USE OF LOW TEMPERATURES FOR FOOD PRESERVATION

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Abstract. Modern technology knows many methods of freezing. Their application depends on the kind of product, scale of production, type of packaging, availability and price of refrigerants. One of the newest methods employed at present for freezing food products is based on using liquid gases – mainly nitrogen and carbon dioxide. Technologies in which liquid gases are used contribute to the development of the refrigeration industry. Research results show that in Poland liquid gas freezing may be employed in the meat and forestry industries, fruit and vegetable processing and drink production.
Keywords: food, methods of freezing, cold storage, quality, durability.

ŽEMŲ TEMPERATŪRŲ NAUDOJIMAS MAISTO IŠLAIKYMUI

Santrauka. Šiuolaikinių šaldymo technologijų yra daug. Kurią iš jų pasirinkti, priklauso nuo produkto rūšies, gamybos apimties, įpakavimo tipo, šaldytuvų ir kainos. Viena naujausių maisto produktų šaldymo technologijų pagrįsta suskystintu dujų naudojimu. Dažniausiai naudojimas azotas ir anglies dioksidas. Lenkijoje atliktų tyrimų rezultatai rodo, kad suskystintų dujų naudojimu pagrįstos šaldymo technologijos tinkamos mėsos, vaisių, daržovių, gėrimų, miško pramonėje.
Raktažodžiai: maistas, šaldymo būdai, šaltas laikymas, kokybė, patvarumas.

A Review. Looking from a historical perspective, food preservation - aimed at extending its keeping quality – appeared probably much earlier than farming or animal breeding. Problems with finding food resulted in the need to prolong its storage life. Also the fact that some plants and animals were seasonal only made it necessary to find a method that would allow to store food products even for several months.

Food storage was from the very beginning connected with simple forms of its preservation under natural conditions, such as: drying, smoking, salting, chilling and freezing. With time those techniques developed into independent scientific disciplines, making use of additional processing and enriching procedures.

In 1876 the 'father of refrigerating engineering' Charles Tellier for the first time in history organized intercontinental sea transport of chilled meat from Europe to South America (12000 km) and back. The ship's name was 'Le Frigorifique'. It is also worth noting that in 1978 we celebrated the hundredth anniversary of opening of the first machine-cooled cold store in Chicago. Those events revolutionized world food economy and provided the basis for the development of a modern 'refrigeration chain'. Cryogenic engineering started to develop on the turn of the 19th century, when Olszewski and Wróblewski, and Carl von Linde carried out liquefaction of gas.

Food freezing is a process of lowering inner temperature of products below the cryoscopic point. The freezing effect is achieved through water wintering (above 80% of its content). Products are kept in this state during storage in order to limit physical, biochemical and microbiological changes which could decrease their quality. Viewed from a broader perspective, freezing includes the whole cycle of product preservation by means of low temperatures, taking into account all necessary technological operations [20].

Food freezing is based upon:

- biose (reversible inhibition of natural life processes of products),
- anabiosis (maintenance of some life processes in a latent form, characterized by a different degree of reversibility),
- abiosis (irreversible inhibition of all life processes).

The papers presented during the International Congress on Refrigerating Engineering, devoted to 'Refrigeration in the Food Industry', emphasized that the process of freezing:

- facilitates food reserve stocking,
- increases production quality,
- contributes to the regulation of periodical fluctuations in supply and prices,
- facilitates international trade in food products,
- reduces storage losses.

The global agricultural and fish production in 1997 was at the level of 5 165 mln tons [6]. 50% of that are perishable products which require preservation at individual stages of production. According to the studies conducted by the International Institute of Refrigerating Engineering, only 25 – 30% of perishable goods are properly protected with the help of refrigerating machines. Due to that food losses are still considerable, reaching 20 – 30% of food perishable weight.

The above data indicate that in the future we should aim not only at increasing production, but first of all at reducing losses. It follows that the development of food storage methods will constitute an important task.

Modern technology knows many methods of freezing. Their application depends on the kind of product, scale of production, type of packaging, availability and price of refrigerants. In practice ca. 90% of freezer rooms are equipped with an air apparatus, 9% - in a contact one. Other types of equipment are used sporadically only – in 1% of freezer rooms [20].

As the topic discussed is very extensive, the present paper will give only general characteristics of the basic freezing methods and machines used. The most popular methods, applied worldwide, are:

Ventilation freezing in tunnels, with a longitudinal or crosswise forced flow of cold air. This method is applied most often, despite the fact that its thermodynamic and technological indices are worse than those of other methods. It is characterized by simplicity and universality, it is easy to apply and may be adapted to the conditions of a given plant. The freezing cycle lasts from 2 to 40 hours, depending on the type of equipment, product size and kind of packaging. The disadvantage of this method is high unit energy consumption (operation of ventilators, temperature of ammonia evaporation from -40 to $–45^0$C). Moreover, the phenomenon of lumping may also be observed in the case of crumbled products.

Fluidization method is characterized by 30 – 40 times higher intensity of heat exchange than the ventilation method. In this technique a stream of cold air goes through the whole mass of a frozen layer of loose products placed on a conveyor belt. This allows to avoid lumping, even of dump products. The freezing process is short, due to very intensive heat exchange. The disadvantages of this method are relatively high investment costs and high consumption of power needed to drive compressors and ventilators.

In both methods the refrigerating medium is ammonia, used in a closed cycle (minimum losses).

The method of contact freezing is applied rarely. Products are placed on metal trays. During freezing they are in contact with pressure plates. In the past those plates were cooled with brine, now direct ammonia evaporation is used. It allows to achieve high values of thermal conductivity and low electric energy consumption. The disadvantages of this method are problems with work mechanization: it cannot be adapted to continuous running and it is difficult to apply it in the case of belt-system production. It is employed mainly for fish freezing on factory ships, as well as fish processing on land. However, the method discussed is becoming less and less popular in world refrigeration.

The method of immersion freezing consists in freezing products in air-tight packages in salt solutions or other media. Good conditions of heat exchange result in a relatively short time of freezing, with the medium temperature $–20^0$C. An immersion apparatus is extremely economical (heat losses up to 7% of the total cold requirement, compared with 20 – 30% observed in ventilation and fluidization tunnels). At present this method is applied, in a limited range, for initial surface freezing of poultry carcasses (further freezing is conducted in ventilation tunnels).

In the years 1963 – 1964 in the United States, and in the years 1967 – 1968 in Europe, new methods of food freezing started to develop. Their application was based on using liquid gases, mainly nitrogen (the method of Liquid Nitrogen Freezing – LNF) and carbon dioxide (the method of Liquid Carbon Dioxide Freezing – LCO_2F) [2, 3].

Cryogenic fluids are characterized by physicochemical properties which enable to satisfy the basic requirements of the refrigeration industry, such as:

- short freezing time, ensuring the highest degree of preserving the original product quality,
- continuous, automated operation of machines, enabling almost complete elimination of operating personnel,
- high efficiency, combined with limited room demand,
- universality of application due to the fact that the apparatus is characterized by light-weight structure and may be easily taken from one place to another,
- high refrigerating capacity.

The presentation of the above methods is connected with certain terminological and classification problems. The technique based on using liquid gases is referred to as cryogenic or cryogenous freezing, while such gases are known as cryogenic fluids. According to the official international terminology, cryogenic techniques are those in which temperatures lower than $–153^0$C are applied. This suggests that it is wrong to use the terms ‘cryogenic freezing’ and ‘cryogenic fluids’ in relation to methods based on temperatures of ca. $–78.5^0$C (sublimation temperature of CO_2). Probably the best solution would be to describe this group of methods as freezing with the use of liquid gases.

LNF is based on pure nitrogen, obtained as the product of air liquefaction or natural gas denitriding. Nitrogen is chemically inert gas; it does not react with food products. Its evaporation temperature under normal pressure is $–195.8^0$C.

There are three basic freezing methods:

- immersion – products are put into liquid nitrogen,
- spraying – products are in direct contact with nitrogen sprayed on them,
- freezing in a stream of cold nitrogen steam.

Each of those methods has both advantages and disadvantages. The immersion method has been almost completely eliminated, mainly for two reasons:

- the freezing process is very quick due to a great temperature difference, which causes micro- and macro-damages of tissues,
- the method uses heat of nitrogen evaporation only.

The spraying method is commonly applied for freezing food products. In freezing tunnels of this type cold nitrogen steam is used for pre-cooling and freezing. Then products are sprayed with liquid nitrogen. If the process is carried out until reaching the final product temperature of -20^0C, nitrogen consumption is equal to 1.0 – 1.5 kg per kg of product.

Liquid carbon dioxide freezing is similar to liquid nitrogen freezing. Because CO_2 under atmospheric pressure has the form of gas or a solid body only, those methods differ in the range of temperatures and rate of the process. The effective freezing rate of portioned meat by the LCO_2 method at the temperature of -70^{0}C may vary between 5 - 8 cm of the frozen layer per hour. In the case of liquid nitrogen, at the temperature of –110^{0}C, it is higher than 10 cm per hour. Consumption of both gases is similar.

Freezing of food products causes changes in their quality, connected directly with this process and further cold storage [5]. Freezing does not inhibit completely the bio-physicochemical processes taking place in food; it only limits them or changes their course. The effect of freezing on food quality varies, depending on individual products. It is generally believed that it is the most significant in the case of fruits and vegetables [11, 12], and slighter in that of meat and meat products [13, 14]. An important role is played here by the rate of freezing and formation of ice crystals.

Structural Changes. Research results confirm the destructive effect of freezing on the tissue structure of food products [9, 22]. Good quality of frozen products is connected with the size of ice crystals. When the temperature falls below the cryoscopic point, the so called 'crystallization centers' are formed, surrounded by numerous ice crystals. The more quickly the temperature falls, the more crystallization centers appear and the smaller ice crystals are. This is directly related with less serious damage of the structure of frozen products.

In our studies on the ultrastructure of pig's muscular tissue frozen employing the ventilation method [9], damages of muscle fibers were observed. They included fiber breaking, in some cases rather extensive. Complete disintegration of the sarcoplasmic reticulum and mitochondria was noted, as well as glycogen structure 'blurring'. Also the sarcoplasmic, basement and nuclear membranes suffered serious damage and disintegration. Large infiltration zones were observed both within and beyond muscle fibers.

The ultrastructure of muscles frozen by means of liquid nitrogen was characterized by better preservation of the sacroplasmic reticulum, structure and uninterrupted sequence of the sarcoplasmic and basement membranes. Most infiltration zones were found within muscle fibers, and only few beyond them.

Therefore, our research confirmed the opinion that the slower the freezing process is, the more serious damage is observed in fibrous and non-fibrous elements of muscular tissue.

The phenomenon of the so called 'recrystallization' may occur during cold storage of food. This means that bigger ice crystals, distributed between muscle fibers, still increase in size, contrary to smaller ones located in fibers [4]. The process of recrystallization, caused by temperature fluctuations, may lead to gradual disappearance of differences between the quality of products frozen quickly and slowly. Due to that, although specialists agree that quick freezing brings better results as concerns quality, the freezing process is not considered the most important factor among those influencing the final quality of frozen products. The primary role is played by storage conditions and ways of thawing.

In the case of delicate food products (e.g. berries), the amount of drip in the thawing process is treated as a synthetic index of the product quality. It is also assumed that the amount of drip during thawing under standard conditions may reflect the degree of tissue structure damage in the freezing process. For example, in the case of strawberries the drip amount may be limited considerably if freezing lasts for 10 – 12 minutes. However, its further acceleration (usually connected with a significant increase in costs) produces a marginal effect only.

As regards beef, the correlation between the drip amount and freezing rate is slight, compared with fruits.

It should be kept in mind that if the freezing rate is very high (above 10 cm/h), as in the case of liquid nitrogen, considerable mechanical stresses may appear in the surface layer of frozen products. This can result in breaking and damaging of tissue structure. The phenomenon discussed is especially well visible while freezing food products which contain large amounts of water (e.g. tomatoes) and meat elements whose thickness exceeds 10 cm. It follows that cryogenic methods of freezing should be quick enough to prevent the occurrence of undesirable cryo-biochemical and microbiological processes, particularly at the initial stage of freezing.

As concerns sensitivity to the rate of freezing, food products may be divided into four groups:

1. products whose quality is not affected by the rate of freezing (green pea, blueberries),
2. products not sensitive to changes in the freezing rate, except for the rate lower than 0.3 cm/h (e.g. fish),
3. products whose quality improves significantly if the freezing rate increases to the level of 5 – 8 cm/h with the application of liquid gases (berries, portioned meat, some vegetables, mushrooms, forest fruits),
4. products which crack when subjected to very quick freezing – above the level of 10cm/h (animal carcasses, large-size products).

When Poland joins the European Union, we will have to apply the methods of food evaluation and quality standards which are binding in the Union countries. One of the ways of improving the quality of chilled and frozen food is the use of liquid gases in the technology of low temperatures. This may facilitate the obtaining of the certificates of the ISO 9000 series, and the introduction of the HACCP system.

Quality of frozen food is an ambiguous term, which includes different groups of distinguishing features, determining the product quality. We can talk about sensory quality (positive features of a given product, required by customers, that may be evaluated by the senses), consumer (degree of satisfying customer's nutritional needs) and health (lack of pathogenic microorganisms and harmful substances). According to world trends, an organoleptic evaluation should be combined with objective instrumental and analytical methods [8, 17].

Colour is the feature of food products that is visible and evaluated at first sight, and its changes are the first indicators of quality deterioration [1]. Very quick freezing (e.g. with the use of liquid gases) causes the formation of tiny ice crystals also on the product surface, which produces an optical effect of its 'whitening'. From the consumers' perspective, this effect may be both positive, e.g. in the case of poultry, and negative, e.g. in that of red meat. It should be noted, however, that the 'whitening' of products frozen cryogenically is a purely physical, reversible phenomenon, which disappears in the process of thawing.

An extreme form of colour changes observed in frozen food may be the so called 'frost scald'. This phenomenon, which constitutes a particular form of dehydration of the surface parts of frozen products (caused e.g. by slow freezing and long cold storage), may occur not only in plant and animal tissues, but also in fruit juices or mushrooms.

Freezing by means of liquid gases has a positive influence on the sensory quality of frozen food. Systematic studies were conducted on meat products of different composition, frozen applying the ventilation method, liquid nitrogen and carbon dioxide [9, 10]. Products subjected to very quick freezing were characterized by significantly better quality, palatability and texture, both directly after freezing and after several months of cold storage. Beef frozen in this way showed a lower degree of fat oxidation, brighter color and better water-holding capacity, compared with ventilation freezing. No considerable differences in the above indices were found between freezing in liquid nitrogen and carbon dioxide [18].

To sum up, we can confirm a beneficial effect of freezing in cryogenic fluids on the quality of numerous products of plant (fruits) and animal (cured meat, poultry) origin, resulting from high freezing rate and influence of neutral atmosphere. This kind of influence is reflected by inhibition of bacterial infections, extended storage life and increased salubrity of food. The bacteriostatic and fungistatic activity of carbon dioxide (which decreases the level of pH in frozen food) should also be emphasized.

Biochemical and microbiological processes moderated or inhibited during freezing are 'accelerated' in the course of thawing [9]. It may be assumed that biochemical changes connected with water wintering in food products take place during thawing as well. However, their range can be different. Apart from enzymes resistant to freezing and storage at temperatures lower than cryoscopic, there are also less resistant ones whose activity decreases. Moreover, enzymes may be additionally released from cell organelles damaged in the process of freezing (especially slow). They are often more active in the new environment than previously. For instance, improper meat freezing directly after slaughter (or after 24 hours of chilling) may result in the so called 'thawing contraction'. This leads to irreversible deterioration of meat quality, especially as concerns its technological properties.

An index of reversibility in the freezing process is the amount of thawing drip. With this drip food loses many valuable ingredients, such as soluble proteins, peptides, amino-acids, vitamins and mineral salts. The highest losses are observed in beef, lower in veal and lamb, the lowest – in pork.

The data on thawing drip from fruits and vegetables differ, as regards both its amount and method of thawing. For example, drip from strawberries may reach the level of 34 – 36% and depends on the rate of freezing.

Protein denaturation and biochemical changes of fats and lipoproteids take place during long thawing of meat products. Considerable losses of vitamin C are observed in fruits and vegetables. They are the highest (60 – 70%) in species susceptible to enzymatic browning. The rate of microbiological changes noted in food products in the process of thawing is much faster than in the same products, characterized by similar initial microflora, not subjected to freezing. It follows that biochemical and microbiological changes in products caused by their improper thawing may result in making food unfit to eat. It should be assumed that the optimum quality effect of thawing is achieved when the period of time needed for freezing and thawing of a given product is similar.

At present the possibility of using liquid gases for food freezing in Poland, the application of certain technical solutions and prospects for the implementation of very quick freezing methods depend on the economic efficiency of freezing. The question of employing new preservation technologies in the agricultural and food industry in Poland seems to be very complex. The problems in this sphere include:

- lack of relevant technological and economic information in the environment of home food producers and processors,
- lack of home producers of cryogenic machines,
- high prices of imported equipment, which makes it impossible for small entrepreneurs to buy it.

Due to an increase in the production of liquid nitrogen, which is a by-product of oxygen production, the only real possibility of making use of its surplus is food preservation.

Despite the difficulties mentioned above, the results of research works conducted at the University of Agriculture and Technology in Olsztyn, obtained in the years 1975 – 1999, enable to state that under Polish conditions the technologies based on using liquid gases may be employed in:

1. the meat industry [13, 14]

- gaseous carbon dioxide may be applied for stunning animals before slaughter, which has a significant, positive effect on bleeding and meat quality,
- for freezing deboned meat (beef, pork, horseflesh) which is to be exported or stored for a long period of time,
- for freezing portioned meat (beef, pork, horsemeat) according to the two-stage method, i.e. pre-freezing to the temperature of -3^0C in liquid gas and further freezing to the temperature of -20^0C in a ventilation tunnel. This method allows to maintain high quality of meat, comparable with one-stage cryogenic freezing, and reduce the consumption of liquid gases by ca. three times,

- for freezing meat from hot carcasses (beef, pork), which enables to use its very good technological properties,
- for mechanical 'massaging' and cutting meat by means of mechanical cutters in the atmosphere of liquid gases,
- for back fat granulation,
- for freezing internal glands (e.g. pancreas), to increase the output of insulin;

2. the fruit and vegetable processing industry, forestry industry [7, 19, 21]

- for chilling or freezing strawberries when daily processing capacities of fruit-and-vegetable plants are exceeded, or for freezing them directly on plantations (transportable units). This method allows to decrease weight losses by ca. 20% on the way from the plantation to the processing plant,
- for chilling or freezing raspberries – the application of gas technologies, contrary to traditional methods, reduces fruit damage (90% of raspberries remain untouched),
- for chilling or freezing cherries, in the case of plantations with mechanical harvesting,
- for chilling or freezing tomatoes, which then can be used for the production of salads,
- for chilling or freezing mushrooms – to replace the technology of drying and salting, and obtain high-quality products;

3. the production of drinks

- for storage in the controlled atmosphere,
- for the production of frozen concentrates (in the form of 'balls'), which allows to eliminate cardboard, glass or plastic boxes.

The technologies based on using liquid gases contribute to the development of refrigerating engineering and will find new applications. The research works carried out at present concern: [10, 15, 16, 17]

- the application of liquid nitrogen or carbon dioxide for reducing the number of meat defects (PSE, DFD),
- decreasing the fat content of meat during cold storage,
- the employment of MA (modified atmosphere) and CA (controlled atmosphere) for culinary 'ripening' of beef,
- keeping animals in the liquid gas atmosphere before slaughter, in order to prevent the PSE and DFD defects and improve meat quality.

References

1. Czapski J. Rola i kształtowanie barwy produktów spożywczych w : Food product development – opracowanie nowych produktów żywnościowych. Wyd. AR Poznań 1995 .
2. Dobrzycki J., Baryłko-Pikielna N., Kondratowicz J., Jarczyk A. Urządzenia do zamrażania żywności za pomocą skroplonych gazów. Chłodnictwo 1984. N 9. S. 14-19.
3. Fennema O.R. General principles of cryogenics processing. Proc. Meat Ind. Res. Conf., 1979. P. 109-116.
4. Hoard N.F. Foods as cellular systems impact on quality and preservation. A review. J. Food Biochem. 1995. N 19. P. 191-238.
5. Horubała A. Podstawy przechowalnictwa żywności. PWN, Warszawa 1975.
6. Imbs B. Sytuacja żywieniowa świata-prognoza rozpoznanych czynników rozwoju. Przem. Spoż. 2000. N 1. S. 4-6.
7. Jędrzejewska J., Rydz A., Kondratowicz J., Sikora Z. Wpływ kombinowanej metody mrożenia na jakość owoców malin. Acta Acad. Agricult. Techn. Olst. Technologia Alimentorum 1991. T 24. S. 183-192.
8. Kondratowicz J. Wpływ nowoczesnych metod zamrażania na mikroflorę powierzchniową mięsa wieprzowego po różnym czasie przechowywania w niskich temperaturach. Medycyna Wet. 1987. N 43. S. 304-307.
9. Kondratowicz J. Wpływ nowoczesnych metod mrożenia na jakość mięsa i tłuszczu wieprzowego po różnym okresie przechowywania w niskich temperaturach. Acta Acad. Agricult. Tech. Olst. Zootechnica 1991. T 34. S. 3-61.
10. Kondratowicz J., Bąk T. Meller Z. Effect of enrichment and different methods of freezing on the weight losses and different methods of freezing on the weihgt losses and taste qualities of horsemeat durring cold storage. Pol. J. Food Natur. Sci. 1999. N 2. P. 185-193.
11. Kondratowicz J., Domańska P. Możliwości zastosowania technologii skroplonych gazów do mrożenia owoców w warunkach polskich. Chłodnictwo 1999a. N 8. S. 40-44.
12. Kondratowicz J., Domańska P. Możliwości zastosowania technologii skroplonych gazów do mrożenia warzyw w warunkach polskich. Chłodnictwo 1999b, N 9. S. 68-70.
13. Kondratowicz J., Domańska P. Możliwości zastosowania technologii skroplonych gazów do mrożenia mięsa w warunkach polskich. Chłodnictwo 1999c. N. 11. S. 44-47.
14. Kondratowicz J., Domańska P. Możliwości zastosowania technologii skroplonych gazów do mrożenia mięsa wołowego w warunkach polskich. Chłodnictwo 1999d. N 12. S. 48-51.
15. Kondratowicz J., Bak T. Wpływ przechowywania mięsa wieprzowego w powietrzu i atmosferze gazów kontrolowanych na wybrane właściwości fizykochemiczne. Rocz. Inst. Przem. Mięsn. i Tłuszcz XXXVI. O. 1999. S. 93-99.
16. Kondratowicz J., Bąk T., Denaburski J. Einfluss von Gefrierveffahren-Varänderung der Eigenschaften von normalen, PSE - und DFD – Schwainefleisch. Fleischwirtschaft 2000. N 3. S. 81-83.
17. Kondratowicz J., Uradziński J., Jóźwiak E., Bąk T. Effect of freezing methods on the bacterial contamination level of horsemeat during cold storage. Polish Journal of Veterinary Sciences 2000. N 3. P. 183-186.
18. Kondratowicz J., Bak T. Efecct of pork storage in the air and controlled atmosphere on its sensory quality. Short report. Pol. J. Food Nutr. Sci. 2001. N 1. P. 41-44.
19. Płocharski W., Zbroszczyk J., Kondratowicz J. Wpływ różnych sposobów mrożenia na jakość mrożonek wiśniowych. Acta Acad. Agricult. Techn. Olst. Technologia Alimentorum 1991. N 24. S.193-205.
20. Postolski J., Gruda Z. Zamrażanie żywności. WNT, Warszawa 1998.
21. Rydz A., Jedrzejewska J., Sikora, Kondratowicz J. Wpływ zamrażania kombinowanego na jakość owoców malin podczas chłodniczego przechowywania. Acta Acad. Agricult. Techn. Olst. Technologia Alimentorum 1991. N 24. S. 171-182.
22. Sobina I., Kondratowicz J. Ultrastruktureller Bau der Schweinemuskeln. Morphologische Unterschiede zwischen normalen und Fleisch mit PSE – und DFD – Merkmalen. Fleischwirtschaft 1999. N 11 S. 98-100.

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