NOVEL CRYOGENIC TECHNOLOGIES FOR THE FREEZING OF FOOD PRODUCTS

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Abstract

Innovative cryogenic freezing technologies can be used to produce high quality frozen foods. A recent patent survey from 40 patent-issuing authorities around the world showed that only 1.2% of the total patents granted for cryogenics in the past 11 years refer to food freezing technologies. The potential for the development of new cryogenic equipment and processes is still enormous.

This paper presents the fundamentals of cryogenic freezing and the trends in food freezing technologies, discussing some technical descriptions of representative freezing equipment developed in the past decade. Product quality issues encountered when using cryogenic systems with inappropriate knowledge of the product or inadequate cold chain after cryogenic freezing -i.e. recrystallization, mechanical damage and others- are also addressed.

Key Words:

1. INTRODUCTION

Food processing is Australia's largest manufacturing industry, with a growth of approximately 36% in the past decade [1]. One of the key strategies for improving the profits of the Australian food industry is increasing the value of raw materials and extending the shelf life of high value products through operations such as freezing. The industry is always looking for innovative ways of producing high quality frozen foods and methods of maintaining this quality through to the point of consumption. The use of cryogenic technologies might be the answer to these needs.

Cryogenic refrigeration refers to the use of expandable gaseous refrigerants, such as argon, oxygen, hydrogen, nitrogen, carbon dioxide and others, that at atmospheric pressure evaporate or sublime at very low temperatures. In the food industry, the most popular cryogenic substances are nitrogen (N_2) and carbon dioxide (CO_2).

Some of the benefits of cryogenic freezing and chilling include short cooling/freezing times, reduction in dehydration and drip loss and improved texture of products due to the growth of small ice crystals.

A patent survey was conducted from 40 patent-issuing authorities in the US, Japan, PCT (World Patent Office) and major European countries (Derwent Innovations Index®. ISI Web of Knowledge™, 2002). This survey showed that 4,604 patents have been granted in the past 11 years for cryogenic technologies in the most important 23 industrial fields worldwide, including polymer engineering, chemical engineering and semiconductors, amongst others. From these, only 57 patents were related to either new developments or improvements on cryogenic freezing technologies for foodstuffs, which represents 1.2% of the total. The potential for the development of new cryogenic equipment and processes is still enormous.

The objective of this paper is to present the fundamental heat transfer phenomena of cryogenic freezing. The paper will analyse the trends of cryogenic technology in food freezing, discussing some technical descriptions of representative freezing equipment developed in the past 11 years, such as impingement freezers, tunnel and spiral freezers, and immersion baths. Frozen product quality issues encountered when using both cryogenic and mechanical systems, such as recrystallization, "shrinking" of product, dehydration and mechanical damage, will also be addressed.

2. HEAT TRANSFER MECHANISMS DURING CRYOGENIC FREEZING

The rate of heat transfer during freezing is influenced by several factors. Some of these are the thermal properties of the food, the surface area of the product available for heat transfer, the size and shape of the product, the temperature difference between the food and the freezing medium, the insulating effect of air surrounding the food and the presence of packaging materials. These factors are significant for mechanical and cryogenic freezing alike. However, the heat transfer phenomena occurring in cryogenic freezing differs from that observed in mechanical systems in several aspects. Figure 1 illustrates the heat transfer phenomena expected during cryogenic freezing.

The most common process in cryogenic freezing is spraying the surface of the product with either N_2 or CO_2. Though the method of application for both substances is similar, the behaviour of these is quite different: when liquid CO_2 is fed into a spay nozzle, the CO_2 expands and changes to approximately equal parts (by weight) of solid and vapour. The flow of the "snow" (e.g. a mixture of solid particles and vapour), the CO_2 distribution system and internal convective mechanisms create air/CO_2 currents within the freezer. As solid CO_2 particles contact the food surface, the solid almost instantly sublimes to vapour, which draws heat out of the

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со словарем за 60 мин (начало)

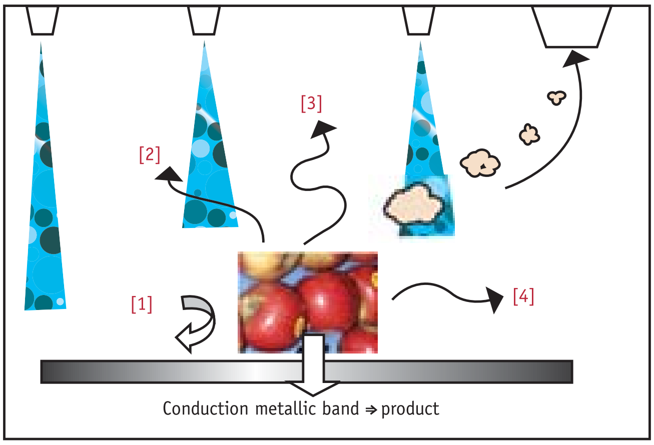
Письменный перевод 3000 п.зн. со словарем за 60 мин (продожение)

product. This system provides approximately 85% of the refrigeration effect from the sublimation of the solid carbon dioxide. The remaining 15% of the cooling is a result of the contact of the product with air/CO_2 mixture. To obtain the maximum refrigeration benefit, a typical CO_2 system will inject CO_2 throughout the length of the freezer [2].

In N_2 systems, the N_2 is sprayed into the freezer and separates as liquid and vapour. As droplets touch the product surface, the liquid changes to vapour, extracting latent heat from the food surface in the process. The vapour distribution through the freezer creates convective currents that increase the freezing rate. In this case, about 50% of the refrigeration effect is supplied by the N_2 phase change from liquid to vapour. The remaining heat is removed by the N_2 vapour flowing through the freezer.

It should be noted that heat removal would not induce phase change by itself: additional factors such as the rate of formation of ice crystals and the propagation of these in the food structure are involved.

Figure 1. Representation of heat transfer phenomena during cryogenic freezing



[1] Heat transfer product-to-mixture of air and refrigerant (either $CO_{2,snow}$ or $N_{2,vapour}$)

[2] Heat transfer product-to-refrigerant (either $CO_{2,solid}$ or $N_{2,liquid}$)

[3] Direct sublimation of CO_2, snow on food surface OR direct evaporation of N_2, liquid on food surface

[4] Radiative heat transfer product => colder surroundings

The freezing of food materials is more complex than the freezing of pure water. All food materials contain solutes such as carbohydrates, salts, colorants and other compounds which affect their freezing behaviour.

Most food products contain animal and/or vegetable cells forming biological tissues. The water content of these tissues is either inside the cells (intracellular fluid) or surrounding these (extracellular fluid). Since the lowest concentration of solutes is found in the extracellular fluids, the first ice crystals are formed there. During a slow freezing, there will be time for the cell to lose water by diffusion and the water will freeze on the surface of the crystals already formed. As the cells keep losing water, the cell shrinks more and more until it collapses [3]. The large ice crystals will exert pressure on the cellular walls, contributing to drip loss during thawing. A rapid freezing promotes a large number of small ice crystals distributed uniformly throughout the tissue, both inside and outside the cells [4]. Hence, products frozen with cryogenic technologies show a matrix of small ice crystals and a better texture than products frozen using slower heat transfer processes.

Jul [5] describes several cases involving frozen beef and lamb meat in which fast freezing rates did not result in better product quality. However, Jul also describes specific examples where cryogenic freezing has shown advantages over mechanical freezing, such as texture improvements in frozen fish and shellfish, tomato slices and dairy products [5]. Detrimental effects of quick freezing can occur in some products, due to considerable internal strain, surface ruptures and cell structural changes.

Quality losses are also related to breakages of the cold chain, such as those commonly encountered in retail and domestic storage. Most frozen products will be stored in commercial and domestic freezers, where temperature abuse is not uncommon, due to the design of defrost and temperature control systems and the practices followed by the users of domestic and commercial appliances. The author has evaluated a variety of domestic refrigerators and found that air temperatures in the freezer compartment of domestic refrigerators can rise from -20ºC to +18ºC during defrost [6]. Billiard et al. [7] observed similar air temperatures during defrosting of horizontal open frozen food display cabinets commonly used in retail sales of frozen foods. Evaporator defrost of commercial and domestic refrigerators will lead to partial thawing of the frozen product, with the product surface temperature following closely that of the surrounding air (+18ºC). A defrost period occurs typically in a cycle of 8 to 12 hours; hence, this temperature abuse is significant and should be considered when calculating actual shelf life losses for frozen products. Even the best freezing technology will not prevent the loss of quality in frozen products that are subjected to temperature abuse before and after the freezing process. Cryogenically frozen products can be more sensitive to these temperature abuses due to the delicate matrix of ice crystals formed initially and the higher temperature difference between freezing and storage.

3.1 Quality issues in frozen products

3.1.1 Dehydration and shrinking

Product dehydration is the result of several phenomena during freezing, such as an increase in solute concentrations in the

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unfrozen medium as a result of the formation of ice, the water vapour pressure difference between the product surface and air, and structural damage to cells leading to rupture and loss of intracellular water [3,4].

Moisture loss in unpacked foods produces surface desiccation. Dehydration also causes a decrease in the product volume (shrinking), which may range between 3 and 6% in mechanical systems, again depending on the freezing conditions [8,9].

One of the strongest claims for cryogenic freezing is the low dehydration and shrinking rates, due to the rapid cooling of the surface and hence rapid lowering of water vapour pressure at the surface. In mechanical systems, evaporative weight loss in unpacked products can range from 1 to 5%, depending on factors such as the type of product, freezing practices and the air relative humidity. In cryogenic systems, weight loses are reported to be less than 1% [9].

As discussed previously, temperature fluctuations during retail and domestic storage can prompt partial melting of ice crystals and moisture migration within the product. This can lead to the presence of superficial liquid in the product. When, after defrosting, the air temperature returns to its initial control set point, superficial ice will be formed; if the heat transfer scenario is such that sublimation of superficial ice crystals occur, then another quality issue can appear: "freezer burn". [2,4]. This quality problem can appear in both cryogenically or mechanically frozen unwrapped products.

3.1.2 Microbiological activity

Freezing is often regarded as a method of prolonging the shelf life of products by slowing microbial growth. The negative effect of freezing on microorganisms relates to temperature shock, concentration of extracellular solutes, toxicity of intracellular solutes, dehydration and ice formation [8]. However, Schmidt-Lorenz [10] and Schmidt-Lorenz and Gutschmidt [11, 12] found that bacteria was still able to grow and reproduce in 3 to 5 log units per gram at -7.5ºC. The authors also found that the reproduction limit of yeast is -10ºC. Hence, microbiological quality remains an issue until temperatures below -10ºC have been reached in the freezing process.

Geiges [13] reviewed the literature available regarding the effect of slow and fast freezing on bacteria. He concluded that quick freezing and thawing would result in higher microbial survival rates than those found for slow freezing and thawing. In fact, the use of cryogenic substances to freeze microbiological samples is the typical procedure used to keep these viable under long-term storage. Hence, consumers and manufacturers should not take for granted microbiological safety in cryogenically frozen products.

There are other factors that affect the microbiological quality of frozen foods, such as the physical and chemical characteristics of the product, the pre-freezing microbiological quality and the handling during and after freezing (such as thawing and storage). The discussion of commercial and domestic handling of frozen foods also applies.

The selection of fast or slow freezing may be critical for some products, whose quality relies on the presence of selected bacteria. In yeast-raised bakery products, certain freezing rates may promote yeast destruction, thus decreasing the raising potential of the dough. In these cases, a quick cryogenic freezing to form a crust followed by a slow mechanical freezing may help to reduce yeast death, but the manufacturer should expect to lose some yeast in the process [14]. The effect of cryogenic freezing on benign flora should be further investigated in specific applications.

3.1.3 Adhesive forces of products during freezing

In mechanical IQF systems, quality problems may arise due to product adhesion onto the metallic belt transporting the product. This arises from the adhesive force between superficial ice and the metallic surface, which follows a temperature - dependent, non-linear behaviour: Initially, the adhesive force increases as the temperature of the metal decreases, until this force becomes larger than the strength of the ice. However, as the metal temperature approaches -80ºC, the adhesive force is reduced dramatically. When the metallic surface reaches -80ºC, the product can be removed with a minimum of effort. This temperature can be easily achieved in cryogenic tunnels and spiral freezers. Zero Adhesive Technology (ZAT) has been implemented in ice cream manufacturing machinery to produce novel ice cream presentations [2].

3.1.4 Recrystallization

Recrystallization during frozen storage refers to the variation of ice crystals properties following the completion of freezing. These variations include a growth of larger ice crystals at the expense of smaller ones, sharper surfaces are less stable than flatter ones and will show a tendency to become smoother over time, and a change in crystal orientation. Maintaining low constant storage temperatures can minimize these changes. Cryogenically frozen products might present more recrystallization problems, due to the very low temperatures used during freezing and the radical change to higher storage temperatures [3,8].

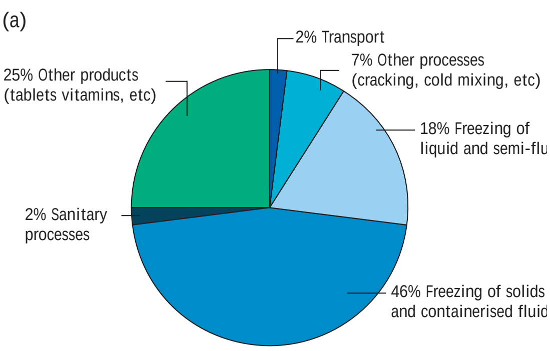
3.1.5 Mechanical damage (freeze-cracking)

Mechanical damage from ice crystals occurs when flexible cell components are stressed in areas where ice is present. Ice crystals continue to grow in size, exerting additional stress on fragile cellular structures. As flexing of cellular tissues occurs, ice can grow into this newly created volume and prevent the structure from relaxing back into its original shape. The theory that ice crystals spear through structures is incorrect: ice crystals grow by adding water molecules to their surfaces; however, the cellular wall surrounds the surface of the ice crystal and aggregation of water molecules to form sharp ice crystals becomes difficult. Research has also shown that product moisture content is not a factor for freeze cracking [3,8].

4. CRYOGENIC EQUIPMENT AND METHODS: STATE OF THE ART

The unsolved quality matters described in Section 3 have motivated the refrigeration industry to seek alternative technologies. Nevertheless, the introduction of new cryogenic technologies in food freezing has been introduced at a slower pace than in other fields, such as superconductors and cryobiology. A patent survey comprising data of 11 years (1991 to date) revealed the following:

- The patented cryogenic technologies applicable to the food industry sector (including freezing, chilling and other equipment and methods) represent less than 4% of the total (Fig. 2a).
- About 64% of the cryogenic technologies applied in food processing refer to developments of refrigeration equipment and methods (Fig. 2b). There is an emerging field of application that uses the physical characteristics of frozen materials to aid mixing, cracking and others. This field has accounted for 7% of the total patents granted in the past 11 years.
- In the 11-year period studied, about 50% of the registered patents worldwide have been granted to individuals or companies which do not have cryogenic refrigeration as their main R&D product (Fig. 3a). Some of these companies are cryogenic users that require a very specific application, such as Nestec (the R&D organisation of Nestle), Dippin' Dots (a manufacturer of ice cream in the US), Institutes and Universities, amongst others.
- The most frequently cited country in the assignee's residence data is USA, followed by Russia (Fig.3b). France and Japan also appear to have an active role in the development of cryogenic freezing.



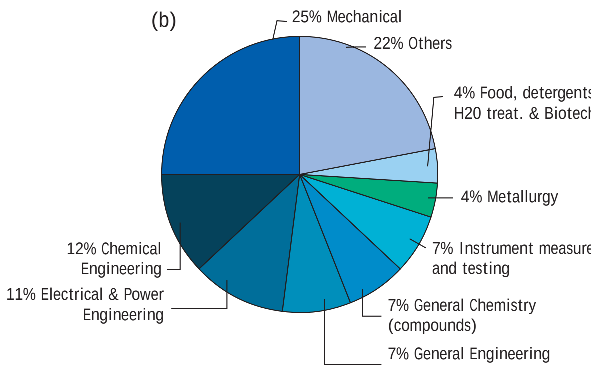


Figure 2. (a) Patents granted in cryogenic refrigeration technologies in the food industry and (b) Patents granted in cryogenic technologies per field of application per application, from 1991 to date.

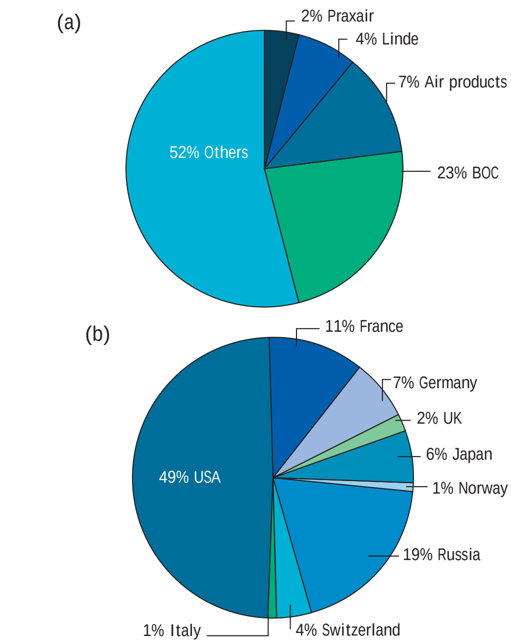


Figure 3. Patents granted in cryogenic food freezing methods and equipment (a) per representative companies and (b) per representative countries, from 1991 to date.

Some examples of representative patents granted in the past 11 years are described below.

4.1 Immersion freezers

The principle of these systems is the immersion of the product in a liquid v bath, freezing the product superficially in 5 to 50 seconds, depending on the product surface available. The main idea is to form a "crust" in the product, reducing the dehydration rate and the clumping of product. The system leads to a significant thermal shock on the product and hence, it is not suitable for delicate food items that may crack under these circumstances. Immersion systems are typically used in the meat and poultry industry.

Kiczec [15] patented a hybrid freezing system using one cryogenic immersion freezer in combination with a spiral mechanical freezer. The advantages of this combination over previous technologies are the creation of a superficial crust in the product, thus avoiding dehydration, and the use of the cold vapour from the immersion bath to increase the refrigeration capacity of the mechanical system.

4.2 Tunnel and spiral freezers

A typical cryogenic tunnel freezer has a conveyor belt that transports the product throughout the freezer, while a liquid cryogenic substance is sprayed onto the food. The spiral freezers have the same principle as the tunnel freezers, with the exception of less area required to mount them in a production line. A vertical-axis spiral belt replaces the straight belt. The design of both types of freezer can comprise one or more spray zones and one or more transfer fans to move the cold vapour along the tunnel.

Traditional designs use only one cryogenic substance. Foss et al. [16] patented a tunnel freezer that uses a mixture of liquid oxygen (O2) and liquid N_2 in a composition similar to that found in normal air. The advantages of the system are related to the safety of the operators, avoiding dangerous build-up of gaseous N_2 with the subsequent lack of O2 in the surroundings of the freezer. The tunnel has an immersion bath and O2 sensors to monitor the levels and control the system accordingly.

4.3 Cryogenic impingement freezers

These systems use a combination of high velocity air jets (air impingement) and atomised N_2 applied vertically downwards on the surface of the product. The use of air jets drastically decreases the superficial resistance to heat transfer and thus, the freezing rate relies mostly on the temperature gradient between product and N_2 (typically of 190ºC) and the thermal properties of the product. Impingement freezers are generally better suited to products with high surface-to-weight ratios [17].

4.4 Free-flowing freezers for liquid products

Jones et al. [18] patented a cryogenic freezer that involves delivering flavoured liquid dairy and other fluid products to a feed tray and then dripping the composition into a freezing chamber. The feed tray comprises a number of orifices through which the liquid product passes. When liquid is fed into the orifices, droplets form and fall into the freezing chamber. As these fall into a chamber filled with a mixture of gaseous and liquid cryogenic refrigerant, they solidify forming solid beads of flavoured ice cream, yoghurt or flavoured ice. The frozen beads are removed from the freezing chamber and packed for distribution and later consumption.

Other promising R&D trends in the use of cryogenic technologies for the food industry are:

- Researchers at the Florida Department of Citrus have refined a cryogenic process to freeze citrus fruit to -46ºC. When the fruit is subjected to impact, it shatters into a handful of frozen vesicles. The department hopes the process can be patented this year and predicts that cryo-separated juice vesicles will be available in supermarkets by around 2003 [19].
- Cryogenic cooling of delicate products by fine-tuning temperature control has been investigated. There are patents granted for cooling of whole eggs, extending the product shelf life from the current 30 days to 60 days [20]
- The combination of ultrasonics and cryogenic freezing techniques as a manner to decrease the size of ice crystals during nucleation is promising. Some equipment was patented in 1980, but the mechanism in which sound waves passing through supercooled water actually form ice crystals is still under research.

5. CONCLUSIONS

The cost/benefit analysis of cryogenic technologies in respect to other freezing processes is not a trivial process. While some products are better suited for fast freezing, others are not. New cryogenic equipment for the food industry should be developed considering the effect of processing variables on the physicochemical properties and on the quality attributes of the individual products. Quality attributes, food safety and legislation should all be considered in the design of novel technologies in this field.

The analysis of recent patents worldwide revealed that there are significant opportunities to further develop cryogenic technologies for food freezing and chilling applications, possibly borrowing principles from the most advanced applications, such as superconductor and spatial technologies or biotechnology. The drive for cryogenic solutions appears to be high from the user end, since a number of developments have actually been developed for specific user applications.

Management practices during the frozen food cold chain also need to be addressed. There is no benefit in fast freezing a product using very low temperatures if the same product is subjected later in the cold chain (i.e. transport and storage) to high temperature fluctuations. The quality of the product at the end of the cold chain might be just as poor as the quality of a product that suffered a slow freezing from the start. The benefit of new frozen product formulations and new freezing technologies should be assessed taking into account the frequent temperature abuse occurring in commercial and domestic storage.

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