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Novel Technologies in the Freezing Process and Their Impact on the Quality of Fruits and Vegetables

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Abstract

Fruits and vegetables (F&V) are living tissues that continue to respire after picking, and while this can be controlled by freezing, for the conservation of its components, maintaining its sensory quality. This review aims (i) to review the use of novel combined technologies used in the F&V freezing process, (ii) to evaluate its unconventional variants to obtain high-quality frozen products, including different aspects that influence this thermal process. The basic principles and uses of new technologies (i.e., ultrasound, magnetic fields, high pressure, microwaves, osmotic dehydration, isochoric freezing and cryogenic freezing and unconventional processes) are described. Moreover, was evaluated the impact of each technology on the control of the formation and growth of ice crystals, and its impact on the microstructure and quality characteristics of F&V, as well as their proposed mathematical models. It is concluded that new technologies combined with freezing have a positive and promising effect on process optimization, since their application can minimize the negative effects of traditional freezing methods.

Keywords Emerging technologies · Food processing · Fruit and vegetables preservation · Non-thermal technologies · Numerical models · Quick-freezing technologies

Introduction

Fruits and vegetables (F&V) are living organisms, metabolically active and perishable foods with a soft and delicate texture that contain high amounts of water in their composition (from 70 to 90%), characteristics that make them susceptible to mechanical damage, microbial attack and, consequently, loss of its organoleptic [1] and bioactive quality [2]. Likewise, its intense rate of respiration (generation of heat and carbon dioxide (CO_2) by oxidation of its stored nutrients) and transpiration (elimination of water vapor for the regulation of internal thermal balance) lead to deterioration, senescence, and reduction of its useful life [3, 4].

Freezing process is a conventional preservation method widely used to extend the shelf life of highly perishable foods after harvest. It consists of subjecting the food to temperatures below 0 °C, causing a reduction in the mobility and water activity (a_w) and, producing a decrease in chemical and enzymatic reactions and proliferation of microbial growth [5, 6]. In this context, freezing represents a common and viable method for prolonging the shelf life and also is non-invasive process, that preserves the intrinsic properties of the food with it the nutritional and organoleptic qualities,

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maintaining food safety and security [7]. However, the nucleation and formation of ice crystals inside the tissues is associated with various factors of the food (size, shape, structure, and composition) and the freezing method [8, 9]. During freezing process, heat and mass transfer phenomena are strongly linked to properties such as surface area, composition, density, and porosity of the food. These properties have a significant impact on the cost and efficiency of the finished product process and its nutritional and organoleptic characteristics. For this reason, the numerical models established for the freezing process are based on said transport phenomena, which will allow predicting, calculating freezing times and temperatures that are essential to maintain effective control of the process [10, 11].

There are efforts to optimize the freezing process in terms of speed that lead to reducing the structural damage produced in conventional freezing [12]. However, optimizing the process is complicated due to the ionic composition of the F&V, which causes high osmotic stress, consequently, an increase in the diffusion coefficient of cellular water, resulting in smaller ice crystals, which would solve the problem of cellular microstructure degradation [13]. Among the novel technologies, ultrasound-assisted freezing has shown excellent results due to the acoustic cavitation effect, which promotes ice nucleation by microbubbles and generating very small ice crystals [14]. Magnetic field assisted freezing has gained quite a lot of popularity, which through vibrating movements in the water molecule causes the water to remain liquid in a subcooled state and, furthermore, suppresses the nucleation of large ice crystals, favoring the formation of fine and microscopic crystals [15]. High pressure freezing is also an interesting technology with a great potential, its effects on the chemical and microbiological aspects of food are governed by Le Chatelier's principle [16]. The high pressure allows accelerating the nucleation stage, giving rise to the formation of a homogeneous matrix composed of numbers of ice crystals of microscopic size that will preserve the textural quality. Electromagnetic wave-assisted freezing is considered a technology with great potential, which causes friction between water molecules to produce a heating effect, thus, the energy is dissipated by the microwave, inducing the partial melting of the ice crystals [17, 18], since it allows control of the stage of formation of ice crystals during the process [19]. Osmotic dehydration as a pretreatment to the freezing process is based on the elimination of a large part of the water present in food by means of osmotic solutions with a high concentration of solutes for a period of time and a determined temperature, favoring the least amount of ice crystals, thus avoiding microstructural damage and preserving the organoleptic attributes, mainly in the color of the product [20].

There are other types of unconventional freezing such as cryogenic freezing, which consists of a very fast reduction of the temperature below the freezing threshold of the food, achieving beneficial effects such as reducing thawing losses, improving the appearance of F&V and maintaining the complete cell structure [21, 22]. Likewise, isochoric freezing is capable of completely preserving the cellular microstructure of the food, reduces microbial attack and allows considerable energy savings [23–25]. For all the above-mentioned, the aims of this review are to consolidate the knowledge related to fundamentals of the freezing process, the numerical models that explain this unit operation, the transport phenomena that occur, and the novel technologies combined with the freezing process.

Fundamentals of Freezing in Fruits and Vegetables (F&V)

Although freezing consists of subjecting the food to temperatures below 0 °C, internationally the reference temperature for freezing is -18 °C; at this temperature a large percentage of water contained in the food has been transformed into ice crystals [26]. However, since water contains dissolved solids, and as it freezes, the solutions that remain in a liquid state become more concentrated in solutes. This increase in concentration produces a phenomenon called cryoscopic descent, that is, as solutions are concentrated in dissolved solids, the temperature at which freezing occurs decreases, this explains why freezing occurs at temperatures below 0 °C [11, 27]. After the freezing process it is possible to notice three significant changes in the plant tissue, (1) dehydration of the cell due to the location of the ice nucleation, (2) solute damage induced by the increase in intracellular fluid concentration during freezing and (3) mechanical damage through stress imparted by the expansion of the ice phase [28] closely related to the location of nucleation, within cells (intracellular nucleation) or outside of cells (extracellular nucleation). Extracellular nucleation is more convenient for the optimal conservation of plant tissue because it has heterogeneous nucleation sites [29].

A homogeneous nucleation in the intercellular space with formation of smaller ice crystals than the size of the cell, is favorable. This would avoid perforation of the vacuole membrane, maintaining its structure and cellular integrity. On the contrary, if this does not happen, the formation of large ice crystals would cause the release of simple sugars, minerals, vitamins, polysaccharides, bioactive compounds, pigments, among others, from the vacuole into the extracellular space. This would negatively affect the osmotic balance, the turgidity of the cell and the functionality of the plant tissue, thus leading to the detriment of the organoleptic properties of texture, aroma and flavor of the F&V. In addition, the stability of bioactives would be altered, compromising the effectiveness of their antioxidant capacity and other chemoprotective properties favorable to human health [30–34].

Thus, the faster the extracellular ice formation occurs, the less damage to the cell walls of the food, whereas the opposite effect would occur if the process is done slowly [5, 35].

On the other hand, during the freezing process synchronous mass and heat transfer phenomena occur in non-steady state. The food loses heat by convection through its surface and by conduction from its interior [36]. Three stages can be distinguished in this process: a) pre-cooling, b) phase change and c) post-cooling [37, 38] indicate that Plank, in 1913, proposed a numerical model to predict the freezing time, being one of the most used mathematical models due to its ease. Based on this model, new numerical models have been developed. For example, Ede in 1949 adapted this equation for use in food (Eq. 1):

$$t_f = \frac{\rho_f L_f}{T_f - T_a}\left(\frac{P'a}{h} + \frac{R'a^2}{k_f}\right) \tag{1}$$

where: t_f is the freezing time, ρ_f is the density of the frozen material, L_f is the latent heat of the food (kJ/kg), T_f is the freezing temperature (°C), T_a is the freezing air temperature (°C), h is the convection heat transfer coefficient for the material (w/m^2 °C), a is the thickness or diameter of the object (m), k is the thermal conductivity of the frozen material ($w/m°C$), and the constants P' y R' whose values are according to the form of the product: P' = ½, R' = 1/8 for the infinite plate; P' = ¼, R' = 1/16 for infinite cylinder; and P ' = 1/6 y R' = 1/24 for the sphere or cube.

The F&V represent a group of highly perishable foods due to their high-water content, up to 90%, which makes them susceptible to attack by microorganisms such as bacteria, fungi and enzymes [3, 4]. The freezing of F&V has become one of the most favorable technologies in the food industry, due to this process it is possible to store F&V seasonal, in order to extend its consumption time [39]. However, the freezing of F&V is very complex and different from the freezing of a drop of water due to the solutes present. In F&V the only thing that changes phase is pure water, the extracellular solution is concentrated in solids and the system becomes unbalanced, then, to try to restore the equilibrium of concentrations, water begins to migrate from inside the cell, that is, from the vacuole through the tonoplast into the cytoplasm and then into the intercellular space through the cell membrane and cell wall, and into the extracellular space through mechanisms called osmotic [11].

Novel Freezing Technologies

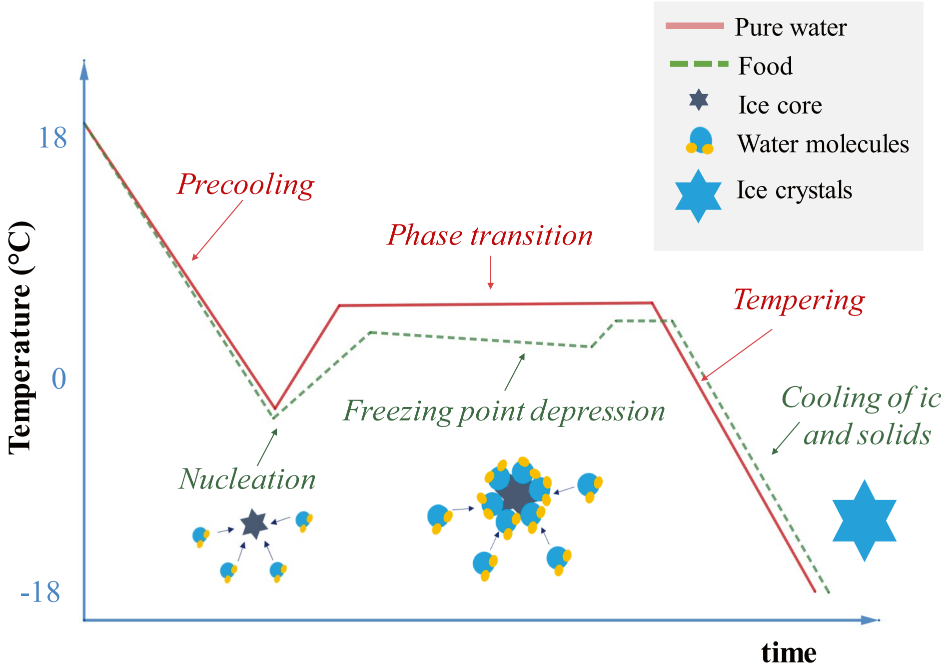
Ultrasound-Assisted Freezing

Otero et al. [40] described ultrasound as acoustic waves which are of low frequency ($20 - 100000Hz$) and high intensity (generally $< 1W/cm^2$). Ultrasound is generated by the attraction of polarized molecules in the high-frequency electric field, which causes elastic deformation of ferroelectric materials. Zhang et al. [41] mention that these waves induce a series of compression and rarefaction cycles during their propagation. On the other hand, the ultrasonic effect is linked to the cavitation phenomenon that occurs when a high ultrasonic power is reached during ultrasound transmission [42]. The attractive forces cause the formation of bubbles or cavities in two ways: (a) stable, when this phenomenon occurs gradually in a way that the bubbles do not reach the critical size to implode, or (b) transient, when the bubbles reach a critical size and implode violently [41]. The application of power ultrasound in the food freezing process, both solid and liquid, has shown to have relevant effects in optimizing this process. During freezing, ultrasonic irradiation triggers cavitation and micro-flow effects, which increase the rate of heat and mass transfer. It also increases the nucleation rate, which promotes the formation of ice crystals to occur microscopically and uniformly distributed in the microstructure of the food, thus considerably reducing structural damage (Fig. 1).

However, for its application to result in beneficial and non-adverse effects, the different ultrasonic parameters that influence the efficiency of the freezing process must be considered. One of them, the ultrasonic intensity, if this also increases the efficiency of the process, but also increases the thermal effect, which impairs said efficiency. For this reason, it is essential to maintain a balance between the ultrasonic intensity and the thermal effect in such a way that the efficiency of the freezing process is preserved [41, 43, 44]. Likewise, in the freezing of F&V it is important to take into account the percentage of void that the plant tissues present; the greater the vacuum, the less effective the ultrasound treatment [45]. Figure 2A represents the way in which ultrasound influences ice crystals, and how the cavitation phenomenon develops. The effects of ultrasonic irradiation on the freezing and quality of strawberries, blueberries, apple, pear, Hami melon, broccoli, and red radish frozen by ultrasound-assisted immersion have been evaluated (Table 1). From these studies, it has been verified that the increase in the ultrasonic intensity decreases the time necessary to reach the supercooling stage, thus reducing the freezing time. Likewise, it improves the nucleation rate and the growth rate of the crystals, therefore, the application of this technology allows to improve the quality of frozen F&V and reduces the loss due to dripping and nutrients [46–48].

On the other hand, Zhang et al. [41] mention that the ultrasonic parameters depend on the nature of the food that will be subjected to said procedure, because their intrinsic characteristics and also influence the efficiency of the process. Cong et al. [79] established a mathematical model for the quantitative analysis of the heat and mass transfer of the drops in the ultrasonic-assisted freezing process, a model that allows knowing the influence of the ultrasonic effect on the performance of the heat and mass transfer (Eq. 2):

Fig. 1 Freezing stages of pure water (continuous line) and that of a solid food (dashed line). Adapted from [37]



$$R_b\frac{d^2R_b}{dt^2}+\frac{3}{2}\left(\frac{dR_b}{dt}\right)^2=\frac{1}{\rho}\left[\left(P_0+\frac{2\sigma}{R_0}-P_d\right)\left(\frac{R_0}{R_b}\right)^3-\frac{2\sigma}{R_b}-\frac{4\mu}{R_b}\frac{dR_b}{dt}-P_0-P_a\right] \tag{2}$$

where: R_b is the bubble radius, R_0 is the initial bubble radius, P_0 is the constant hydrostatic pressure, P_d is the liquid vapor pressure, μ is the dynamic viscosity of water, P_a is the ultrasonic pressure, d represents the droplet, ρ is the density.

Alternatives are currently being studied to improve the effect of cavitation, since it plays an important role in optimizing the freezing process. It has been shown that cavitation affects the efficiency of the freezing rate and the acceleration of the formation of ice crystals [80]. A research carried out by Jiang et al. [81], evaluated the effect of pre-injection of pressurized CO_2 combined with ultrasound-assisted immersion freezing on the microstructure of sweet melon, obtaining significantly positive effects. It was determined that the application of pressurized CO_2 contributes to the improvement of the ultrasonic cavitation effect, consequently, it improves the formation and growth of ice crystals, allowing to reduce the microstructural damage of the product more effectively. However, despite being a remarkable technology for the optimization of the freezing process, it has only been used on a laboratory scale because considerable funding is required for the development of equipment that operates on an industrial scale [49].

Magnetic Field-Assisted Freezing

Magnetic fields are created by passing an electric current through a coil, which acts as an electromagnetic field. To create the magnetic field in an electromagnet, a coil of wire is wound around the magnetic core and when an electric current is passed through the wire, the magnetic field from all the turns of the wire passes through and penetrates the iron coil. This causes the domains to rotate and small magnetic fields to form from the core, creating the geomagnetic field effect [82]. Magnetic fields cause changes in the physical and chemical properties of liquid water molecules that are frozen through mechanisms of vibration, orientation, and rotation of their dipoles. This results in the magnetisation of water and alters its properties, including specific heat capacity, surface tension, conductivity, viscosity, and diffusion coefficient [52]. They also influence the distribution of electron clouds within water molecules (charge), the network of hydrogen bonds between molecules and the interactions/clusters between molecules and ions in aqueous solutions, which influences the kinetics of freezing.

During the freezing process, this technology strengthens the hydrogen bonds between water molecules, which enhances stability and order. This leads to a high level of supercooling, creating microscopic, fine, and evenly dispersed ice crystals in the food [83]. This protects the cell membranes of the F&V tissue, thereby enhancing the texture, taste and appearance of frozen foods [15, 84]. However,

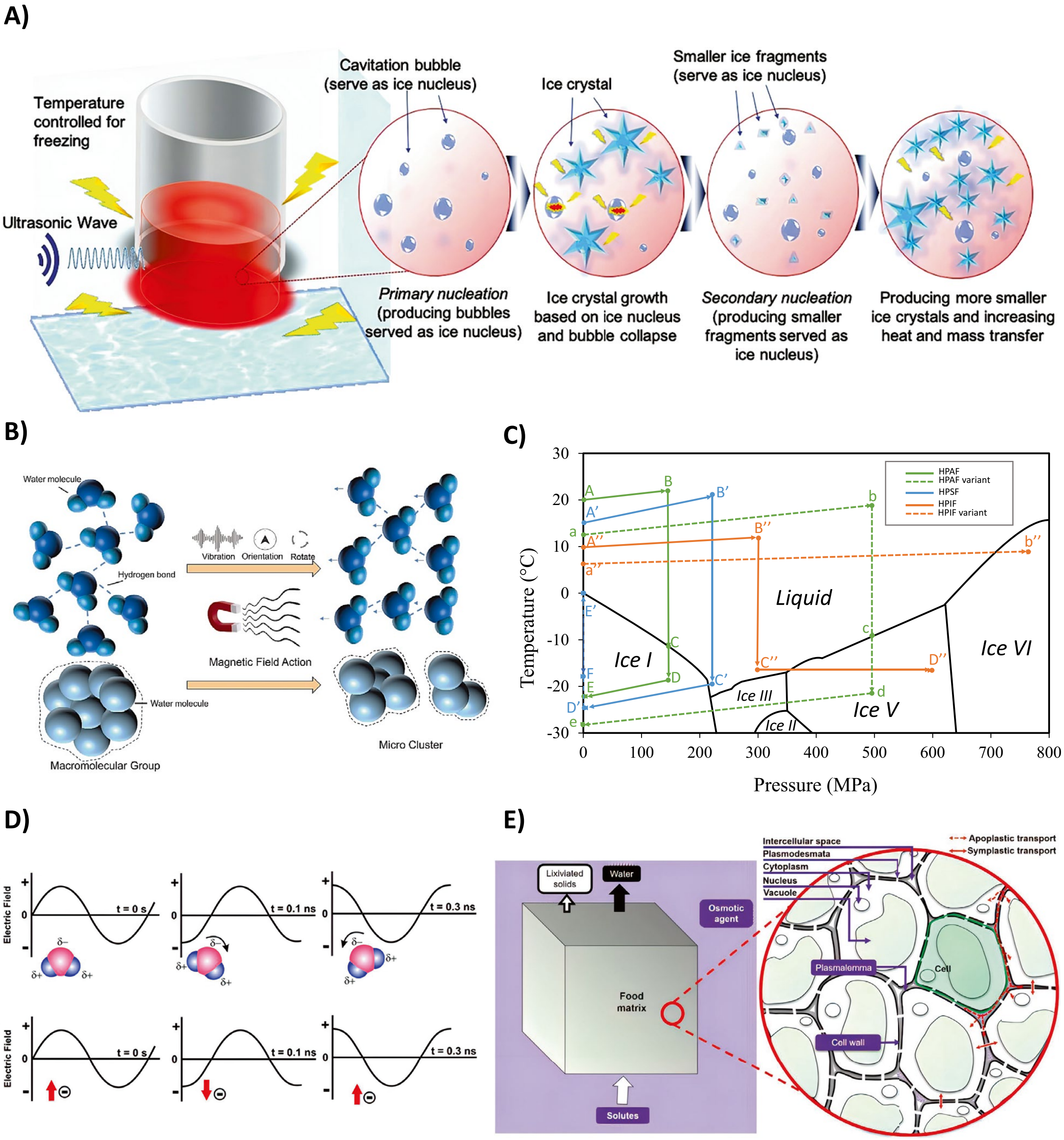


Fig. 2 Novel technologies. **A** Diagram of ultrasonic effect on ice crystals. **B** Hypothetical physical mechanisms of the magnetic field in changes in dipole rotation and clustering of water molecules. **C** Possibilities for high-pressure freezing processes based on the water phase diagram. **D** Heating mechanisms of water molecules under microwave irradiation. **E** Mass transfer during the osmotic dehydration process of F&V. Adapted from [49–52], https://doi.org/10.4018/978-1-5225-2136-5.ch003

it is important to acknowledge that the impact of the magnetic field is contingent on its intensity, as well as the length and temperature of exposure during the procedure [82]. Figure 2B shows the action mechanisms of magnetic fields on water molecule clusters.

A study was conducted to compare the impact of permanent magnetic field (PMF) and alternating magnetic field (AMF) assisted freezing on the microstructure of blueberries showed that applying AMF at 0.05 mT led to a 55.8% reduction in ice crystals. However, as AMF intensity increased, the phase change time also escalated, promoting the growth of ice crystals in food freezing, hence conveying an undesirable outcome. While in PMF significantly reduced the

Table 1 Summary of the applications of novel and unconventional technologies in fruit freezing

Type of technology		Fruits	Parameters	Results	References
Novel technologies	Ultrasonic assisted freezing	Blueberry	Ultrasonic power: 33.3 W/dm^3	Ultrasonic irradiation saves time and energy by accelerating the freezing time, resulting in a high-quality product.	[47]
		Strawberry	Ultrasonic intensity: 0.09, 0.17, 0.28, 0.42 and 0.51 W/cm^2 Temperature: -1.6 °C	Nucleation was promoted at a lower degree of supercooling, and it was also shown that the freezing time decreased with a higher irradiation intensity.	[53]
		Apple	Ultrasonic intensity: 0.28 W/cm^2 Temperature: -1 a 0 °C	The rate of drip losses was reduced, and rapid nucleation was induced.	[54]
		Pear Melon	Ultrasonic intensity: 0,145 W/cm^2	The firmness increased and the structure of the product was preserved.	[46]
	Freezing assisted by permanent magnetic field (PMF), alternating magnetic field (AMF), and static magnetic field (SMF)	Blueberry	Intensity: 10 mT for PMF and 0,05 mT for AMF	Significantly reduced the size of ice crystals.	[55]
		Cherry	Intensity: 10 mT for PMF and 1.26 mT for AMF	In PMF, lower nutrient losses were obtained compared to AMF, in addition, in the latter there was a higher energy consumption. On the other hand, in PMF the phase change time decreased.	[56]
		Cherry tomatoes	Intensity: 40Gs for SMF and 80 Gs for AMF	AMF was the best treatment for reducing weight loss and increasing catalase activity, while SMF delayed the post-harvest ripening process better and maintained product color.	[57]
		Guava	Intensity of AMF: 7,02 mT	The integrity of the tissue was preserved during the process, the speed of freezing was improved, and the quality of the product was preserved.	[15]
		Apple Peach Indian jujube Cucumber	Intensity of SMF: 0.45 mT	It allowed the reduction of the ize of the ice crystals formed during the process.	[58]

Table 1 (continued)

Type of technology		Fruits	Parameters	Results	References
	High-pressure assisted freezing	Peach Mango	Pressure: 200 MPa Temperature: -20 °C	Generated a high level of supercooling, which resulted in a uniform nucleation, and the structural quality of the product was preserved.	[59]
	Microwave Assisted Freezing	Apple	Microwave power: 167 W/kg	Drip losses were reduced, and the firmness of the product was not affected.	[60]
		Pineapple	Microwave power: 6 W/g	Structural quality preserved the uniform distribution of ice crystals.	[61]
		Banana	Microwave power: 1,5, 1,7, 2,0, 2,2 W/g Temperature: -40 °C	A better-quality product was obtained.	[62]
		Blueberry	Microwave power of 0,7 W/g	Facilitated heat transfer.	[63]
	Osmotic dehydration-assisted freezing	Strawberry	Concentrations of the osmotic medium: 45-65 BrixOsmodehydration temperature: 30 °C Freezing temperature: -40 °C	It prevented loss of fruit quality and contributed to the formation of important components in the aroma of the product.	[64]
		Papaya	Concentrations of the osmotic medium: 65 Brix Osmodehydration temperature: 20 °C Freezing temperature:-33,74°C	Intensified the color of the product, and preserved its structure.	[65]
		Apricot	Concentrations of the osmotic medium: 65% w/w Osmodehydration temperature: 25 °C Freezing temperature: -40 °C	Drip losses were significantly reduced.	[66]
		Cucumber	Concentrations of the osmotic medium: 65% w/w Osmodehydration temperature: 35 °C Freezing temperature: -40 °C	The structural quality of the product, sugar enrichment, was preserved.	[67]
		Mango	Concentrations of the osmotic medium: 10 -20 Brix Osmodehydration temperature: 20 °C Freezing temperature: -18 °C	Quality degradation was avoided.	[68]

Table 1 (continued)

Type of technology		Fruits	Parameters	Results	References
		Pear	Concentrations of the osmotic medium: 2/1 (solute/water) Osmodehydration temperature: 30 °C Freezing temperature: -40 °C	Improved some organoleptic properties such as color.	[69]
		Pineapple	Concentrations of the osmotic medium: 60 Brix Osmodehydration temperature: 45 °C Freezing temperature: -31.5 °C	The cellular structure of the product was not affected, however, there was a loss of ascorbic acid content after freezing thawing. The drip loss was reduced.	[70]
		Azará	Concentrations of the osmotic medium: 60 Brix Osmodehydration temperature: 40 °C Freezing temperature: -30	Improved retention and bioacceptability of polyphenols and antioxidant capacity.	[71]
		Rambutan	Concentrations of the osmotic medium: 50 % p/p Osmodehydration temperature: 30 °C Freezing temperature: -40 °C	It preserved the organoleptic qualities of the product.	[72]
		Kiwi	Concentrations of the osmotic medium: 45-65 Brix Osmodehydration temperature: 30 °C Freezing temperature: -40 °C	Changes arose in the content of some volatile compounds such as aldehydes and alcohols that decreased, however, the ester fraction increased.	[73]
		Apple	Concentrations of the osmotic medium: 55 Brix Osmodehydration temperature: 35 °C Freezing temperature: -63 °C	The color and structure of the product were preserved.	[74]
		Tomato	Concentrations of the osmotic medium: 55% (p/p) Dehydration temperature: 35 °C Freezing temperature: -40 °C	Quality losses and volume shrinkage were reduced and textural quality was maintained.	[75]
Unconventional technologies	Cryogenic freezing	Mango Litchi	Temperature: – 24 °C	The size of the ice crystals was minimized, moreover, the nutritional value, organoleptic characteristics, and structure of the product were preserved.	[76]
		Date	Temperature: – 40 °C	Reduced the deleterious effects of crystallization and recrystallization on the microstructure of product tissues.	[77]

Table 1 (continued)

Type of technology	Fruits	Parameters	Results	References
Isochoric freezing	Myrtle	Temperature: –120 °C	The freezing rate was increased, and the structure of the product was preserved.	[22]
	Durian	Temperature: –110 °C	The structural quality of the product was guaranteed, which ensures its durability during storage.	[21]
	Cucumber	Temperature: –196 °C	Drip loss was reduced, and firm retention was improved.	[12]
	Cherry	Temperature: –4 and –7 °C	Drip losses were reduced, and the organoleptic characteristics were preserved, mainly color and texture.	[39]
	Grenade	Temperature: –2,5 °C	The color and structure of the product were preserved.	[23]
	Tomato	Temperature: – 2,5 °C	Structural damage was minimized, and it retains nutritional properties similar to that of the product in its fresh state.	[78]

size of crystals, as the intensity was increased. An optimal PMF intensity for blueberries in terms of freezing parameters and microstructure was found to be 10 mT, resulting in a 33.6% reduction in crystal size [55]. Similar research was conducted on cherries, indicating that PMF-assisted freezing requires less energy than AMF-assisted freezing. In cherry, as well as blueberry, the optimal PMF intensity was 10mT, resulting in a reduction of approximately 67% in ice crystals. The use of both types of magnetic fields led to a decrease in nutrient loss, with PMF resulting in lower losses than AMF [56].

Similarly, the effects of applying AMF to freeze minimally processed guava were evaluated, and positive results were obtained when 7.02 mT of AMF was used. Both phase change time and drip losses were reduced, and texture properties were better preserved. However, the precise effects could not be described as there is still insufficient study material on real food matrices with a wide range of magnetic parameters [15]. The effects of static magnetic field (SMF) application have been investigated in several F&V including apple, peach, cucumber, Indian jujube, broccoli, and cauliflower. The results showed that the optimal SMF intensity varied depending on the F&V studied. Furthermore, SMF application led to a decrease in respiratory intensity, membrane permeability y ice crystal size, which had a positive effect the preservation of the quality and microstructure of the Fruits and delicate vegetables such as spinach [31, 58, 85, 86]. However, in cherry tomatoes, SMF and AMF were found to increase the enzymatic activity of catalase, which is an enzyme that delays ripening. Therefore, these techniques can be used to control ripening during postharvest of fruit [57].

High-Pressure-Assisted Freezing

The use of pressure in the freezing process has great potential, as the pressure exerted (150 to 760 MPa) plays a key role in the transition from water to ice (Fig. 2C). Its application can improve the characteristics of the ice crystals formed during the process, as well as the freezing and thawing kinetics [83]. Acording to Sanz and Otero [87], three different high-pressure freezing processes can be distinguished (Fig. 2C), depending on how the phase transition occurs: 1. High-pressure-assisted freezing (HPAF), 2. High-pressure-induced freezing (HPIF), and 3. High-pressure-shift freezing (HPSF). In HPAF, the phase transition occurs at a constant pressure above atmospheric pressure, as the temperature drops below the corresponding freezing point, ice I known as ice polymorphs are obtained. Under HPAF conditions (200 MPa), the point of freezing of water will be very low (-22 °C), which reduces the water crystallisation but increases its vitrification upon freezing. Consequently, the formation and configuration of crystals is different, increasing the density of water molecules and preventing the expansion of their volume. Ice crystals formed under HAPF can be produced by two pathways, which lead to the formation of ice I (Fig. 2C—green line A to E) and ice V (Fig. 2C—dashed green line—a to e). Such thermodynamic water conditions can prevent mechanical damage caused by ice crystals in the F&V tissue.

Samples subjected to HPIF undergo a phase transition during the freezing process, which begins with a gradual increase in pressure (300 MPa), then the sample temperature decreases at a constant pressure, at which point the pressure gradually increases (up to 600 MPa), initiating the transition phase, leading to nucleation and formation of ice V (at -20 °C and 600 MPa) (Fig. 2C – red line A’’ to D’’) [51]. For the desired ice polymorph, compression can be performed directly at the target pressure (770 MPa) where ice VI is obtained (Fig. 2C red dashed line - a’’ to b’’). In the case of an HPSF, there is a slight increase in sample temperature due to pressurisation (210 MPa). Then, when the system pressure is released (fully or partially), the phase transition begins, increasing the freezing point and, suddenly and instantaneously, supercooling and expansion occurs, where the water at this point is still liquid (Fig. 2C, blue line C’-D’). Subsequently, a rapid nucleation starts after a slight heating (blue line D’-E’) and an immediate subsequent cooling (blue line E’-F), forming fine and uniform crystals of ice I. These pressure changes reduce the phase transition time and prevent sample heating, which is especially suitable for samples of large size or low thermal conductivity [87, 88].

It is important to note that the effects of high pressure on food chemistry and microbiology are based on the Le Chatelier’s principle. When the equilibrium of a system is disturbed, phenomena such as phase transitions, chemical reactivity, changes in molecular configuration and chemical reactions occur, which are accompanied by a decrease in volume, but which are counteracted by reactions involving an increase in volume. In that regard, all cellular components are affected by the resulting high pressure, including the cell membrane and its proteins (denaturation), enzymes (inhibition) and ribosomes, as well as the entire cell metabolism [16, 89]. For the mathematical modelling of high-pressure freezing processes, Sanz and Otero [87] mention that it is essential to take into account the temperature variation caused by pressure changes and the thermophysical properties of the products inside the pressure vessel, which cause different temperature increases after a pressure change. This variation can be determined using the following numerical Eq. (3):

$$\frac{dT}{dP} = \frac{T_k \times V \times \alpha}{c_p} \tag{3}$$

where: T is the temperature (K), P is the pressure (Pa), V is the specific volume $\left(m^3/kg\right)$, α is the thermal expansion coefficient $\left(K^{-1}\right)$ and c_p is the specific heat capacity $\left(\frac{J}{kg} \times K\right)$.

High-pressure freezing has been demonstrated to have favorable effects on the preservation of cell structure in food due to its ability to cause rapid nucleation leading to the uniform formation of microscopic ice crystals. This ensures that textural deteriorations to food products are minimized [90]. In peach and mango, high-pressure exchange freezing has been assessed for its microstructural effects. The product’s original structure was effectively preserved, and its textural quality remained almost intact. This technology considerably reduces the issues of freeze cracking or the creation of large ice crystals, which are frequently seen in conventional freezing [59]. The results are similar to those obtained in previous studies using this technology on vegetables such as carrots and Chinese cabbage (Table 2) [91, 92].

Microwave-Assisted Freezing

The use of microwave technology is a method that relies on an alternating electromagnetic field that produces thermal energy through the rotational movement of water molecules and ionic species. Since the frequency of microwaves typically ranges from 300 to 3000 MHz, this field causes rapid dipole movement in water and ionic/polar molecules [105]. In addition, heating occurs due to the deformation and friction of the water molecules, while the energy dissipated by the microwaves promotes the partial melting of formed ice crystals [18]. Two hypotheses have been proposed to explain this beneficial effect: (i) the microwave-induced (constant or pulsed) rotation of water molecules around crystals could disrupt ice crystal growth, as it impacts on hydrogen bonds between water molecules and water clusters during freezing and (ii) temperature oscillations due to increased microwave power could cause partial melting of crystals and lead to increased secondary nucleation. In both cases, this would lead to an increased number of smaller crystals, which were demonstrated by [106, 107], where a reduction of crystal size in food matrices in the order of 15-20% was evidenced.

Figure 2D shows the heating mechanisms of water molecules by (1) dipolar polarization and (2) ionic conduction triggered by microwave irradiation. Sadot, Curet, Le-Bail, Rouaud, and Havet [108] propose a mathematical model that is founded on an enthalpy formulation of the heat Eq. (4), incorporating terms deriving from Maxwell’s Eq. (5):

$$\frac{\vartheta H}{\vartheta t}\rho - \nabla . \kappa \nabla T = Q \tag{4}$$

Table 2 Summary of the applications of novel and unconventional technologies in the freezing of vegetables

Type of technology		Matrix: Vegetables	Parameters	Results	References
Novel technologies	Ultrasonic assisted freezing	Broccoli	Ultrasonic intensity: 0,250 y 0,412 W/cm^2	Allowed to preserve the organoleptic characteristics of the product, mainly the texture and color.	[93]
		Red radish	Ultrasonic intensity: 0,26 W/cm^2	It was possible to preserve the microstructure of the product, mportant characteristics such as color and firmness were preserved, and the loss of phytonutrients (anthocyanins, vitamin C, and phenols) was also reduced.	[48]
	Freezing assisted by permanent magnetic field (PMF), alternating magnetic field (AMF), static magnetic field (SMF)	Carrot	Intensity of PMF: 0–7,2 mT	It was possible to decrease the volume of ice crystals, it is also more flocculent.	[94]
		Potato	Intensity of SMF: 150–200 mT	The structural quality of the product was preserved.	[95]
		Cauliflower	Intensity of SMF: 8 mT	Drip losses were significantly reduced, and quality was preserved minimizing the loss of flavor of the product.	[85]
		Broccoli			
		Spinach	Intensity: 0, 40, 60, 80 y 100 Gs	Magnetic field strength of 40Gs reduced respiratory intensity, rate of weight loss, membrane permeability of spinach and increased titratable acidity.	[86]
	High-pressure assisted freezing	Potato	Pressure: 400 MPa Temperature: -30 °C	Drip losses are reduced, and product structure is preserved.	[96]
		Chinese cabbage	Pressure: 200, 340 and 400 MPa Temperature: -30 °C	The histological structure of the product was preserved.	[91]
		Carrot	Pressure: 200, 340 and 400 MPa Temperature: -30 °C	Problems related to thermal gradients have been reduced, while textural quality is maintained.	[92]
		Eggplant	Pressure: 200Mpa Temperature: -20 °C	Quality was preserved, a firm product with good texture was obtained, and cell damage was significantly reduced.	[97]

Table 2 (continued)

Type of technology		Matrix: Vegetables	Parameters	Results	References
	Microwave Assisted Freezing	Potato	Microwave power: 167 W/kg	The quality of the cellular, textural, and organoleptic structure of the product was preserved.	[60]
		Cabbage	Microwave power: 600, 700, 800, 900 W	The histological structure of the product was preserved.	[98]
		Carrot	Microwave power: 2 W/g	Allowed greater nutrient retention.	[99]
	Osmotic dehydration-assisted freezing	Broccoli	Concentrations of the osmotic medium: 50% p/p Temperature: -18 °C	A much higher retention of the rheological properties of the products was obtained.	[100]
		Carrot			
		Potato			
		Green peas	Concentrations of the osmotic medium: 56.5% p/p Temperature: -40 °C	It preserved the color and nutritional properties of the product.	[101]
Unconventional technologies	Cryogenic freezing	Carrot	Temperature: -30 °C, -50 and -70 °C	Improved preservation of cell structure.	[102]
		Asparagus	Temperature: -50 °C	Weight loss and dripping were decreased, product structure was preserved, and freezing time was reduced.	[103]
		Red pepper	Temperature: -196 °C	Drip loss was reduced and firm retention was improved.	[12]
		Carrots			
	Isochoric freezing	Potato	Temperature: -3 °C	It reduced the contraction of the volume and caused the increase of the antioxidant capacity but the reduction of the ascorbic acid content.	[24]
		Spinach	Temperature: -4 °C	After thawing it was found that the leaves remained crisp as in their fresh state.	[104]

Table 3 Advantages and disadvantages of novel assisted freezing technologies and unconventional methods of freezing fruit and vegetables

Type of technology	Advantages	Disadvantages	References
Novel technology			
Ultrasonic-assisted freezing	Environmentally friendly and non-polluting technology in foodstuffs. Improved freezing/thawing rates, water retention, protein stability, hardness, and brittleness of food. Regulates the crystallisation process in the food freezing process at acoustic intensities of 0.09–0.37 W/cm^2 Decreases freezing time, promotes smaller ice crystals, and reduces damage to cell and tissue structures. Reduces drip loss, prevents loss of phytonutrients such as anthocyanins, vitamin C and phenols. Reduces polyphenol oxidase and peroxidase enzyme activities	Developing equipment that works on an industrial scale requires substantial funding. High energy consumption. Insufficient uniformity in the distribution of the ultrasonic power intensity in the freezing chamber. The heat produced by the thermal effect of the ultrasound is absorbed by the liquid medium, negatively influencing the freezing process. Operating conditions and parameters need further optimisation for large-scale use. Very high acoustic intensities and excessive times may cause degradation or oxidation of the compounds and thus limit their applications.	[48, 49, 80, 128]
Magnetic field-assisted freezing	Increases the freezing speed to maximise freshness and preserve the quality of the frozen F&V. It achieves refrigeration below the freezing point. Strengthens hydrogen bonds between water molecules, which helps to form small ice crystals and distribute them uniformly in the food. Minimises the formation of ice crystals. Minimises drip loss. It is a low energy, controllable, safe, and non-toxic technology. This makes it suitable for a wide range of applications in the food industry. Enables zero additives to be added to frozen foods. It can inhibit enzyme activity and microbial growth, maintaining product firmness and quality. AMF treatment inhibits polyphenol oxidase and peroxidase activities. Reduces respiration intensity and membrane permeability, as well as maintains quality in delicate vegetables (spinach). AMCT showed improved inhibition of freezing damage, resulting in a lower respiration rate and improved keeping quality. SMF and AMF reduced cooling time and increased catalase activity in cherry tomatoes, improving their preservation and prevent fruit maturity in the post-harvest. Their effects vary depending on the type and strength of the magnetic field and the specific product being frozen.	There is a lack of study material on real food matrices with a wide range of magnetic parameters. The phase change time increases with increasing AMF intensity from 0.05 mT, resulting in a disadvantage for the freezing of blueberries. Over-intensity of magnetic fields accelerates the intensity of respiration, compromising the freshness of the product.	[15, 52, 55, 57, 83, 86]

Table 3 (continued)

Type of technology	Advantages	Disadvantages	References
High-pressure-assisted freezing	Shorten the time of the transition phase. It resolves issues related to thermal gradients and results in rapid nucleation, significantly reducing freeze cracking problems while preserving structural and textural quality. Control of the size and distribution of ice crystals. Preserves cell structure.	Protein denaturation and inhibit enzymatic activity. This method is not suitable for delicate foods such as lettuce, spinach, and others. It is not applicable to dried fruits with low water content. The inherent discontinuous nature of the process, coupled with a long pre-cooling stage. Capital costs limit commercial use.	[59, 87–89]
Microwave-assisted freezing	No increase in ambient temperature. Simplifies the heat transfer process. Minimises freezing damage. Reduces large ice crystal formation in delicate cellular food matrices such as F&V, preserving quality attributes. Frozen food microstructure is preserved. Reduce drip loss. Microwaves under pulsed conditions at 667 W/kg with a pulse width of 10 s and a pulse interval of 20 s showed the improved results in F&V quality.	Unclear. At high intensity it can cause rupture of cellular tissues and damage the structure. Heat inhomogeneity within the product, particularly along eggs, corners, and surfaces.	[60, 106, 107]
Osmotic dehydration-assisted freezing	Low cost, user-friendly, and can be applied to a variety of food items. Osmodehydrofreezing improved the polyphenol bioaccessibility and the retention of ferric reduction. Freezing times reduced by up to 50% compared to conventional freezing. Reduces drip loss, loss of colour and antioxidants. Useful for sensitive fruits and vegetables (cucumber).	Unclear. Migration of non-food solutes in high concentrations. Minor loss of vitamins, minerals, and some organic acids.	[70, 71, 129]
Unconventional technology			

Table 3 (continued)

Type of technology	Advantages	Disadvantages	References
Isochoric freezing	Reduced energy consumption during the process (65 – 70%) Reduces browning of food. Isochoric freezing does not cause cell dehydration and maintains morphological integrity. Water is kept at a constant volume, which prevents tissue rupture due to water expansion. Water at temperature and pressure conditions (-4,0 °C and 29,7 MPa) does not freeze and prevents the formation of ice crystals. Allows homogeneous nucleation. Preserves the texture and flavour of the food. Pathogenic microorganisms are destroyed by the synergy between the 135 MPa pressure and the moderate temperature of -15 °C. Preserves nutritional components such as vitamin C, pigments, antioxidants, and phenols in climacteric fruits such as tomatoes, which are susceptible to cold damage.	The design of refrigerator walls that can withstand the high pressures of isochoric freezing is difficult. Expensive technology. Hydrostatic pressure can cause decomposition of the food tissues, reducing the quality of the food.	[78, 120, 121, 124, 125]
Cryogenic freezing	Very high freezing rates. The cooling mediums are inert and non-toxic and as cooling media that are in direct contact with foodstuffs, they produce instant freezing. Generates numerous small ice crystals at inter- and extracellular level. Induces the formation of an ice crust that improves the mechanical strength of the product and acts as a moisture retention barrier. Flavour preservation. Minimizes the detrimental effects caused by dehydration and avoids shrinkage. Retains soluble protein of fruits. Reduces exudation, preserves microstructure, and minimises color change. Protects against lipid oxidation. Significantly reduces polyphenol oxidase activity.	Unclear. Crack formation.	[21, 77, 118]

AMF alternating magnetic field, *SMF* static magnetic field, *AMCT* alternating magnetic continuous fields

$$Q = \frac{1}{2}\omega\varepsilon_0\varepsilon''\left|E_{total}\right|^2 \tag{5}$$

where: ω is the pulsation (rad·s $^{-1}$), ε_0 is the vacuum permittivity (F·m $^{-1}$), ε'' is the relative dielectric loss factor, Q is the heat source term, (W·m $^{-3}$), E is the local electric field, (V·m $^{-1}$), ρ is the density (kg·m $^{-3}$), H is the specific enthalpy, (kJ/kg), t is the time (s), k is the thermal conductivity, (W·m $^{-1}$ ·K $^{-1}$) and T is the temperature (K).

In freezing, the use of microwave technology enables efficient regulation of ice crystal formation within the cellular structure of food. This addresses a significant challenge often encountered during traditional freezing practices, positioning this method as a viable alternative for enhancing the freezing process [19]. The diminishment of crystal size is believed to arise from the rotation of water molecules caused by the alternating electric field produced by microwaves, which interferes with hydrogen bonds and may lead to the formation of the crystalline structure [109]. This is confirmed by a study that evaluated the effects of microwave-assisted freezing on potatoes and apples (Table 1). It was observed that freezing parameters including characteristic freezing time, overall freezing time and freezing rate, were not impacted in either of the products. The freezing curves of microwave-assisted freezing were very similar to those of conventional freezing. However, microwave-assisted freezing has less drip loss and consequently foods retain their firmness and texture [60].

Osmotic Dehydration-Assisted Freezing

The aim of dehydration is to produce foods with low moisture levels (a_w below 0.70) or intermediate moisture (a_w from 0.70 to 0.85) [50]. Osmotic processing consists of treating the food product with a hypertonic solution (low a_w) to remove water from the food by an osmotic mechanism. Osmotic solutes of high and low molecular weight such as sugars (sucrose, honey, glucose, fructose, sorbitol, corn syrup), salts (sodium chloride, potassium chloride, calcium chloride), polyols (glycerol, sorbitol, erythritol), organic acids (lactate and ascorbic acid), concentrated fruit juices and combinations thereof are often used in an oxygen-free environment to avoid oxidative reactions [50]. Under these conditions, there is a bidirectional transfer of mass taking place: (i) water moves from the product to the osmotic solution and (ii) the osmotic solute is transferred from the solution to the product [110]. This mass transfer phenomenon is explained by selective osmotic transport through semi-permeable cell membranes [111], where water loss is greater than solute gain. Solutes enter the area between the cell membrane and the cell wall once they cross the membrane [112].

In addition, the leaching of soluble products (such as sugars, acids, minerals, and vitamins) has a significant impact on the sensory and nutritional properties of the product [113]. A combination of water and solute is then transported from the surface of the food product towards the center due to the osmotic pressure created between the osmotic solution and the food matrix. The process concludes when osmotic equilibrium is attained [114]. Mass transfer during the osmotic dehydration process of F&V is schematically presented in Fig. 2E. In general, this method is typically used as a pre-treatment before freezing food to reduce the amount of water present and, consequently, minimize crystal formation during the process. This process promotes an even distribution of crystals, which reduces damage to cell membranes [20] and results in significant benefits in the final product [115]. Such favorable outcomes are associated with the enhancement and maintenance of the inherent features of the food matrix, including sensory, nutritional, and functional attributes [116]. Additionally, this method is cost-effective as it employs basic equipment and consumes relatively low energy [70].

Goula and Lazarides [117] conducted numerical modelling to calculate water loss, solute gain, and the eventual equilibrium point following the process of osmotic dehydration. They obtained the Eqs. 6 y 7:

$$WL = \frac{s_1 \times t \times WL_\alpha}{1 + s_1 \times t} \tag{6}$$

$$SG = \frac{s_2 \times t \times SG_\alpha}{1 + s_2 \times t} \tag{7}$$

where: WL is the water loss, SG is the solid gain, s_1 and s_2 are parameters that can be defined as relative rate constants for water loss and solids gain, respectively, t is the time, WL_α is the water loss at equilibrium and SG_α is the solid gain at equilibrium. Eqs. 6 and 7 can be linearized to obtain the Eqs. 8 and 9 comprise the Azuara Model.

$$\frac{t}{WL} = \frac{1}{s_1 \times WL_\alpha} + \frac{t}{WL_\alpha} \tag{8}$$

$$\frac{t}{SG} = \frac{1}{s_2 \times SG_\alpha} + \frac{t}{SG_\alpha} \tag{9}$$

A study was conducted to examine the impact of osmotic pre-treatment and freezing on the volatile fraction of strawberries (Table 1). It was determined that using osmotic pre-treatment before freezing was advantageous, as it augmented the production of crucial aroma compounds in the fruit, thereby avoiding loss of quality [64]. Similarly, in the volatile fraction of kiwifruit, osmotic dehydration resulted in the creation of esters whilst decreasing the presence of aldehydes and alcohol [73]. A study investigated the effects of osmotic dehydration and freezing on papaya pieces. The findings were positive, as the brightness of the yellow color increased with the prolongation of osmotic dehydration. Recent studies have shown that this technology applied to the arazá fruit improved the freezing rate, avoided drip loss, which resulted in enhanced bioaccessibility of polyphenols with higher antioxidant capacity [71]. However, it is crucial to monitor the time factor as it could have an impact on the sweetness [65]. In a study conducted on apple cubes, it was noted that greater concentration of the osmotic medium resulted in higher firmness [74]. This observation was also supported by a similar study that found dehydro-freezing to effectively enhance the firmness of frozen products under examination, including peppers, carrots, and cucumber, while considerably reducing drip losses (Table 2) [12].

Unconventional Freezing Variants

Cryogenic Freezing

Ultra-rapid freezing, facilitated by cryogenic fluids, provides exceptionally high freezing rates. This process generates numerous small ice crystals in both intercellular and intracellular cavities and reduces water dislocation, thus avoiding detrimental effects caused by dehydration and shrinkage of the microstructure. As a result, the overall quality of the frozen food is effectively preserved. In addition, during cryogenic freezing, an outer layer or crust of ice forms on the surface of the product. This outer layer of ice gives the product mechanical strength and acts as a moisture barrier. The operational advantages of products frozen by this method are non-agglomeration and adherence to mechanical conveyor belts compared to other conventional freezing methods [75, 118].

This is based on the use of cryogenic liquids that allows a temperature reduction to occur quickly, the most used are CO_2 and nitrogen gases [119]. Tangtua et al. [76] mention that these cryogenic liquids are responsible for the rapid absorption of heat, thus reducing the temperature of the food below its freezing point. Consequently, great benefits are obtained, among which we can mention the conservation of nutrients, organoleptic characteristics, and cellular structure, since the leakage of intracellular liquid produced after the defrosting of the food is reduced. In Fig. 3A, a cryogenic food freezer is graphically represented, in which nitrogen is being used as a cryogenic liquid.

Likewise, Tangtua et al. [76] evaluated the methodology to stop the activity of the polyphenol oxidase (PPO) and the peroxidase (POD) enzymes in ripe mango pulp before cryogenic freezing after storage, where the immersion of mango pulp in a citric acid/Calcium chloride solution and the immersion of litchi pulp in a calcium chloride solution improved fruit firmness, moreover, cryogenic freezing with liquid nitrogen were effective treatments to control enzymes and minimized changes in fruit quality during frozen storage at -24 °C for six months. On the other hand, Alhamdan et al. [77] mention that the liquid nitrogen cryogenic freezing (LNCF) method is superior to the conventional slow freezing method using the deep freezer (CSF) method during frozen storage in preserving the basic color parameters of fresh Barhi fruit and the deterioration of its texture, this due to the reduction of the harmful effects of crystallization and recrystallization in the microstructure of the F&V tissues during quick freezing method. Numerical model to analyze the heat transfer process in the freezing of myrtle, which will allow the establishment of a theoretical basis for subsequent experiments of this type of freezing in blueberries, having the Eq. (10):

$$Nu = 2 + \left(0.4Re\frac{1}{2} + 0.06Re\frac{2}{3}\right)Pr^{0.4}\left(\frac{\eta_\infty}{\eta_w}\right)\frac{1}{4} \tag{10}$$

$$0.71 < Pr < 380, 1.0 < \frac{\eta_\infty}{\eta_w} < 3.2$$

where: “*Re*” is the Reynolds number, Nu is the Nusselt number, Pr is the Prandtl number, and η is the viscosity.

Supporting that, the quality of a frozen product depends on the temperature and speed of operation since they determine the distribution and size of ice crystals formed in the tissues. On the other hand, Razali et al. [21] observed that cryogenic freezing is indeed a promising method to preserve the quality of export fruits such as durian, since it positively prolongs storage life and also prevents durian dehiscence compared to conventional freezing (Table 1).

Isochoric Freezing

In isochoric freezing, food is submerged in an isotonic solution and then subjected to temperatures below 0°C. This freezing technique is characterized by being carried out under constant volume conditions. It is based on the principle of Le Chatelier also known as “The law of equilibrium”, which describes that as the formation of ice occurs and it expands, the pressure increases and, consequently, hinder the formation of ice inside the food matrix, which explains why part of the volume remains thawed or, in other words, in the liquid phase. The isochoric freezing sample represented in a phase diagram of pure water follows the trajectory of the liquid state curve, which lies at the interface between ice I, ice III and liquid water. This sample reaches an equilibrium pressure up to the triple point of 209.9 MPa at a sub-zero temperature of -21.985 °C, where a considerable part of the water contained in the sample remains liquid (45%). These process conditions restrict any further ice development and also prevent damage caused by the expansion of ice crystals

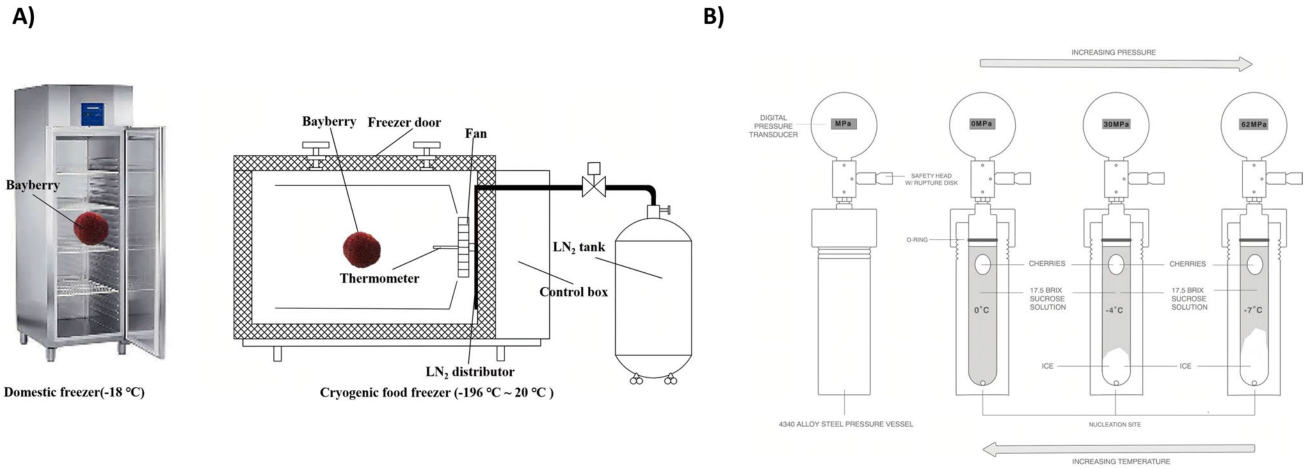


Fig. 3 Unconventional technologies. **A** Schematic diagram of cryogenic a food freezer. **B** Scheme of the isochoric chamber and generalized freezing process. Adapted from [22, 39]

during the transition phase of the water state [120].This increase in pressure will cease once a thermodynamic equilibrium is established between ice and water at the given freezing temperature [121]. Figure 3B graphically represents what was previously described.

Due to the above, this technique is currently gaining preponderance, being classified as an emerging technology with remarkable efficiency capable of completely preserving the cellular microstructure of the food. Likewise, its application does not imply damage due to the formation of ice since the ice crystals are distributed evenly and are also capable of minimizing microbial growth. For several years, this technique has been developed by Rubinsky and his group [23, 122, 123].

In addition to being an efficient freezing technique, it is economical due to it allows significant energy savings where approximately 35% less energy is needed compared to traditional freezing [124, 125]. The authors, in turn, introduced a numerical model that represents the freezing process in isochoric thermodynamic systems, having the following numerical equations that establish the relationship between the energy required to freeze a volume (V) and a certain temperature in an isochoric system concerning an isobaric system is given to the Stefan number (11):

$$Ste = \frac{c_1\left(T_{init} - T_1\right)}{L} \tag{11}$$

and the isochoric frozen fraction IF = IP/100, for (12):

$$R = \mathrm{IF} + (1 - \mathrm{IF})\frac{c_2}{c_1}\frac{Ste}{(1 + Ste)} \tag{12}$$

where: Ste is the number of de Stefan, c is the specific heat $(\frac{J}{kg}.K)$, T is the temperature (K), $init$ means initial, L represents the change of de enthalpy between frozen and thawed phases (kJ/kg), R is the relation of energy $(\frac{W}{m}.K)$, IF represents the isochoric frozen fraction, subscripts 1 and 2 represent the frozen and liquid domain respectively.

Regarding fruits, this technique has been applied in sweet cherry freezing performed by Bilbao-Sainz et al. [39] where it was observed that in an isochoric system under a temperature of -4 °C, the physical, nutritional, and organoleptic characteristics of the fruit were preserved, being these very similar to fresh cherries. Similarly, Bilbao-Sainz et al. [78] studied the effects on tomato conservation by applying this technique, where it was observed, that the preservation of the physical, nutritional, and organoleptic characteristics of the fruit, being very similar to the product in a fresh state. On the other hand, Bilbao-Sainz et al. [23] carried out a comparative study on the conservation of pomegranate through isochoric freezing and isochoric supercooling, the latter differs because during this process the food is brought well below its freezing point without the formation of ice crystals inside the food container. As a result, it was observed that in isochoric supercooling the physical, nutritional, and organoleptic properties of the product were maintained, likewise, the contents of ascorbic acid and anthocyanins increased. However, in isochoric freezing, although the physical and nutritional properties were preserved, in terms of organoleptic properties, the texture of the pomegranate arils was affected. In this sense, the isochoric supercooling technique turns out to have a greater efficiency for the preservation of the properties of freshly cut arils.

On the other hand, positive effects have also been found in potatoes and spinach, where isochoric freezing effectively leads to less loss due to dripping and volume contraction, as well as a better-preserved texture and microstructure [24, 104]. Even though this technique has been studied for several years, there is still not enough information to fully understand the mechanisms involved in conservation processes under isochoric conditions, which is why it is important to continue carrying out studies and research on this topic [126, 127].

Trends And Future Prospects

Over the years, new study approaches have emerged in the frozen F&V industry, as shown in Fig. 4, where the main studies that have been carried out for periods between 1955 and the present are observed. Initially from the years 1955–2000, the main approaches were sensory, instrumental analysis, and frozen storage, having the papaya greater research field. From 2001 to 2010, emphasis was placed on increasing the freezing speed and preserving the nutraceutical value of F&V, emerging rapid freezing methods (cryogenic freezing), and incorporating assisted technologies such as microwave. In the last decade, from 2011 to 2022, the studies had more emphasis on quality, frozen storage, microstructure, antioxidant activity/capacity, enzymatic activity, and optimization of the freezing process. Studies began on emerging combined

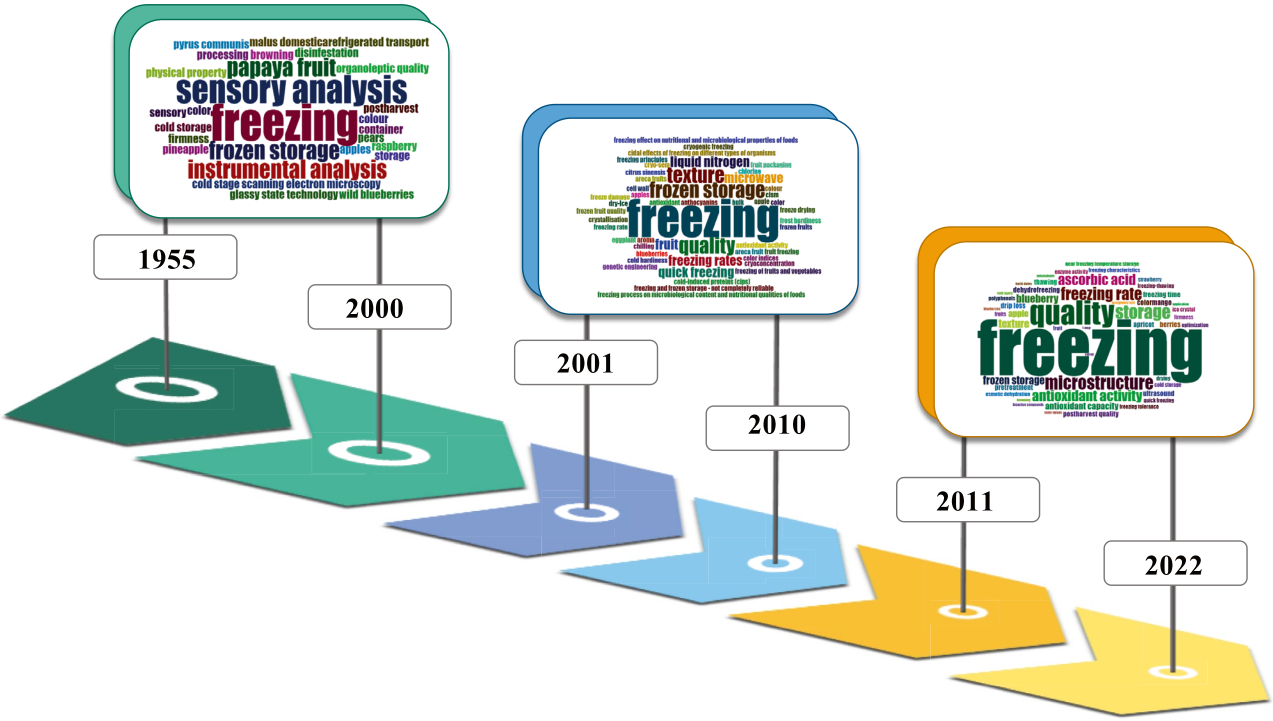


Fig. 4 Timeline: Most prevalent research approaches in the frozen food area (1955 – 2000), (2001 – 2010) and (2011 – 2022)

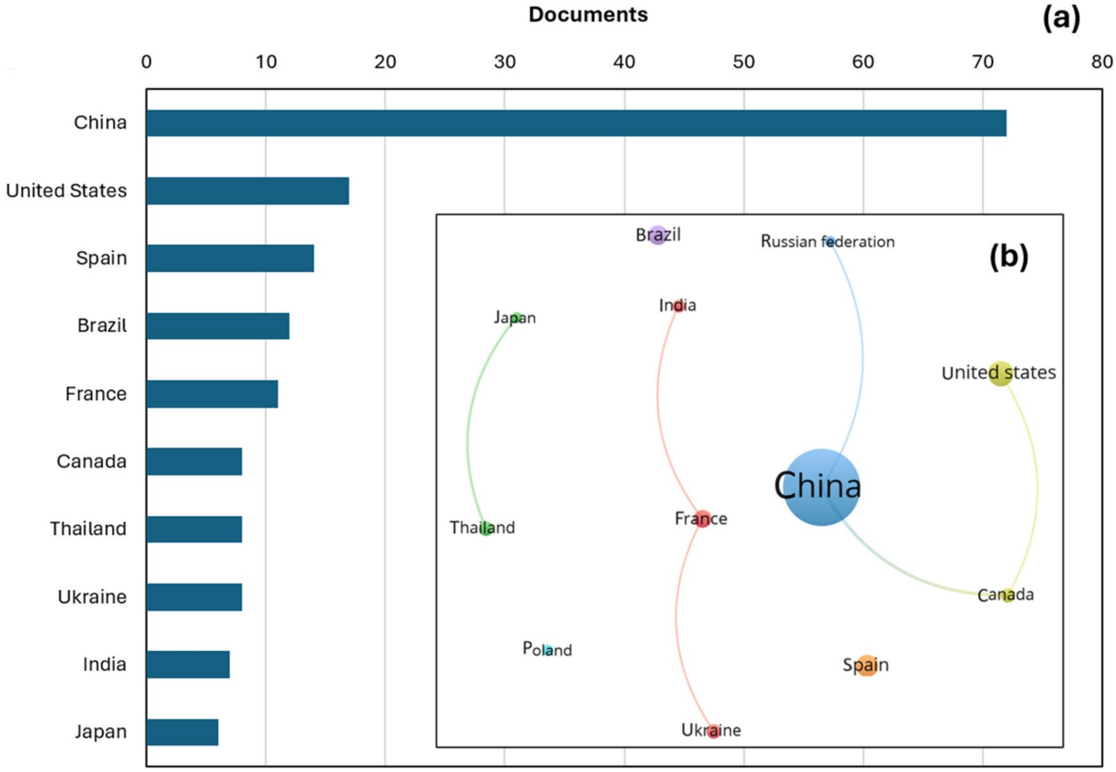


Fig. 5 Scientific production by country (Source: Scopus; TITLE (freezing) AND TITLE-ABS-KEY (fruits AND quality). **a** Number of documents per country. **b** Co-occurrence map generated with VosViewer (https://www.vosviewer.com/) (Unit of analysis: Countries; Visualization: Documents)

technologies, such as ultrasound, osmotic dehydration, and dehydrofreezing.

On the other hand, it is important to mention that China is the country with the highest scientific production in food freezing with around 72 papers published in high impact journals (Fig. 5a). In addition, this country together with Thailand (8), India (7) and Japan (6) are the Asian territories that focus their research efforts on food freezing with a total number of 93 scientific publications, and it is this continent that leads the world. In addition, China has established direct collaborative networks with Russia and Canada (Fig. 5b), thereby increasing its scientific research and contributing to that of other countries in this regard. Similarly collaborative networks are established by countries such as France with India and Ukraine, as well as Thailand with Japan and the United States with Canada. In the Americas, the United States was the leading country in terms of number of publications (17), followed by Brazil (12) and Canada (8), and together they represented the American continent with a total of 37 scientific productions. Among the European countries, Spain had the highest number of scientific publications (14), followed by France (11) and Ukraine (8), for a total of 33 European scientific publications. It is hoped that the countries with the most research will establish collaborative networks with countries in the Caribbean, South America and Africa, which have a high potential for F&V production due to their tropical climates, and thus carry out in-depth studies on the main export and native crops, which are the axis of development in these continents, and at the same time, with the help of these new technologies, large F&V wastes can be avoided.

This review provides new approaches related to new technologies related to the freezing of F&V that have not been addressed in the course of the last 20 years, but that are being incorporated at an industrial level in the area of frozen foods, standing out among them the freezing assisted by magnetic field, high pressures, and unconventional technologies such as isochoric freezing. These technologies have shown promise for the optimization of the freezing process and the preservation of food quality (Table 3), however, according to the literature on emerging technologies such as ultrasound, further research is required to optimize the operating conditions and parameters for its application at an industrial scale.

Conclusions

Overall, novel freezing assisted technologies and unconventional freezing variants have been shown to have great potential in the frozen F&V industry in terms of mitigating structural damage (dripping and loss of firmness) caused during the conventional freezing process, as they allow to reduce the freezing rate and promote the formation of microscopic ice crystals with uniform distribution. They also contribute to preserve the morphological integrity of cellular tissues, thus maintaining the organoleptic, functional and/or nutraceutical quality of F&V. They can also inhibit enzyme activity (peroxidase and polyphenoloxidase) and cause the destruction of potentially pathogenic micro-organisms. Among the novel technologies, ultrasound, high pressure, and microwaves allow obtaining high quality frozen products through various mechanisms related to the distribution of water in the food matrix, without transferring foreign components to the food. However, they are expensive technologies, and their scale of operation is limited. Meanwhile, osmotic dehydration or dehydrofreezing and magnetic field freezing are the most accessible and economical technologies, as they do not require sophisticated equipment and expensive refrigerants to carry out the freezing process.

Regarding unconventional processes, isochoric freezing by volume-invariant mechanisms retains 45% of the water in liquid state, avoiding tissue damage caused by the ice crystals expansion and can reduce the energy required to freeze a food product by up to 65–70% compared to conventional isobaric freezing. In cryogenic freezing, due to its very high freezing rate, it prevents dehydration and shrinkage of tissue microstructure, and also forms a crust that protects against mechanical damage and acts as a moisture barrier, thus maintaining the texture, colour, flavours and microbiological safety of food frozen by this method. On the other hand, the numerical models presented in this article allow a mathematical understanding of each revised technology and important parameters to control in the freezing process such as temperature, freezing time, heat transfer, and mass. Undoubtedly, these new combined technologies mean a significant advance in the frozen food industry, however, it is important to continue research on these technologies to better understand their mechanisms of action and their relationship with the optimization of the F&V freezing process.

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Declarations

Ethical Approval In this systematic review article, no living organisms were used to collect or obtain experimental data.

Competing Interests The authors declare no competing interests.

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