries [151, 165, 166]. The high freezing rate of cryogenic freezing is mostly due to the low temperature of the coolant, cold nitrogen or  $\text{CO}_2$  gas or sprays—which is generated from solid  $\text{CO}_2$  or liquid nitrogen. The freezing temperature is due to the low boiling point of the cryogenic liquids, which are  $-78$  °C or  $-196$  °C for  $\text{CO}_2$  and  $\text{N}_2$ , respectively. Both gases are quite inert and do not penetrate the food. Cryogenic liquids can also be sprayed on the foods, and the freezing is then enhanced by the required heat for the evaporation of the cryogenic liquid droplet on the foods surface [100].

In immersion freezing the cooling medium should remain liquid below 0 °C, which can be mixtures of water/glycerol, water/ethanol or similar liquids as used in osmotic dehydration (sugar or salt solutions) [167, 168]. The heat transfer coefficients in liquids are considerably

higher than those in airflow, which are in the range 150–1500 W/m<sup>2</sup> K [169]. During immersion freezing in such liquids there will be impregnation of food with solutes from the liquid if the food does not have any proper barrier. For large-sized foods like fish or meat, it is economical to use vacuum-sealed packagings as a barrier. However, if a similar liquid has already been used for osmotic dehydration, the use of immersion freezing in the same liquid can be a serious option for freezing fruits or vegetables, via combining freezing and osmotic dehydration [167]. Freezing rates can also be improved via the use of impingement technology.

There will be a limit to the freezing rate, as high freezing rates will impact the development of mechanical stress in the food, due to the volume expansion of ice [170]. At high freezing rates, the stress has insufficient time to relax. High stresses can lead to freeze cracking or damage during fast thawing [171].

At sufficient low freezing temperatures, the food attains the glassy state. The food is not in equilibrium but is supercooled. The amount of ice formed depends on the freezing rate [171]. However, if one thaws these supercooled foods too slowly, ice growth can occur at temperatures just below freezing point. All the protection offered by the glassy/supercooled state against freezing damage can be eliminated by the slow thawing [172].

For the stimulation of ice nucleation one has been tried several novel technologies, like ultrasound [173], pressure shift freezing [174], static or oscillation electric fields [175], and oscillating magnetic fields [176, 177]. Whether (electro)magnetic fields have a significant influence on nucleation is doubtful [178, 179]. Ultrasound and pressure shift freezing have significant effects on nucleation. However, ultrasound is only effective if the frozen food is submerged in liquid as in immersion freezing. For pressure shift freezing quite specialized equipment is required, which only works for batch operations. Hence, novel technology is difficult to combine with conventional air blast freezing tunnels. I view mainly potential for ultrasound technology if applied to immersion freezing of fruits [180, 181]. Ultrasound will also enhance the heat transfer if the immersion fluid via the acoustic streaming effect.

In formulated foods like gels and ice creams, one can control nucleation also via additives, but that is difficult for fresh vegetables. Some trials are performed using pulsed electric fields, to permeate the cell membrane and to impregnate vegetables with antifreeze agents like trehalose and antifreeze proteins [155]. However, the additives can be costly.

Hence, for most foods control of ice nucleation must rather be sought in processing technologies, which can be applied with conventional freezing equipment. Examples of these technologies derive from the field of cryopreservation or freeze-drying. Examples of such methods as applied to

are (1) shock freezing [19], (2) ice fog method [182], and (3) mechanical shock [49].

It is not likely that the ice fog method is applicable to vegetables and fruits because their epidermis does not permit direct contact of the liquid in the tissue and the deposited ice crystal seeds. In freeze-drying it is relatively easy to provide a mechanical shock to vials placed on the shelf of the freezer [49]. But, for belt freezing it is not evident how to apply mechanical shocks.

I view that for food processing the shock freezing method is the easiest to implement in practice. During shock freezing the product is first slowly cooled to a supercooling of about 5 °C, and it is held in the supercooled state for some time. After the holding time, the freezing temperature is suddenly dropped to temperatures far below – 20 °C. This temperature shock very often induces the nucleation, which is expected to give a more uniform and fine ice crystal distribution [19].

There are a few reports in food science, where the shock freezing method has shown to initiate indeed ice crystal nucleation [183–186]. The temperature shock leads to the nucleation of many small ice crystals. Due to the subsequent fast, deep freezing step the nucleated ice crystals have little time to grow and coalesce, as at low temperatures the water diffusion coefficient is too low for ice crystal growth [54]. However, a recent application of shock freezing to strawberries still shows freezing damage comparable with conventional slow freezing, despite the controlled nucleation of ice crystals [186]. The fast growth of ice crystals has caused much mechanical stress on the cell membranes and cell walls, which appears to be split in pieces similar to what happens during slicing. Apparently, the rigidity of the cell is an important factor to consider when applying shock freezing.

## Frozen Storage

It is common practice that frozen foods are stored lower or equal to – 18 °C, which is the limit set by legislation (such as the European directive for Quick Frozen Foods). This storage temperature is still above the glass transition for many fruits and vegetables [187]. Consequently, during frozen storage there can still be (bio)chemical activity and coarsening of ice crystals. Especially, the effects of temperature fluctuations due to the mechanical temperature control are expected to have a large impact on frozen food quality [188].

Often, it is advised for minimization of freezing damage to store foods at the intersection of freezing line and glass transition line, which lies in the range of – 20 to – 40 °C for most fruits and vegetables [189]. However, one must mind that the chemical kinetics and ice coarsening are driven by diffusion, which decouples from the viscosity

at temperatures around the glass transition [190]. Hence, the glass transition is not a good measure for diffusivity, but rather for viscosity. I have shown that near the glassy state diffusion is quite independent of the molecular weight of solutes [190]. Consequently, the effects of the chemical kinetics and ice coarsening are quite independent of the type of food, i.e., the type of solutes. But, ice coarsening can still be controlled by antifreeze proteins [191, 192], as synthesized by cold acclimation or infused via PEF.

The large independence of the type of food concerning the physical and chemical changes during storage allows for a simple strategy for improving food storage: lowering of the storage temperature will have similar effects on all stored fruits and vegetables. If the storage temperature is lower than  $-25\text{ }^{\circ}\text{C}$ , the effect of temperature fluctuations is considerably lower due to reduced diffusion coefficients and lower (bio)chemical activity. Of course, via packaging with good insulating properties the effects of these fluctuations can also be lowered [193].

During frozen storage, the thermal stresses accumulated during the freezing operation can relax. However, this is a very slow process with relaxation times of about half a year. The relaxation time also depends on how far the storage temperature deviates from the glass transition temperature of the frozen food [89, 194].

## Thawing

Generally, thawing is performed more slowly than freezing. This is mainly inherently to the process for the following reasons [195]: (1) the thawed outer layer of food has a lower thermal conductivity than the frozen part, (2) the ambient temperature cannot be high, because of high temperatures promoting biochemical processes, as enzymatic activity, microbial decay or protein denaturation having adverse effects on product quality. One should mind that enzymes and microbes are often not (fully) inactivated, and proceed with their activity upon rewarming [95]. Furthermore, it is also because thawing is often left to the consumers, who either leave it in the open air in the kitchen, or in the refrigerator or immersed in tap water [195]. The latter is considerably faster, but allows solutes to leach out in the immersion liquid, but which can be minimized via having the food wrapped in plastic packaging foil [196].

On the other hand, slow thawing should give the food time to relax mechanical stresses induced by freezing and allow to reabsorb moisture, which would either be lost via drip loss [197]. The stress relaxation time is much faster in the thawed state as in frozen storage. But, for meat [198] and potato [33] it is found that thawing rate does not affect much the volume of drip loss. In general it is stated that thawing has little influence on texture, as much irreversible damage is already performed during freezing [196].

Thawing frozen food is applied in the industry if frozen food is mixed into a multi-component meal like a pizza, pie or salad [196]. Also some frozen foods are tempered, i.e., raised in temperature from  $-18$  to  $-5\text{ }^{\circ}\text{C}$  to allow for easy slicing [199]. Conventional thawing methods are reviewed by James [199], which rely on heat transfer via (moving) air, water or condensing steam. Via forced convection and smart temperature/time strategies the thawing can be significantly faster than at the consumer site.

Novel processing technology has been investigated for industrial thawing [200]. Thawing can be achieved via pressure-shift freezing [201], where frozen food are subject to high pressures of about 200 MPa at  $-15\text{ }^{\circ}\text{C}$ , by which the freezing point shifts. Thawing can happen at subzero temperatures, and subsequently rewarmed to room temperature. Application of this method is limited due to high costs of equipment, and their batch-like operation.

Fast thawing can also be achieved by electromagnetic means, via microwave, radio-frequency (RF) waves or ohmic heating [170, 200]. Especially during microwave heating, there is strong non-uniform heating as the frozen part hardly absorbs microwaves. One can experience overheated edges of the food, while the inner core is still frozen.

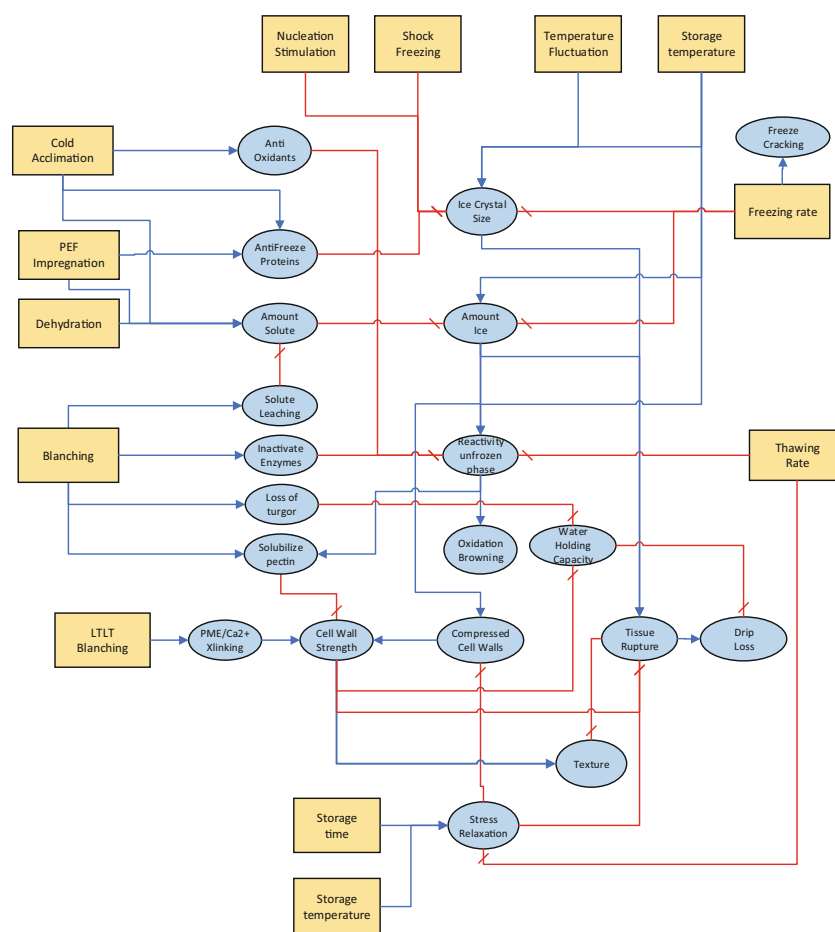
Due to the longer wavelength of RF waves, the temperature distribution is much more uniform than with microwaves, but its non-uniformity is still limiting its application to thawing [170]. Thawing via Ohmic heating is quite promising, but it often requires immersion of the frozen food in a liquid, promoting leaching of solutes. However, the treatment times can be quite short, in the order of minutes. Thawing can also be done via ultrasonic acoustic waves, which are mainly absorbed by the frozen part. The efficient application of ultrasound requires immersion of frozen food in liquid, leading to leaching of solutes. The technique is still experimental, and still with some disadvantages like high power consumption and low penetration depth—leading to non-uniform heating [170, 200].

## Discussion

### Summary via the Causal Network

The above review of the effect of processing steps on the final quality of frozen vegetables and fruits is summarized by means of a causal network (also known as a concept map), cf. [202–205], as shown in Fig. 4. The (aspects of) processing steps are indicated with rectangles, which are connected to physicochemical factors of influence to the final product quality. These connectors either indicate a positive correlation (blue arrows) or a negative correlation

**Fig. 4** Causal network of how processing steps in the production chain (rectangles) impact the physicochemical factors related to final product quality. Positive correlations are indicated by blue arrows, and negative correlations are indicated by barred red lines



(red barred connectors). For example, the dehydration processing step promotes the amount of solute in the sample (via removing water). Most of the physicochemical factors do not have a direct effect on the final quality. Most times, their impact is indirect, which is indicated by the network of causal relations between these physicochemical factors. This network is based on the physics and chemistry behind freezing of vegetables and fruits, as summarized in the supplementary material. In the network one can distinguish several final quality aspects: drip loss, texture, water holding capacity (related to juiciness), and browning. In the causal network, I have included all processing steps from Fig. 3, except for slicing. The latter is done because otherwise the causal network becomes too much cluttered up. The main effect of slicing is to reduce the size, which will affect the heating rate during blanching or thawing, and freezing rate. Hence, the effect of reducing size via slicing is absorbed in these processing factors.

As an example of the use of the causal network, I focus on a single quality aspect, drip loss. Via traversing the causal network from the processing factor to the drip loss factor, one obtains the final effect on the processing factor on the drip loss, via multiplication of the signs of the correlations.

The final results are captured in Table 1. The left column lists all steps of the production chain of frozen vegetables and fruits. The next column indicates the input parameters one can adjust in these process steps. Each processing step can impact some physicochemical factors, which are stated in the third column. The fourth column indicates how the increase of the physicochemical factor in the third column impacts drip loss. This impact can either be negative (−) (decreasing drip loss), positive (+), or indifferent (0). If the impact is either negative or positive, we have placed (+/−) in the fourth column. In the table, the slicing operation is now incorporated.

Using the considerations from the above review and the results listed in Table 1, I have come to the following recommendations for modification of the production chain of frozen vegetables and fruits for improved drip loss:

- Perform cold storage at low temperature, just above the freezing point of the vegetable, to induce *cold acclimation*.
- Match the size of the product during slicing to a shorter blanching time and/or faster freezing rate.
- Match the blanching time to the size of the product and the enzyme inactivation kinetics and pectin degradation

kinetics, i.e., perform blanching as short as possible by the use of the HTST treatment.

- Before HTST perform LTLT blanching to promote pectin cross-linking, which might be combined with calcium immersion.
- Combine dehydration and blanching via using superheated steam impingement or hot air/infrared heating.
- Find an optimal freezing rate with minimal ice crystal size, and minimal stress accumulation
- Low frozen storage temperature,  $T \ll -18$  °C, to reduce Ostwald ripening and the product sensitivity to temperature fluctuations.
- Improve packaging during frozen storage, with increased thermal insulation and moisture barrier, for minimization effects of temperature fluctuations.
- Perform thawing at moderate temperature (0–10 degrees) and allow time for stress relaxation and resorption of drip loss.

From the list above, one can observe there are largely two main strategies to reduce drip loss: (1) improved freezing operations, with faster freezing rates and lower freezing temperatures, and (2) the increase of solute concentrations before freezing, which is achieved via other processing steps prior to freezing. However, one must also consider the adverse effects of increased solute concentration (i.e., reduced water content) on other quality factors like texture or water holding capacity/juiciness. It is clear that industry has to make a compromise between different quality traits.

### Process Intensification and Production Chain Optimization

Above, I have discussed the individual processing steps in the production chain. Here, I discuss potential improvements if larger parts or the complete product chain is taken into consideration. First, I discuss the possibilities of process intensification, where one tries to integrate several unit operations into a new one. In the production chain of frozen foods, there are opportunities for process intensification, if there are subsequent processing steps which use the same medium for heat transfer. Via combining such processing steps one shortens the residence time, often leading to improving final product quality. From this perspective, I see two possibilities for process intensification: (1) combination of blanching and dehydration of vegetables if performed in hot air or (superheated) steam and (2) combination of osmotic dehydration and freezing for fruits if immersed in a liquid.

If the blanching is performed in air or steam, there is little leaching of solutes and nutrients. This dry blanching is easily combined with dehydration, which can be viewed as the first step in dehydrofreezing. However, dehydration

can lead to loss of texture, if there is structural collapse of the tissue [27]. Volumetric heating can help in preventing collapse during dehydration due to the generation of pressure inside the tissue due to internal evaporation [27]. Another suggested measure to reduce texture loss is to strengthen the cell wall via PME-enhanced cross-linking of pectin with  $\text{Ca}^{2+}$ , as in the LTLT blanching method. The dehydration/blanching step should be designed such that the reduction in texture breakdown in the following freezing step significantly outweighs the texture loss imposed by the dehydration. Recall, that dehydrated vegetables will have less freezing damage due to a reduced ice crystal size, and a reduced amount of ice formation.

The other possibility for process intensification is foreseen for fruits, that are immersed in osmotic solutions, to perform both osmotic dehydration and immersion freezing [167]. There is good potential to combine it with novel technology. Mild PEF treatments can make the cell membrane more permeable but can be repaired if the cells remain viable [150]. Furthermore, thanks to the immersion liquid ultrasound can be applied efficiently to promote ice nucleation [173]. This possibility for process intensification offers opportunity for fruits, where the conventional freezing process leads to too much freezing damage due to their fragile tissue, such as strawberries. Still, the design of the intensified process should be done with care to overcome the two drawbacks of immersion freezing [167]: (a) to keep the immersion liquid free from microbial contamination and (b) the influx of solutes from the immersion liquid into the fruit. The latter can affect the health impact of the fruit, due to the increase in sugar levels. However, this might be solved by the use of polyols as the osmolyte [145].

Next to process intensification, whose implementation is still quite involving for the food industry, I view there are still ample opportunities for simultaneous optimization of the complete production chain. Taking into account the interaction between various processing steps, one could optimize the settings of each processing step for the optimal value of the final product quality.

This optimization requires good quantitative knowledge on how the processing impacts the product quality. Over the years a large body of knowledge on this matter is generated, but still, some knowledge is lacking especially the impact of processing on mechanical damage and water holding properties. Below, I will summarize some of the findings, that can be found in literature. Most of this knowledge is on the kinetics on biochemical processes impacting product quality, which links to the functionality of several processing steps like blanching and freezing, i.e., to lower the activity of these biochemical processes. For optimizing the production chain for the final quality one has to minimize the thermal impact of the processing steps. This can be achieved via matching the time scale and/or resi-

dence time of the thermal processing with the time scale of biochemical kinetics. Below, we discuss the time scales of relevant biochemical processes in several processing steps.

Cold acclimation happens at relatively long time scales of several weeks [104]. Hence, to invoke cold acclimation, one has to match cold storage times of freshly harvested vegetables and fruits to this long time scale of cold acclimation. Diurnal fluctuating storage temperatures can help to shorten this time scale, as the metabolism is higher at elevated temperatures.

Blanching affects the inactivation of enzymes, the degradation of color and simultaneously modifies the cell wall structure. These kinetics have been investigated for several vegetables [212–216]. The cell wall structure is modified enzymatically via the PME enzyme, and via  $\beta$ -elimination. PME removes methoxy side groups from pectin, which makes them less vulnerable to  $\beta$ -elimination. The interaction between these processes is captured in the model by Verlinden [214]. The time scale of the heat transfer process can be estimated with simple models, as proposed earlier [217, 218]. The time scale of the heat transfer depends on (1) the size of the product, (2) the external heat resistance as quantified by the heat transfer coefficient  $h$ , and (3) the internal heat resistance. For determining the endpoint of blanching the limiting time scale of the most important biochemical processes has to match the time scale of heat transfer [219].

Blanching modifies the mass transfer during a subsequent dehydration step, due to the permeation of the cell membranes, allowing faster diffusion of moisture during drying [220]. Even blanching enhances the mass transfer during osmotic dehydration, but induces loss of cell membrane integrity. But, this makes the purpose of osmotic dehydration obsolete, which is to remove moisture, while maintaining turgor and cell membrane integrity [221]. For conventional dehydration methods like air drying or via superheated steam it is very beneficial to apply blanching beforehand due to the enhancement of the mass transfer. During dehydration the time scale for mass transfer is usually much longer than the time scale for heating. However, the time scale for mass transfer can still be computed using a similar approach as used for heat transfer [217, 218]. But, it requires knowledge of moisture diffusion coefficients, for which predictive theories are at hand [190, 222, 223].

The time scale for the freezing operation can be estimated using the Planck method, as detailed in [53]. With the help of the freezing time, and the difference between initial freezing point and coolant temperature (or desired final product temperature), and thermal conductivity [224] one can compute the freezing rate. Knowing the freezing rate one can estimate the ice crystal size via a power-law [53]. The ice crystal size can be taken as a measure for freezing damage [62].

During frozen storage, there can be further recrystallization, i.e., ice coarsening via Ostwald ripening. For sugar solutions, which can be regarded as a model system for fruits, a study has been performed concerning the kinetics [56]. The growth rate of the ice crystal volume is linear with the diffusion coefficient of water [225], which is known for carbohydrate solutions [190]. The model shows that the diffusion coefficient depends on temperature and mass fraction of water. Hence, recrystallization is minimized at lower storage temperatures, which lowers both the diffusion coefficient and the mass fraction of water (due to progressed ice fraction). For computing the ice fraction and the remaining water fraction in the unfrozen phase a simple relation with the storage temperature and initial freezing point can be used [224, 226].

## Conclusions

In this paper, I have reviewed the production of frozen vegetables and fruits from a chain perspective, which is instigated by our experience with industrial projects that final product quality can significantly be improved via optimization of the complete production chain [205].

This optimization requires good knowledge of the fundamental physicochemical and biochemical processes underlying the changes in product quality during their processing in the production chain. This knowledge is summarized in a network diagram, showing the causal relations between processing steps and physicochemical factors impacting various quality aspects. The use of the causal network is shown for the example of drip loss, an important final product quality.

In general, it is found that it is difficult to implement novel processing technology in current production chains. But, I do see opportunities for the use of novel processing technology if combined with process intensification, where several unit operations can be combined into a new single operation. In particular, I see the potential for combining blanching and dehydration for vegetables or combining osmotic dehydration and immersion freezing for fruits. But, the implementation of process intensification can still be quite involving modification of existing production chains.

Still, I view there is an opportunity to improve final quality of frozen food via optimization of the existing production chain, via careful matching the processing times to the time scales of the fundamental physicochemical and biochemical processes. For this optimization the causal network can be a good guiding tool.

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