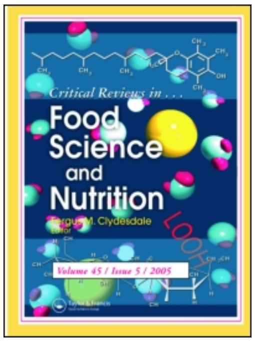


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# Recent developments in novel freezing and thawing technologies applied to foods

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**ABSTRACT**
This article reviews the recent developments in novel freezing and thawing technologies applied to foods. These novel technologies improve the quality of frozen and thawed foods and are energy efficient. The novel technologies applied to freezing include pulsed electric field pre-treatment, ultra-low temperature, ultra-rapid freezing, ultra-high pressure and ultrasound. The novel technologies applied to thawing include ultra-high pressure, ultrasound, high voltage electrostatic field (HVEF), and radio frequency. Ultra-low temperature and ultra-rapid freezing promote the formation and uniform distribution of small ice crystals throughout frozen foods. Ultra-high pressure and ultrasound assisted freezing are non-thermal methods and shorten the freezing time and improve product quality. Ultra-high pressure and HVEF thawing generate high heat transfer rates and accelerate the thawing process. Ultrasound and radio frequency thawing can facilitate thawing process by volumetrically generating heat within frozen foods. It is anticipated that these novel technologies will be increasingly used in food industries in the future.

**KEYWORDS**
Ultra-low temperature; ultra-rapid freezing; ultra-high pressure; ultrasound



## Introduction

Freezing is one of the most commonly used and efficient methods of food preservation. Chinese began to use ice cellars for freezing preservation of foods as early as 100 BC(Archer, 2004). Meat and poultry were frozen in order to be shipped very long distance since late 1800s (Lund, 2000). By1930s, the freezing industry had evolved considerably and diverse types of food products in large quantity were available in frozen form (Lund, 2000).

The freezing preservation applied to food involves three operations: actual freezing, frozen storage and thawing (Hanenian and Mittal, 2004). The freezing process significantly retards the chemical and biochemical reactions and microbial growth; thus, it greatly slows down the deterioration of color and texture, loss of nutrients and development of off-flavor during the storage (Cheng et al. 2015). These beneficial effects are produced by the low temperature and the conversion of water into ice. When the temperature of a food product is lower than −10°C, the chemical and metabolic reactions and microbial proliferation are greatly reduced (Delgado and Sun, 2001). The conversion of liquid water into ice crystals makes it unavailable as a solvent for chemical and enzymatic reactions and microbial growth (Delgado and Sun, 2011). However, the formation of ice crystals during the freezing of food materials should be studied and controlled carefully since it affects the quality of frozen foods and the efficacy of freezing process considerably(Kiani and Sun, 2011). Although large ice crystals are preferred in limited processes such as freeze concentration and freeze drying of some foods, they can cause significant damage to the tissue in frozen foods (Saclier et al., 2010). The extent of the negative impact of freezing process to foods depends on the nature of foods as different food materials respond differently to the freezing process. For instance, freezing causes less damage to meat compared to fish as the meant proteins are more stable at low temperatures than the fish proteins. In general, food materials with high water content such as fruits and vegetables suffer more serious structural damages during freezing (Fuchigami and Teramoto, 1997). Small and evenly distributed ice crystals cause less damage to the tissue structure compared to the large onesand better preserve the product quality.

Crystallization of ice consists of two stages: nucleation and the growth of nuclei. The rates of nucleation and ice crystal growth and the relationship between these two determine the size and distribution of ice crystals (Kiani and Sun, 2011). Slow freezing rates produce large ice crystals overwhelmingly in extracellular areas, while the fast freezing rates produce small crystals uniformly distributed throughout the tissue. Therefore, the freezing rate has to be carefully controlled for better preservation of quality of frozen products. It is desired that the thawing process is slower than the freezing process. Thawing process brings about physical and chemical changes in frozen foods and it can significantly affect the quality of the product if carried out sub-optimally (Stinco et al., 2013).Freezing and thawing processes are carried out using various conventional methods such as air blast freezing, fluidized-bed freezing, immersion freezing, cryogenic freezing, and water immersion thawing (Li and Sun, 2002).

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In order to improve the effectiveness of freezing, several novel freezing methods such as pulsed electric field pre-freezing treatment, ultra-low temperature, ultra-rapid freezing, ultra high pressure, ultrasound-assisted freezing are being researched. Similarly, to improve the effectiveness of thawing, novel methods such as ultrasound assisted thawing, ultra high pressure, high voltage electrostatic field thawing and radio frequency thawing are developed. These novel methods are designed to improve the product quality by promoting uniform nucleation and formation of small ice crystals.

This article is aimed at reviewing the recent developments in novel and emerging technologies applied to freezing and thawing processes of foods. The advantages and disadvantages of above mentioned novel freezing and thawing technologies in improving the quality of frozen and thawed foods and in improving the energy efficiency are presented in considerable detail.

## Novel technology for pre-freezing treatment

### *Pulsed electric field pretreatment*

Pulsed electric field (PEF) has been used as a nonthermal food processing technology over last 50 years (Donsì et al., 2010). It is widely applied in the food industry as a pretreatment method to improve the extraction efficacy of valuable compounds (Grimi et al., 2011; Loginova et al., 2011). PEF is also used to accelerate drying process (Mujumdar and Law, 2010;Sagar and Kumar, 2010) and to inactivate microorganisms (Saulis 2010). PEF treatment generates high-voltage intense electric pulses for extremely short time in foods placed between two conductive electrodes (Puértolas et al., 2012; Faridnia et al., 2015). It helps to enhance the mass transfer by affecting the permeability of cell membranes (Donsì et al., 2010).

The increased cell or tissue permeability caused by PEF increases the accessibility of intracellular materials to freezing (Shayanfar et al., 2014), increases the freezing rate and shortens the freezing time (Fig. 1). Wiktor et al. (2015) reported the time of apple samples subjected to PEF pretreatment was 33% shorter in the phase transition stage of freezing compared to that of the untreated samples. The total freezing time was reduced by 17.2% due to the application of PEF. A 24% reduction in freezing time was achieved when the apple samples were subjected to 10 kV/cm, 50 pulses PEF prior to air blast freezing (Wiktor et al., 2012). Similarly, potato tissue subjected to the PEF before freezing showed a noticeable reduction in freezing time (Jalté et al., 2009). Despite the fact that the PEF caused some damage to the membrane of the potato tissue, the cell wall structure was not affected significantly (Vorobiev and Lebovka, 2006). It has been shown that the membrane of the tissue provides new nucleation sites and helps to increase the rate of nucleation (Toner et al., 1990). In addition, the PEF accelerates the freezing process by raising the freezing temperature. Dymek et al. (2015)showed that spinach leaves treated by PEF were frozen completely at a notably higher temperature compared to the untreated leaves. The reasons behind this effect remain unclear because the freezing point of vegetables is affected by many factors.

Although the PEF improves the freezing process by shortening freezing time and raising the freezing temperature, it may cause undesirable effects such as mass loss, structural damage and color change. Wiktor et al. (2015) reported that apples

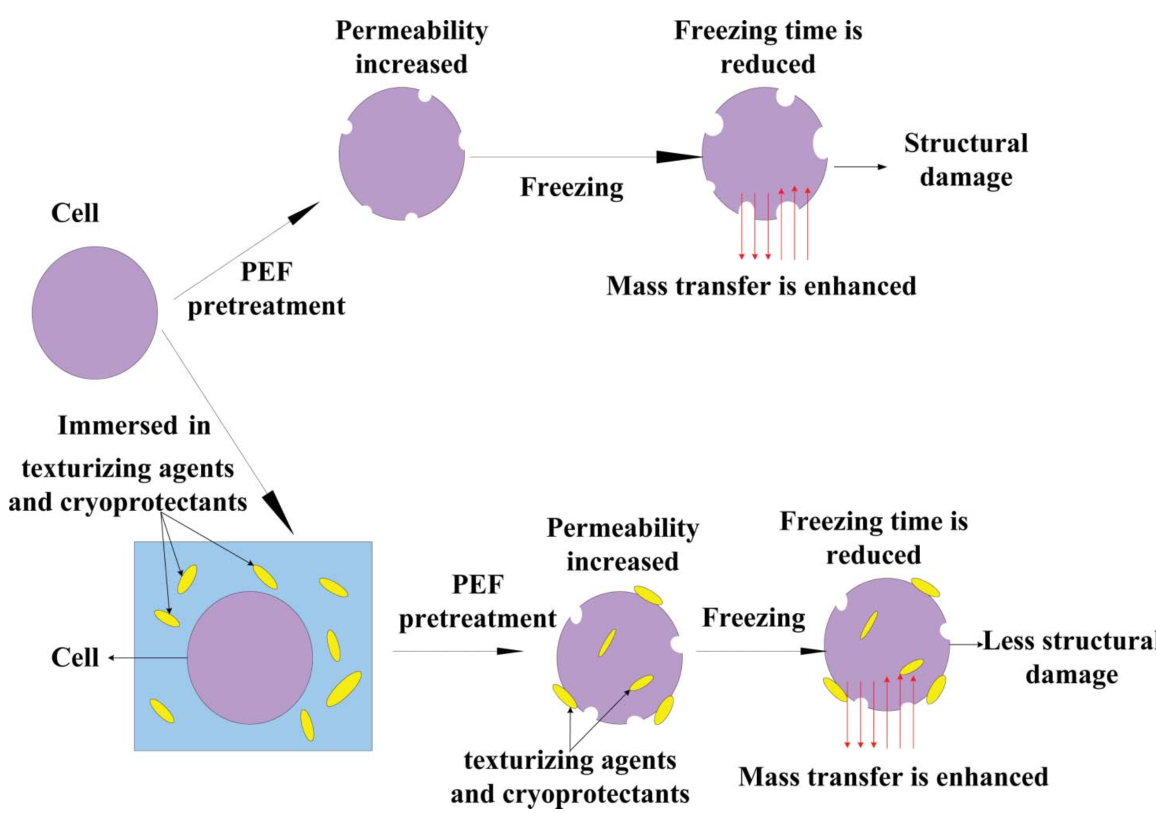


**Figure 1.** Schematic diagram of the PEF pretreatment to facilitate freezing process.

treated with PEF at 5kV/m by 50 pulses before freezing suffered higher mass loss than the untreated ones. Jalté et al. (2009) showed that the PEF pretreatment increased the rupture of cell walls and perturbed the polyhedral shape of cells. It has also been reported that the treatment of apple samples with PEF prior to freezing increased the darkening. This could be attributed to the rupture of cell membrane and the membrane-bound vacuole system due to perforation (Tekle et al., 2005). The browning of the tissue occurs with relative ease when the ruptured apple tissue is exposed to the air and the polyphenol oxidase is activated (Grimi et al., 2010).

The PEF improves the ability of cells to take up the texturizing agents and cryoprotectants. Shayanfar et al. (2014)reported that the carrot discs immersed in aqueous solutions of$CaCl_2$, glycerol, trehalose followed by PEF treatment prior to freezing could better maintain the firmness and color attributes. Phoon et al. (2008) combined the vacuum impregnation with PEF and cryoprotectant (trehalose) to treat spinach leaves before freezing and found that the cryotolerance of spinach leaves was significantly improved. Results of these studies indicate that the application of PEF before freezing greatly benefits the freezing process.

## Novel technologies applied to freezing

### *Ultra-low temperature freezing*

Since the thermal conductivity values of water and ice are higher than that of the food matrix they are part of, they determine the thermal conductivity of food. At normal pressure, thermal conductivity can be increased by lowering the freezing temperature (Table 1). In addition, the temperature of a freezing process determines the amount of ice that can be formed in the frozen food (Soyer et al., 2010). Thus, the freezing temperature greatly affects the structure of a product and its quality. For example, lowering the temperature during freezing has shown to improve the quality of frozen fish. Haugland (2002) reported that the quality and shelf-life of salmon was considerably improved by lowering the temperature from −22°C to −40°C. When the temperature is lower than −40°C, all of the free water in food materials is frozen and only the bound water remains unfrozen (Froid and Sørensen, 2006). Indergård et al. (2014) defined the temperature below −40°Cas the ultra-low freezing temperature. They showed that drip loss and gaping score of salmon were lower when frozen at −45°Cand −60°C compared to when frozen at −25°C.

**Table 1.** Thermal conductivity (*k*) of water and ice at normal pressure (1 bar) (Evans 2008).

| Temperature (°C) | *k* (W/(m K)) |
|---|---|
| 0 (water) | 0.554 |
| 0 (ice) | 2.25 |
| −10 | 2.35 |
| −15 | 2.41 |
| −20 | 2.47 |
| −40 | 2.73 |
| −50 | 2.85 |
| −100 | 3.95 |
| −150 | 5.70 |

Ultra-low temperature freezing increases the freezing rate owing to its very low operating temperature and high surface heat transfer coefficient between the food product and freezing medium. Boonsumrej et al. (2007) studied the freezing of tiger shrimp at −70°C, −80°C, −90°C, and −100°Cand reported that the freezing time was shortened and freezing rate was increased when the freezing temperature was lowered. The tiger shrimp samples frozen at −100°C had the lowest loss caused by freezing. The ultra-low temperature freezing can affect the shear force of foods upon thawing. For example, when the freezing temperature of green asparagus spears was decreased from −30°C to −70°C, the shear force decreased from 5.96 kg $cm^{-1}$ to 4.77 kg $cm^{-1}$(Kidmose and Kaack, 1999). Shear force indicates to the expressed toughness of green asparagus spears which affects the consumer acceptance. Shrimps frozen by liquid nitrogen and then stored at −80°C showed less damage to texture than those frozen by forced convection and stored at −20°C. Lower shear force and fracturability are favored by consumers and these values were found to be lower in cryogenically frozen samples than the samples frozen by using forced convection (Díaz-Teborio et al., 2007).

Ultra-low temperature freezing can also cause some undesirable physical damages to foods. The rapid expansion of volume due to fast conversion of liquid water into ice at faster drying rates generates considerable internal stress in foods. These stresses can lead to cracking of cellular structure in foods and the cracking occurs more easily at high cooling rates. For example, carrot slices when frozen at −80°C showed structural collapse and large pores when they were observed under scanning electron microscope (Xu et al., 2014). Pan and Yeh (1993) also reported that the cracking of the surface was observed in most of the muscle cells when shrimps were frozen at −120°C. The ultra-low temperature freezing of carrot slices caused the highest drip loss and loss of textural firmness due to cracking when compared to the carrot slices frozen using high pressure carbonic and liquid nitrogen immersion freezing.

Despite of these disadvantages, ultra-low temperature freezing better preserves some flavor and chemical characteristics of foods. Jiang et al. (2010) carried out ultra-low temperature freezing of banana slice before freeze drying and found that the hydrolysis of starch in banana slice was prevented due to ultra-low temperature freezing. As the reducing sugar content contributed to the sweet taste of banana chips, the undesired hydrolysis of starch to reducing sugar affected the taste sensation. The ultra-low temperature generated by liquid nitrogen reduced the mean size of ice crystals during freezing and produced creamier and richly textured ice cream(Jones, 1992). The ultra-low temperature freezing also better retained the water, glucose, $\alpha$-and $\beta$-carotene contents in carrot slices (Xu et al., 2014). This can be attributed to the collapse of cellular structure due to ultra-low temperature and consequently reduced rate of Maillard browning which consumes glucose. Moreover, the collapse of cellular structure could also lower the oxidation of $\alpha$-and $\beta$-carotene by preventing the diffusion of oxygen through the sample solids. The collapsed matrix resulted in a reduction in porosity, which had a significant effect on diffusion-controlled reactions like Maillard reaction and oxidation. With the decrease of moisture and oxygen diffusion, the Maillard reaction and oxidation were prevented. When amylopectin gels produced from rice were frozen at ultra-low temperature, no amylopectin retrogradation was observed as the gel was frozen rapidly and the network was frozen instantly (Yu et al., 2012). In this way, the intramolecular interactions were reduced and association of the amylopectin was effectively prevented.

### *Ultra-rapid freezing*

The size and structural integrity of ice crystals are closely related to the freezing rate. Rapid freezing produces numerous small ice crystals and causes less damage to the cellular structure (Fig. 2). It has been shown that the cell integrity was better preserved by the fast freezing than the slow freezing (Holzwarth et al., 2012). Freezing rate has also shown to affect the retrogradation of starch in foods. Muadklay and Charoenrein (2008) analyzed the retrogradation of starch gels at different freezing rates and showed that that the rapid freezing rate retarded the retrogradation.

Fresh foods which are rapidly frozen below −25°C, and stored and transferred below −18°C are called fast or rapidly frozen foods(Wang et al., 2007). When foods are frozen rapidly at high freezing rates, smaller ice crystals are formed and their distribution within the frozen sample becomes more uniform; thus, the flavor and texture of foods can be better preserved. This is the reason why the fast freezing technology is increasingly being used in food industry.

Ultra-rapid freezing uses freezing rates higher than 10 cm/h (Evans, 2008) and it is recognized as an efficient freezing method for a number of food products. The ultra-rapid freezing has many advantages including rapid freezing of product, formation of large number of nuclei and ultimately formation of smaller and evenly distributed ice crystals. This leads to better preservation of structural integrity and the quality of frozen products(Khadatkar et al., 2004).Navarro et al. (1995) compared the effect of slow and ultra-rapid freezing rates on the viscoelasticity (paste rheology) of frozen dough and showed that the viscoelasticity and texture of dough were better preserved by the ultra-rapid freezing. Work et al. (1997) showed that the ultra-rapid freezing better maintained the textural quality of hard and soft shell lobsters and that no fishy off-flavors were developed when stored for 9 months.

The ultra-rapid freezing has also been successfully applied to freeze rapidly dissolving drug formulations. Purvis et al. (2007) applied the ultra-rapid freezing to produce rapidly dissolving repaglinide powders. These authors showed that the ultra-rapid freezing could overcome the limitation of heat transfer by making direct contact with cryogenic substrate and by avoiding the resistance of gas interface to heat transfer. The physicochemical properties of rapidly dissolving formations produced through the ultra-rapid freezing were desirable and neither degradation nor spontaneous recrystallization was observed.

Despite above mentioned advantages, ultra-rapid freezing can cause mechanical cracking, especially with large and less porous samples with high water content (Orlowska et al.,

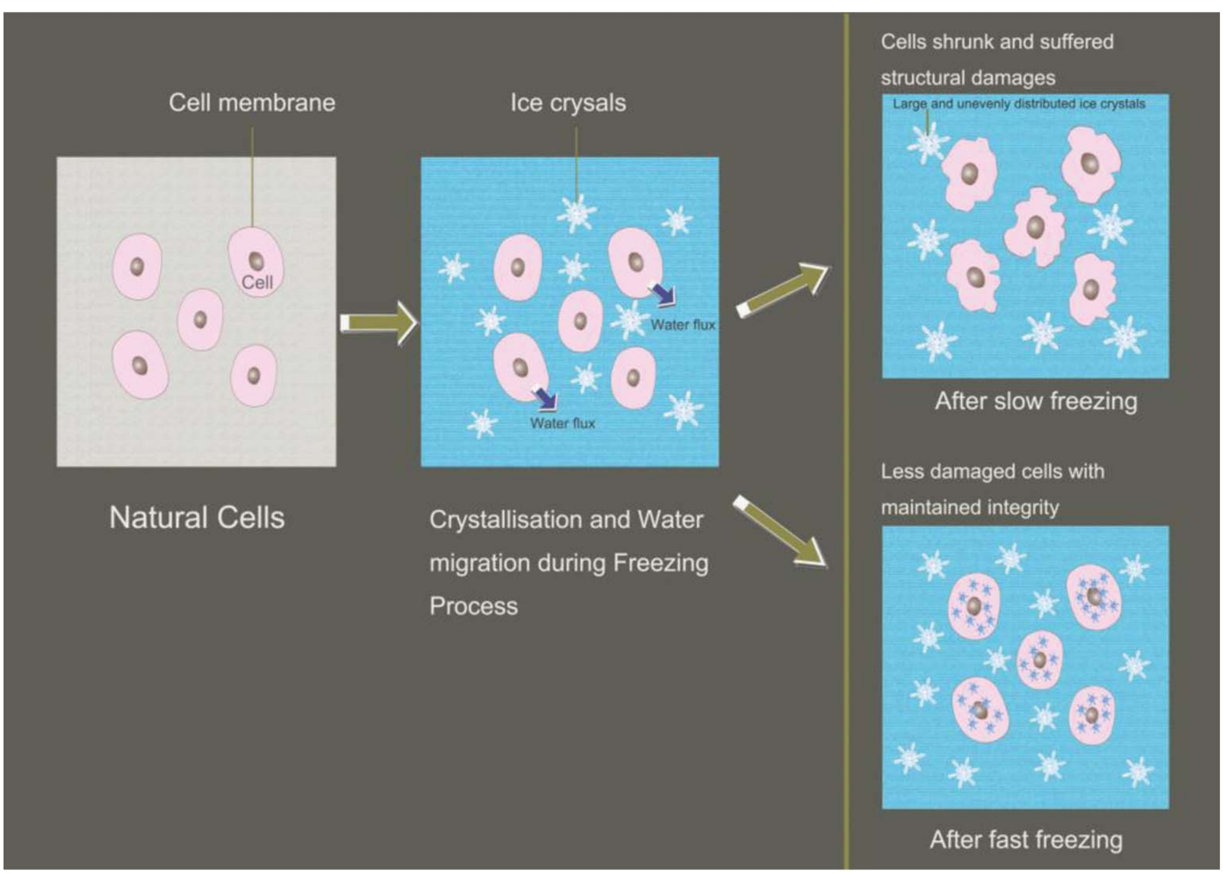


Figure 2. Crucial impact of freezing rate on the end product quality (Fikiin 2003).

2009). This is because the volume of a sample changes rapidly in fast succession, it decreases first during cooling and then increases very rapidly during freezing. Zhu et al. (2004) applied the ultra-rapid freezing to Atlantic salmon and observed that the temperature of the salmon decreased very rapidly due to the fast heat transfer. The salmon frozen by applying the ultra-rapid method suffered much higher drip loss compared to that in other freezing methods. In the case of lamb, the color parameters of samples frozen using slow, rapid and ultra-rapid freezing methods were not significantly different. Some surface cracks and separation of dorsal muscle from fat were observed in lamb chops subjected to ultra-rapid freezing using liquid nitrogen both of which affected the meat quality negatively (Lind et al., 1971, Rasmussen and Olson, 1972).

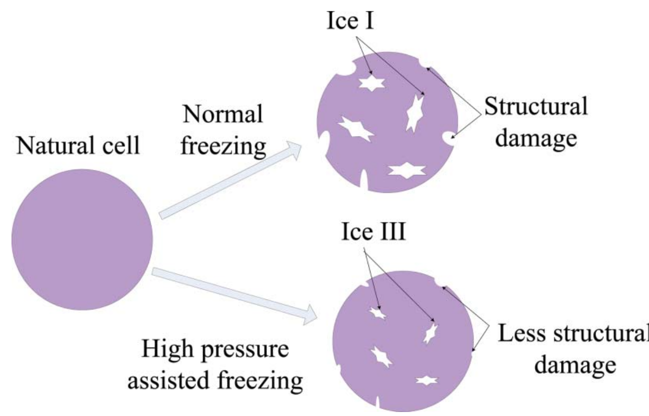


Figure 4. The ice types and structural damage formed during normal freezing and high pressure-assisted freezing.

### High pressure and ultra-high pressure-assisted freezing

High pressure processing can inactivate the microorganisms at the same time maximally preserving the color, flavor and nutritive value of foods. Being isobaric process, the high pressure processing is independent of shape, size, and composition of foods (Norton and Sun, 2008). High pressure-assisted freezing which is able to maintain the natural product quality has been used to cryoimmobilize samples for microscopic observation since 1960s (Taylor, 1960).

Pressure assisted freezing has attracted increasing attention in last few decades. The freezing point of water decreases from 0°Cat 0.1 MPa to −21°Cat 210 MPa (Fig. 3). When the pressure is higher than 210 MPa, an opposite effect is observed and it is possible to freeze a sample above 0°Cat pressures above 600 MPa. At normal atmospheric pressure, the crystallization of ice occurs when temperature falls below 0°C. Ice III has a higher density than ice I and liquid water (Pham, 2008). These type III crystals cause less damage to the product tissue since they are smaller than type I crystals (Chevalier et al., 2000) (Fig. 4). TypeIIIice crystals are formed when appropriate pressure is applied during freezing. At normal atmospheric pressure, ice VI is unstable and it readily converts into ice I form. Ice II and ice V can be obtained when pressure and temperature levels are adequately controlled. The density of ice increases with the increase in pressure, for example, the densities of type III, II and V ice crystals are 1.14, 1.17, and 1.23 g/cm$^3$, respectively (Fuchigami and Teramoto, 1997).

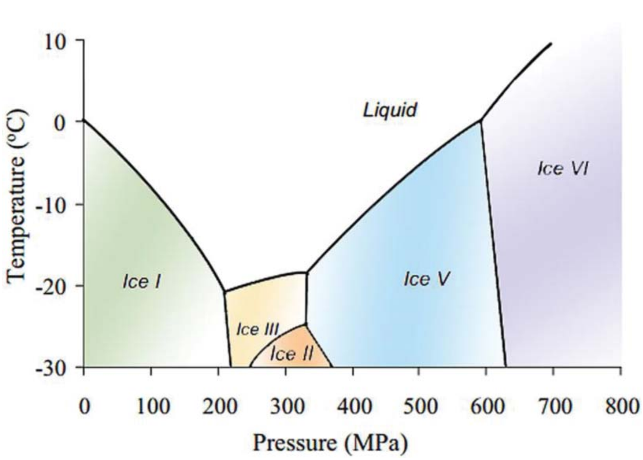


Figure 3. High pressure freezing and thawing processes on the phase diagram (LeBail et al. 2002).

The volume of unit mass of water increases when it is frozen at normal atmospheric pressure. Type I ice is formed at this condition and the volume increases by 9% and 13% at 0°C and −20°C, respectively (Kalichevsky et al., 1995).These large type I ice crystals damage the cell structure and cell wall. Since the size of crystal is inversely related to the number of ice crystals formed, thus increasing the number of nuclei may be an effective way to reduce the damage caused by large ice crystals. Chevalier et al. (2000) reported that a relatively faster release of pressure resulted into more uniform and fine nucleation. These authors also showed that the mean diameter of ice crystal decreased with the increase in pressure.

A pressure range of 100 to 1000 MPa is generally used in high hydrostatic pressure processing of foods (Yaldagard et al., 2008). The size and uniformity of ice crystals in pork meat frozen by ultra-high pressure-assisted freezing (200 MPa) were compared with those obtained by liquid $N_2$ and air-blast freezing (Martino et al., 1998). It was found that the ice crystals were smaller and their distribution was more uniform in pork muscle when they were frozen using high-pressure freezing compared to air-blast and cryogenic freezing.

Fuchigami and Teramoto (1997) studied the effect of high pressure freezing on the quality of kinu-tofu in 100–700 MPa range. Large ice crystals were observed when tofu samples were frozen at 100 MPa and 700 MPa. On the other hand, the ice crystals formed in the outer parts of tofu frozen at 200 MPa to 400 MPa were quite small. When the pressure was above 500 MPa, the size of ice crystals started to increase. The application of ultra-high pressure at 200MPa to 400 MPa range was found to be beneficial in preserving the texture of frozen tofu. The tofu frozen at 700 MPa was found to suffer the greatest histological damage. Similarly, the carrots frozen at 200 MPa to 400 MPa showed less pectin release and less histological damage than those frozen at 700 MPa (Fuchigami et al., 1997).

Freezing at ultra-high pressure is particularly beneficial in freezing large pieces of food when small and uniform ice crystals are required. Although pressure assisted or ultra-high pressure-assisted freezing is more expensive than traditional normal atmospheric freezing, it can become economically more viable in the future (Yaldagard et al., 2008).

### Ultrasound-assisted freezing

Ultrasound is a cyclic sound wave when its frequency exceeds 20 kHz. The ultrasound applied in food processing can be classified into low energy (or low power) when the frequency is >100kHz and high energy (or high power) when the frequency ranges from 20–500 kHz (Awad et al., 2012). Cavitation bubbles (Fig. 5) generated by ultrasound, can accelerate the freezing process by promoting ice nucleation and enhancing the transfer of heat and mass (Deora et al., 2013). When the cavitation bubble collapses, high pressure is generated. This pressure can induce the nucleation of ice by raising the equilibrium freezing temperature of water and breaking the already formed nuclei into smaller ones (Delgado and Sun, 2011) (Fig. 6).Higher heat and mass transfer rates can be realized during freezing through the strong ultrasound vibration produced by high energy ultrasound. Acoustic streaming (Fig. 5) is extreme turbulence caused by high amplitude acoustic waves in the propagating medium. Both the acoustic streaming and cavitation greatly affect the formation of ice crystals (Deora et al., 2013).

Ultrasound can monitor the freezing process by estimating the freezing time and degree of freezing. Sigfusson et al. (2004) measured the flight time of ultrasoundpulses moving parallel to the heat flux in blocks of gelatin, chicken and beef. The results from this study indicated that the degree of freezing and the time required for a complete freezing could be reasonably estimated using ultrasound. The quality of frozen products can also be better preserved by ultrasound assisted freezing. For example, red radishes frozen using ultrasound assisted immersion freezing better preserved the textural firmness and lowered the drip loss compared to the samples frozen without the application of ultrasound (Xu et al., 2015). This can be attributed to less damage caused to the cellular structure during ultrasound assisted freezing. Similarly, the microstructure and firmness of broccoli were better maintained and the drip loss was significantly reduced when ultrasound freezing was used (Xin et al., 2014).

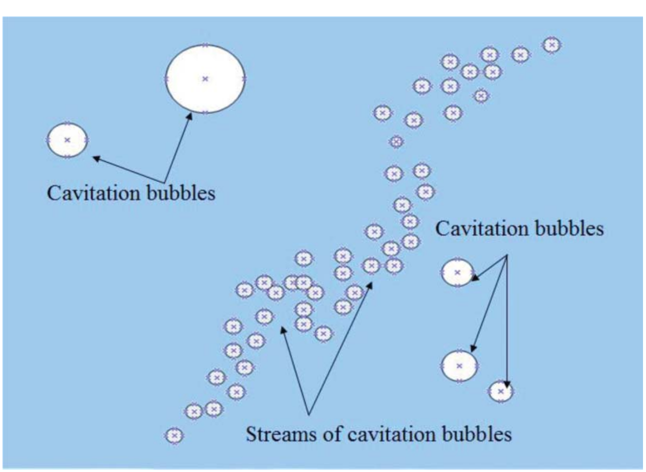


**Figure 5.** Cavitation and acoustic streaming inside the ultrasound bath (Cheng et al. 2015).

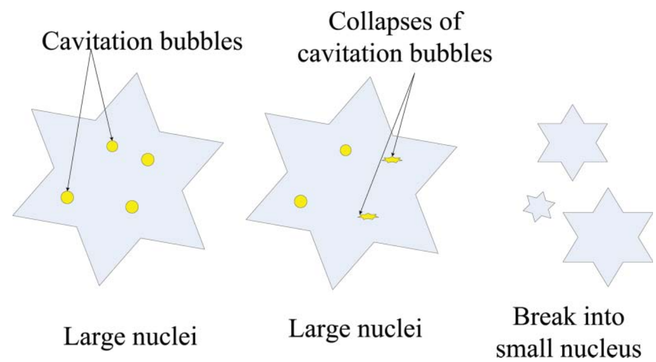


**Figure 6.** Schematic diagram of cavitation bubbles breaking the already formed nuclei into smaller ones.

The nucleation temperature was found to be higher and freezing time was shorter compared to normal freezing when radish samples were subjected to ultrasound first and then frozen(Xu et al., 2014). The nucleation temperature had a linear relationship with ultrasound irradiation temperature when the temperature of the system was within $-0.5\sim-2$°C. Kiani et al. (2015) evaluated the effect of ultrasound immersion freezing on potato spheres using analytical, numerical and experimental methods and showed that the application of ultrasound could effectively decrease the characteristic freezing time of potatoes. The effect of ultrasound-assisted freezing on apple samples was evaluated by Delgado et al. (2009).They showed that the application of ultrasound significantly increased the freezing rate and shortened the freezing time by 8%.

Higher ultrasound power in an appropriate range is preferred for ice nucleation since lower ultrasound power can be insufficient to induce nucleation (Tao and Sun, 2015). Higher heat transfer rates are achieved at higher ultrasound power levels. For example, the rate of heat transfer to potato samples was higher at ultrasound power of 25.89 W than at 15.85 W and the 7.34 W power failed to provide minimum rate of heat transfer required within the temperature range of $0\sim-5$°C(Li and Sun, 2002). According to Kiani et al. (2012), ultrasound power intensities of 0.07 W $cm^{-2}$ and 0.14 W $cm^{-2}$ were inadequate to induce nucleation at a low degree of supercooling compared to control samples. Nucleation occurring at lower degrees of super cooling was observed when the ultrasound intensity varied from 0.25 $Wcm^{-2}$ to 0.42 W $cm^{-2}$ inagar gels.

The duration of ultrasound irradiation is one of the factors that enhances the nucleation process during freezing. Longer-time of ultrasound irradiation is not beneficial to ice nucleation because of the heat generation. Kiani et al. (2011) evaluated the effect of ultrasound irradiation time on the nucleation of ice in agar gels and showed that the ultrasound irradiation time of 1 s was insufficient to initiate the nucleation, 3s was optimal and longer than 5 s impeded the nucleation process.

## Novel technologies in thawing process

### Ultra-high pressure-assisted thawing

The application of high pressure in thawing process of frozen foods has so far received less research attention (Farag et al., 2009). Thawing involves complex heat and mass transfer processes and the physicochemical properties and quality of frozen foods is significantly affected by the thawing process (Stinco et al., 2013). The microorganisms and enzymes which survived the freezing and frozen storage can multiply and promote spoilage if the thawing time is long (Hanenian and Mittal, 2004). Therefore, low temperatures and higher thawing rates are beneficial to the thawing process.

Frozen samples can be thawed at relatively low temperatures by using high pressure. The phase change temperature of pure water decreases with the increase in pressure up to 210 MPa (Fig. 5). As a consequence, the temperature difference between the sample and the surrounding is increased due to the increase in driving force (Zhu et al., 2004). Van Buggenhout et al. (2006) thawed frozen strawberries using ultra-high pressure (200 MPa) at −30.5°C and showed that thawing time was significantly reduced (11 min) compared to that of the samples thawed at normal atmospheric pressure at 20°C (36 min).It was possible to maintain relatively low thawing temperature of hami melons by applying ultra-high pressure as it lowered the melting point of ice (Wen et al., 2015). High thawing rates were achieved because strong driving force was created by the large temperature difference between the thawing medium and the frozen samples.

The effectiveness of ultra-high pressure-assisted thawing in preserving the quality of thawed food products was recently studied by Li et al. (2014). They compared the effects of conventionally water bath-thawed and ultra-high pressure thawed chicken breasts on the water holding capacity by using low-field nuclear magnetic resonance. It was found that the ultra-high pressure-assisted thawing can transform the loosely bound water fraction to the more tightly held one which significantly reduces the thawing loss. Okamoto and Suzuki (2002) compared the effect of ultra high pressure and running water on thawing of frozen pork meat. It was found that the ultra high pressure thawing reduced the drip loss and improved the water holding capacity. High pressure thawing carried out at 220 MPa significantly reduced the drip loss in both frozen aiguillat and scallops compared to when they were thawed at normal atmospheric pressure (Rouillé et al., 2002). Chevalier et al. (1999) reported that the drip volume of fish samples was significantly reduced when they were thawed using ultra-high pressure-assisted thawing for optimal length of time compared to normal atmospheric freezing.

Though high pressure-assisted thawing can reduce the thawing time as well as drip loss; however, it produces some harmful effects such as hydrophobic interactions and degradation of salt bonds and give rise to the conformational changes and denaturation of proteins (Fernández-Martín et al., 2000). For example, it has been shown that the high pressure thawing caused denaturation and aggregation of fish myofibrillar proteins (Chevalier et al., 2000). The samples thawed using high pressure exhibited significantly high drip and ascorbic acid losses and texture deterioration suggesting that high pressure thawing was unable to prevent the tissue damage caused by high pressure (Wen et al., 2015).

### *Ultrasound-assisted thawing*

Thawing process can be accelerated by generating heat inside the frozen food. However, due to surface heating and runaway heating, there still are severe limitations in controlling the thawing rate by using dielectric, microwave or resistant heating (Chemat and Khan, 2011).

Ultrasound was better attenuated in frozen meat than in unfrozen tissue (Chandrapala et al., 2013). The attenuation increases significantly with temperature and reaches its highest value near the freezing point of a product (Miles et al., 1999). Thus, ultrasound-assisted thawing process is more uniform than the microwave thawing process. The front of phase change during ultrasound-assisted thawing process approaches more rapidly than that of conventional thawing (Fig. 7). Kissam et al. (1982) applied ultrasound (1500 Hz and 60 W) water immersion thawing to thaw fish blocks and found that they required 71% less thawing time compared to when only the water-immersion thawing was used. Quality analyses on both sensorial and chemical changes of fish flesh showed no significant difference between the samples obtained with and without ultrasound-assisted thawing. Gambuteanu and Alexe (2015) noted that thawing time required to pass through −5°C∼−1°C range and the total thawing time were significantly reduced when ultrasound of 25 kHz and 0.6 W/cm$^2$ was used. The textural properties of meat were not affected negatively when the thawing time was significantly reduced by the application of ultrasound. The thawing time of edamame was significantly shortened in the ultrasound-assisted water immersion thawing compared to that in conventional one(Cheng et al., 2014). The ascorbic acid, chlorophyll and initial textural firmness of edamame were better retained and the drip loss was minimized by using ultrasound-assisted thawing at the power level of 900 W. Gambuteanu and Alexe (2013)compared the physicochemical and microbiological properties of unpacked pork thawed using low intensity ultrasound and conventional thawing (immersion in water). The results suggested that ultrasound-assisted thawing made no difference in pH, total drip loss, moisture content, thiobarbituric acid reactive substances (TBARs) value and microbial growth when compared with the conventional thawing.

Though ultrasound-assisted thawing is a novel and effective technology, it has some disadvantages such as high power consumption, localized heating and poor penetration(Li and Sun,

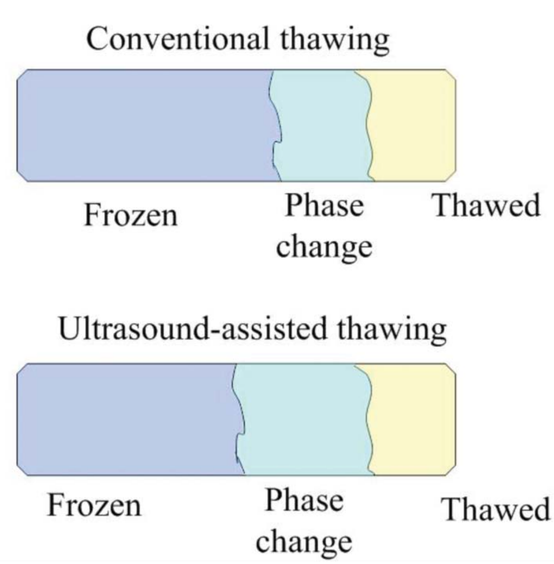


**Figure 7.** Effect of ultrasound-assisted thawing on the phase change region as compared to conventional thawing (Li and Sun 2002).

2002). A considerable proportion of ultrasound energy is lost and dissipated as heat when the ultrasound wave propagates through frozen foods. Hence, the surface temperature of the frozen food rises rapidly even though this increase is slow in the interior(Chandrapala et al., 2013). Miles et al. (1999) investigated suitability of applying 0.22∼3.3 MHz ultrasound frequencies at 1∼3 $Wcm^{-2}$ of intensity range aiming to overcome the overheating near the surface of beef, pork and cod. It was found that the application of ultrasound at 500 kHz and $0.5Wcm^{-2}$ could minimize the surface heating and could effectively thaw frozen meat and fish samples within 2.5 h.

## High voltage electrostatic field thawing

High voltage electrostatic field (HVEF) technology is being applied in drying (Alemrajabi et al., 2012;Singh et al., 2012), preservation (Walkling-Ribeiro et al., 2010) and sterilization of foods(Misra et al., 2011). However, there is not much research regarding the application of this technology in thawing of foods. The application of this technology in thawing (Fig. 8) avoids the electrical interference on the food and can reduce the thawing time.

The HVEF generates corona wind (He et al., 2014). This corona wind produces turbulence and vortices which enhance the heat transfer and increases the thawing rate (Mousakhani-Ganjeh et al., 2015). It has been reported that the thawing rate is related to the voltage, the distance between the two neighboring needles and the electrode spacing (Bai et al., 2011). He et al. (2014) reported that at the electrode spacing of 6cm, the thawing time was decreased when the voltage was increased. Bai et al. (2011)reported that the thawing time was shortest when the electrode distance and voltage were 9 cm and 45 kV, respectively. Mousakhani-Ganjeh et al. (2015) undertook thawing of frozen fish cubes using HVEF and traditional thawing and showed that thawing rate was significantly (1.78 times)increased by the HVEF. The nitrogen gas produced by microbial activities was also reduced due to HVEF treatment as it inhibited the microbial growth. Hsieh et al. (2010)compared the effects of HVEF assisted thawing and common refrigerator thawing on the chicken thigh meat. This study showed that the HVEF significantly reduced the thawing time at −3°C and it reduced the thawing time by one third when thawed at−5°C. Furthermore, the chicken thigh meat thawed by HVEF showed lower cooking loss and higher water holding capacity when stored at 4°C.He et al. (2013) evaluated the effects of HVEF-assisted and air thawing on frozen pork. It was found that the thawing time was greatly reduced by using the HVEF compared to the time required in air thawing. In addition, thawing time decreased with the increase in electrode voltage and the inhibition of microbial growth was more effective at higher voltages in post-thawing storage without any adverse effect to the meat quality.

In addition to its ability to significantly reduce the thawing time, HVEF thawing is also energy efficient. He et al. (2014) studied the effects of electric field strength on thawing time and thawing energy of frozen pork tenderloin meat. These authors also evaluated the energy consumption during hot/cold water, microwave and HVEF thawing processes. Results showed that the energy consumption in HVEF thawing was 0–190 kJ/kg while it was 1104, 248, and 184 kJ/kg in the case of microwave, hot-water and cold-water thawing, respectively. In addition,

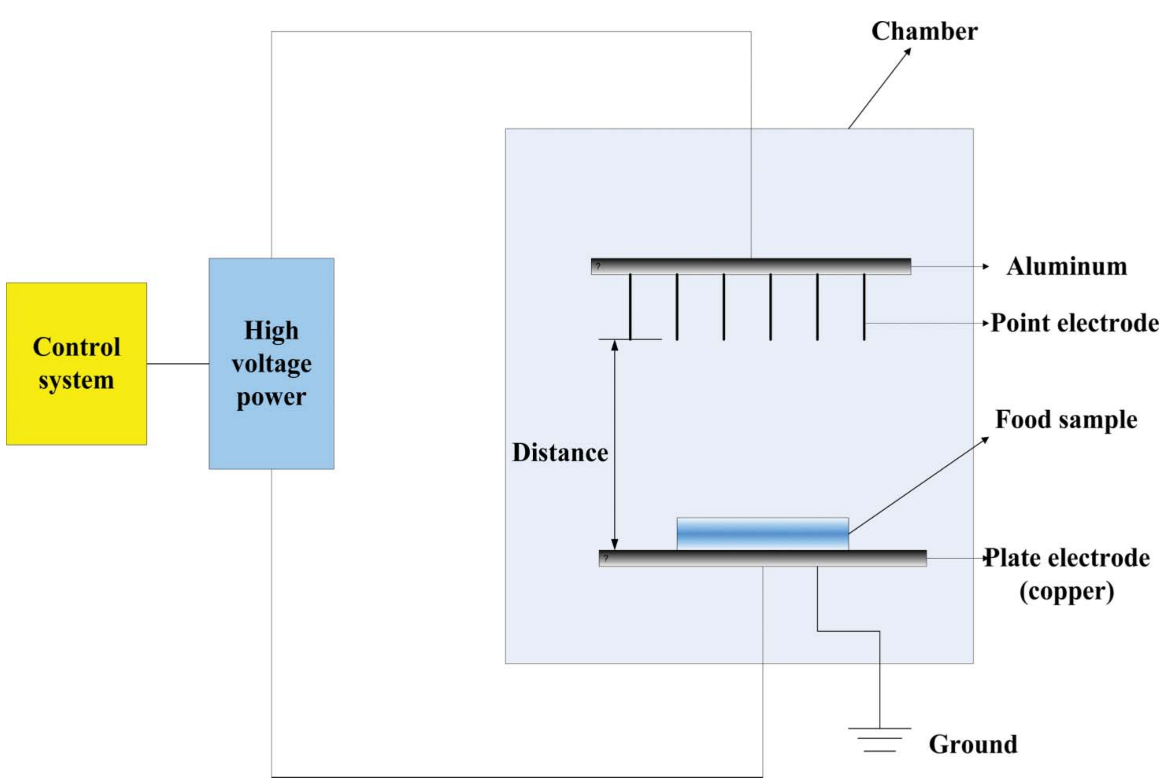


Figure 8. Schemetic diagram of HVEF thawing system (Mousakhani-Ganjeh et al. 2015).

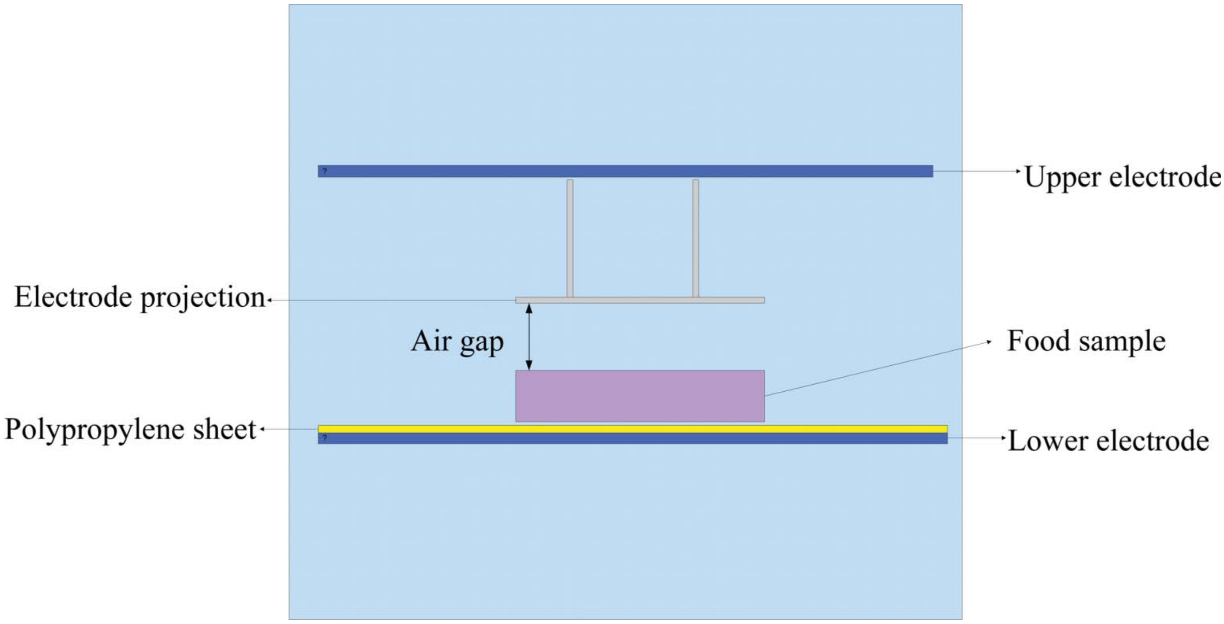


**Figure 9.** Schematic diagram of the RF system (Llave et al. 2015).



the temperature difference between the surface and geometrical center of pork sample was quite low (0.3∼1.2°C), indicating that the HVEF could achieve better uniformity during thawing.

### *Radio frequency-assisted thawing*

Radio frequency (RF) system produces heat volumetrically through ionic displacement and dipole rotation and it is more efficient in heating food materials compared to conventional air heating systems (Marra et al., 2007). RF systems operate at the frequency range of 1∼300 MHz (Jiao et al., 2014), converts electrical energy to electromagnetic radiation and then generates heat within food (Marra et al., 2009). Because of its ability to heat food volumetrically, RF is widely applied in food industry especially in drying (Zhu et al. 2012; Wang et al., 2014), baking (Kocadağlı et al., 2012), sterilization (Schlisselberg et al., 2013), and thawing (Basaran-Akgul et al., 2008) processes.

RF-assisted thawing (Fig. 9) can achieve shorter thawing time and better temperature uniformity due to its inherent volumetric heating ability. Cathcart and Parker (1946)were perhaps the earliest researchers to report the application of RF in thawing of frozen fish, eggs, fruits and vegetables. As early as 1946, they reported that thawing time was notably reduced when RF was used in a frequency range of 14∼17 MHz. The color and flavor of food samples were better maintained by the RF-assisted thawing compared to those thawed by conventional method. Jason and Sanders (1962)showed that herring and white fish thawed by RF in 36∼40 MHz frequency range had shorter thawing time, less drip loss and better retention of odor as well as flavor compared to those thawed by using air or water. Farag et al. (2011) thawed lean beef meat by using RF and conventional air method. The results of this study showed that the RF-assisted thawing resulted in an 85-fold reduction in thawing time and a more uniform temperature distribution within the sample. Similarly, tuna defrosted by using radio frequency at 13.56 and 27.12 MHz showed a threefold reduction of thawing time compared to that of air thawing (Llave et al. 2014). In addition, the tuna muscle which contained lower proportion of fat had much better temperature uniformity during RF thawing. Llave et al. (2015)also reported that the color of flesh muscle was better maintained and the drip loss was lower by RF thawing than by air thawing.

One of the most commonly encountered limitations of RF thawing is the runaway heating (Uyar et al., 2014) and at times this system is reported to be unfit for thawing frozen foods (James and James, 2002). It appears that the runaway heating is associated with the nature of foods and that it is more severe in high fat ones (Farag et al., 2011). Temperature distribution in fat-rich beef meat thawed by RF was much less uniform than that in lean meat. Llave et al. (2014) also corroborated the fact that the tuna muscle with low-fat content exhibited higher uniformity at the end of thawing. To minimize the runaway heating and subsequent over heating during thawing, Uyar et al. (2015)developed a computational model and computer simulation. They reported that greater penetration depths of RF are required to achieve better temperature uniformity and to minimize the effect of runaway heating. The RF can be immensely promising thawing technology if the runaway heating can be controlled and reduced.

## Conclusions

This paper has systematically reviewed recent developments in novel freezing and thawing technologies which are applied to and are relevant to the food industry. The novel technologies including ultra-low temperature freezing, ultra-rapid freezing, ultra-high pressure-assisted freezing and ultrasound-assisted freezing create high heat transfer rates and lead to the formation of small as well as evenly distributed ice crystals and ultimately improve the quality of frozen foods. The non-thermal and novel technologies such as ultra-high pressure-assisted thawing and high voltage electrostatic field thawing greatly increase the thawing rate and also maintain the quality of the thawed foods. Additional novel thawing technologies such as ultrasound and radio frequency-assisted thawing generate heat inside the frozen product, heat the product volumetrically and accelerate the thawing process.

New and innovative freezing and thawing technologies have been developed rapidly in the past few decades. The freezing and thawing processes are complex and negatively affect the quality of frozen foods. Therefore, development of innovative and more effective freezing and thawing technologies is necessary to improve the quality of frozen/thawed foods and to save the energy.

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