CRYOGENIC FREEZING OF SOME BERRY SPECIES USING AN EXPERIMENTAL MODEL OF MULTI-FUNCTIONAL QUICK-FREEZING EQUIPMENT
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CONGELAREA CRIOGENICĂ A UNOR SPECII DE FRUCTE DE PĂDURE UTILIZÂND UN MODEL EXPERIMENTAL DE ECHIPAMENT MULTIFUNCȚIONAL DE CONGELARE RAPIDĂ

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ABSTRACT

For the preservation of horticultural products, the best results in keeping the attributes and quality at a level as close as possible to that of the fresh product are obtained when artificial cold (refrigeration, freezing) is used, unlike other methods. Among the existing freezing methods, freezing with cryogenic agents allows obtaining average linear freezing rates superior to the other methods. The fastest procedure for cooling food products involves the use of liquid nitrogen, which comes into direct contact with the surface of the food product that needs to be frozen. The paper analyzes the quick freezing process of three species of berries, namely blueberries, strawberries and raspberries, using an experimental model of multifunctional quick-freezing equipment - ICR, developed by INMA Bucharest as part of a national research programme. Total times and average linear freezing rates, as well as liquid nitrogen consumptions for each of the three species subjected to freezing, were tracked. Following the analysis of the experimental data, there were found the following: the minimum total freezing time, 498 s, was recorded for blueberries and the maximum total freezing time, 773 s, was recorded for strawberries; for blueberries and strawberries the average linear freezing rates recorded values of 6.32 cm/h and 6.29 cm/h corresponding to a very fast freezing process and for raspberries the average linear freezing rate recorded a value of 1.62 cm/h corresponding to a fast freezing process; liquid nitrogen consumption recorded a minimum value of 6.90 kg for blueberries and a maximum value of 7.20 kg for raspberries. In the case of blueberries, at the end of the freezing process, cracks and fissures of the epidermis and pulp were observed as a result of the thermal shock induced during the very rapid freezing process.

REZUMAT

Pentru conservarea produselor horticole, cele mai bune rezultate în păstrarea atributelor și calității la un nivel cât mai apropiat de cel al produsului proaspăt se obțin atunci când se utilizează frigul artificial (refrigerare, congelare), spre deosebire de alte metode. Dintre metodele de congelare existente, congelarea cu agenți criogenici permite obținerea unor viteze medii de congelare superioare celorlalte metode. Cel mai rapid procedeu destinat răcirii produselor alimentare presupune utilizarea azotului lichid, care ajunge în contact direct cu suprafața alimentul ce necesită a fi congelat. Lucrarea analizează procesul de congelare rapidă a trei specii de fructe de pădure, respectiv afine, căpșune și zmeură, utilizând un model experimental de echipament multifuncțional de congelare rapidă – ICR, dezvoltat de INMA Bucuresti, în cadrul unui program național de cercetare. S-au urmărit timpii totali și vitezele medii liniare de congelare, precum și consumurile de azot lichid pentru fiecare din cele trei specii supuse congelării. În urma analizei datelor experimentale s-au constatat următoarele: timpul total minim de congelare, 498 s, a fost înregistrat în cazul afinelor, iar timpul total maxim de congelare, 773 s, a fost înregistrat pentru căpșune; pentru afine și căpșune vitezele medii liniare de congelare au înregistrat valori de 6,32 cm/h și 6,29 cm/h corespunzătoare unui proces de congelare foarte rapidă iar pentru zmeură viteza medie liniară de congelare a înregistrat o valoare de 1,62 cm/h corespunzătoare unui proces de congelare rapidă; consumul de azot lichid a înregistrat o valoare minimă de 6,90 kg pentru afine și o valoare maximă de 7,20 kg pentru zmeură. În cazul afinelor, la finalul procesului de congelare s-au observat fisuri și crăpături ale epidermei și pulpei ca urmare a șocului termic indus în timpul procesului de congelare foarte rapidă.

INTRODUCTION

Fruits and vegetables, although they have a much lower content of energy substances than products of animal origin, play a very important role in human nutrition through their intake of vitamins, mineral substances and antioxidants *(Cirillo et al., 2023; Gherghi, 1994; Hoffmann et al., 2014)*, contributing to the smooth running of metabolic processes in the human body. Fruits and vegetables contain water in proportion of 80–90% (*Khan et al., 2017*), favoring microbial activity and enzymatic reactions inside the cells, resulting in chemical degradation and loss of quality. Under these conditions, fruits and vegetables are highly perishable, often requiring preservation processes. Preservation technologies aim to lower the intensity of metabolic processes like respiration and transpiration and also the activity of pathogenic microorganisms which represent the main cause of decomposition processes.

In order to prolong the shelf life period of perishable products, a series of preservation procedures can be used (*Alhamdan et al., 2018a; Alhamdan et al., 2018b; Biglia et al., 2016; Bilbao-Sainz et al., 2019; Sousa-Gallagher et al., 2016; Ingeau et al., 2015*): lowering the water content of the product (concentration, dehydration); the use of high temperatures (sterilization, pasteurization); the use of inhibitors of deterioration phenomena (chemical preservatives, bacteriocins, natural antimicrobials, acidification, sugar addition etc.); the use of low temperatures (modified atmosphere, freezing, refrigeration); the use of non-conventional methods (high pressure, high voltage electrical pulses, ionizing radiation, non-ionizing radiation, ultrasound, photodynamics, ozone etc.). When artificial cold (refrigeration, freezing) is used to preserve horticultural products, unlike all other methods, the best results are obtained in keeping the attributes and quality at a level as close as possible to that of the fresh product (*Aghdam and Bodbodak, 2014; Cao et al., 2018; Jha et al., 2018; Gales et al., 2022*).

Freezing, as a preservation method, increases the admissible storage time of food products by more than 5...50 times compared to refrigeration *(Niculita, 1998)*. The increase in shelf life, achieved through freezing, is due to the effects of low temperatures to strongly slow down or completely inhibit the development of microorganisms, to reduce or stop the metabolic processes in the case of living products, and to reduce the chemical and biochemical reactions.

Taking into consideration the average linear freezing rate, *Wm*, the International Institute of Refrigeration (Institut International du Froid - IIF) indicates the next categorization of freezing methods: slow freezing (*Wm* = 0.5 cm/h); rapid freezing (*Wm* = 0.5...3 cm/h); very fast freezing (*Wm* = 3...10 cm/h); ultrafast freezing (*Wm* = 10...100 cm/h).

The regular freezing of products, throughout which their average temperature decreases below -10 °C in a duration that does not permit the unleashing of undesirable enzymatic and microbiological reactions, is featured by the adoption of average linear freezing rates of 0.1...0.5 cm/h. Quick-frozen products are obtained at average linear freezing rates greater than 0.5 cm/h.

If the temperature decrease is achieved slowly, a progressive formation of reduced number of large ice crystals is obtained, which can ruin the cellular structure of the food product and irremediably damage the tissues upon thawing (*Delgado and Rubiolo, 2005; Chaudhary, 2021; Kotwaliwale et al., 2012; Buggenhout et al., 2006; Parandi et al., 2022; Chassagne-Berces et al., 2009)*. If, on the contrary, these temperatures are quickly attained, crystallization can be evaded through the formation of an amorphous stage, characterized by the formation of small ice crystals *(Li and Sun, 2002; Zhu et al., 2020; Van der Sman et al., 2013; James et al., 2015)*, which favors the stability of the products during the following storage period *(Fellows, 2017; Kennedy, 2003)*, while limiting weight loss due to dehydration *(Mulot et al., 2019)*.

The most important techniques of freezing food products are: the use of chilled air; touching with cold metal areas; touching with intermediate cooling substances; using cryogenic fluids.

Among the methods listed above, freezing with cryogenic agents allows obtaining higher average freezing rates than the other methods. This consists in using both, the latent heat of vaporisation at atmospheric pressure of some cryogenic liquids and the sensible heat that the formed vapors soaks up rising their temperature from the very low point of vaporisation to a point near the temperature when the food product freezes. The cryogenic substances utilized within this situation are: liquid nitrogen, nitrogen oxide, carbon dioxide.

By comparison with usual freezing methods, the cryogenic technique possesses the following benefits: rapid freezing, reduction of bacterial growth, minimal dehydration, significant lowering of quantitative losses due to dehydration, optimum conservation of nutritional value, maintenance of the appearance and taste of food products, significant reduction of investment costs in production facilities.

The fastest procedure for cooling food products involves the utilization of liquid nitrogen, that directly touches the surface of the product needed to be frozen. Being a major constituent of the air, the Nitrogen is odorless, tasteless, colorless and inert, and is inoffensive to the food. At atmospheric pressure, liquid nitrogen has a temperature of -196 °C, its principal characteristic being the capacity to absorb a large amount of heat right at inferior temperature, enabling raised refrigeration efficiencies and heat transfer coefficients far superior to mechanical systems. In the case of nitrogen, 48 *%* of the total refrigerating capacity is represented by the latent heat of phase change, and the remaining 52 *%* is represented by the sensible heat of the vapor. The experimental research presented within this paper aims to determine the working qualitative indices and the energy indices in the cryogenic freezing of some berries species, using a multifunctional quick-freezing technical equipment with liquid nitrogen, having a discontinuous operation and an automatic working regime.

MATERIAL AND METHODS

The experimentations were carried out using three species of berries commercially purchased, respectively blueberries, strawberries and raspberries (fig. 1).

Fig. 1 - Species of berries used in the experimentation

For the quick-freezing of berries, an experimental model of multifunctional quick-freezing equipment, with discontinuous operation, using liquid nitrogen as a thermal cooling agent, developed by INMA within a national research programme, was used (fig. 2). Currently, the equipment is subject to a national patent application (CBI A-00054/07.02.2023) and a European patent application (EPC EP23020352.3/25.07.2023).

Fig. 2 - Experimental model of multifunctional quick-freezing equipment – ICR

The ICR equipment uses the latent heat of vaporisation at atmospheric pressure of liquid nitrogen, in order to reduce the temperature of the products to the frozen storage temperature. The technical equipment includes new solutions for the distribution of liquid nitrogen by using high precision nozzles and homogenising the exposure to the liquid nitrogen jets by driving in a continuous rotation movement of the rack with trays on which the products subjected to quick freezing will be positioned. The equipment also ensures the superior recovery of the "exhausted" coolant, by reusing the cold nitrogen vapor (-30 *°C*) discharged from the quick freezing room, when cooling an adjacent room for pre-cooling/temporary storage in frozen state. To prevent the formation of ice and facilitate the access to the freezing rooms at the end of the quick freezing/pre-cooling or temporary storage in frozen state process, the access doors are equipped with sealing gaskets accompanied by defrost resistors.

The experimental model is endowed with temperature probes that permit continuous monitoring and control of process parameters:

- Thermocouple (chromel–alumel), type K, with rod diameter φ = 1.5 mm, measurement domain -100 ºC...+30 ºC, performs temperature measuring in the center of the product;
- Thermocouple, type K, with temperature transmitting segment, measurement domain -100 ºC...+30 ºC, performs temperature measuring on the outer surface of the product;
- Type TTR Pt 100 thermal resistance, measurement domain -200 ºC...+30 ºC, performs temperature measuring within the freezing room.

The mass of each sample was 5000 *g*, 500 *g* on each of the 10 trays (fig. 3). The average mass of a berry was determined, for each sample, as the mean of five aleatory weighings from the mass of the product. The average height and maximum equatorial diameter of the berries corresponding to each sample of the three species were also measured. This was achieved as a mean of five random measurements from the product mass.

Fig. 3 - Preparation of samples for experimentation

Considering the geometric shapes of the three fruit species, the minimum distance between the thermal center and the external surface of the product was calculated. Assuming that the plant tissue of the respective product is homogeneous, having constant thermal properties throughout its mass, it is considered that the thermal center coincides with the center of the product mass.

When it comes to products having regular geometric shapes, the thermal center (*CT*) concures with their geometric center. The minimum distance between the thermal center *CT* and the external surface of the product is denoted by δ_0, this being a significant parameter to determine the average linear freezing rate (fig. 4). For blueberries, δ_0 was approximated by *h/2*, for strawberries it was approximated by *h/3* and for raspberries it was approximated by *h'/2*.

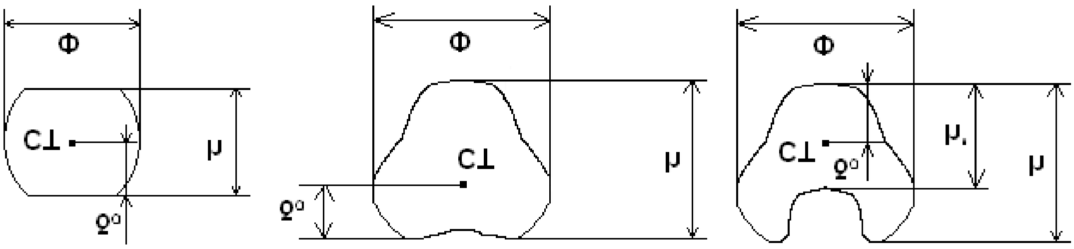

Fig. 4 - Dimensional characteristics according to the geometric shape of the analyzed product

When the temperature in the product thermal centre comes to -15 *ºC*, the freezing process is considered complete. During the freezing process there were followed the main parameters, such as:

- Freezing time from 0 *ºC* to -15 *ºC*;
- Temperature within the quick freezing room, at the end of the freezing process;
- Temperature on the surface of the product at the end of the freezing process;
- Temperature in the thermal center of the product, at the end of the freezing process;
- Total freezing time;
- Mass of the liquid nitrogen container used for freezing;

After processing the experimental data, the following indexes were determined:

- Average linear freezing rate;
- Liquid nitrogen consumption for a freezing cycle.

In order to classify a freezing process depending of cooling intensity, the average linear freezing rate is considered to be a suitable criterion and is defined by the relation:

$$w_m = \frac{\delta_0}{\tau_0}, \text{ [cm/h]} \tag{1}$$

where: δ_0 is the minimum distance between the thermal center and the external surface of the product, [cm];

τ_0 - the freezing time calculated starting from a uniform initial temperature of 0°C to the temperature to be achieved in the thermal centre, [h].

The variation in mass between the liquid nitrogen container before and after the completion of the freezing process, represents the liquid nitrogen consumption for a freezing cycle.

RESULTS

After the processing and interpretation of the experimental data, the following outcomes were achieved:

Table 1

The characteristics of the three species of berries used for experimentation

No.	Characteristic	UM	Value of parameters determined in the tests			
			Blueberries	Strawberries	Raspberries	
1.	Sample mass	g	5000	5000	5000	
2.	Average mass of a berry fruit	g	2.220	15.367	4.313	
3.	Berries maximum equatorial diameter, Φ (average of 5 random measurements)	mm	17.2	35.2	23.1	
4.	Berries average height, h	mm	13.3	40.5	h=18.8	h'=4.1
5.	The minimum distance between the thermal center and the external surface of the product, δ_0	mm	6.65	13.50	2.05	

The limit temperature within the quick freezing room was set to -30°C for all of the three species of berries used.

Process parameters, through the freezing process, can be read on the touch screen of the command and control panel or can be obtained by post-processing the data recorded on the SD memory card. Freezing times were obtained this way:

- the freezing time from 0°C to -15°C was calculated by substracting the recorded value when the temperature came to 0°C in the product's thermal centre, from the total timer recorded at the end of the freezing process (-15°C);

- the temperature within the quick freezing room, the temperature on the surface of the product and the temperature in the thermal center of the product, all measured at the end of the freezing process, were determined by directly reading the values indicated by the respective temperature sensors, at the end of the freezing process;

- the total freezing time was obtained by direct reading of the total timer recorded at the end of the freezing process.

Aspects during the experimentation are presented in figure 5.

Fig. 5 - Aspects during the experimentation

The followed parameters during the freezing process and the determined indexes are shown in Table 2.

Table 2

The parameters of the freezing process and the determined indexes

No.	Characteristic	U.M.	Value of parameters determined in the tests		
			Blueberries	Strawberries	Raspberries
1.	Freezing time from 0°C to -15°C	s	379	773	457
2.	Temperature within the quick freezing room, at the end of the freezing process	°C	-30	-32	-33
3.	Temperature on the surface of the product at the end of the freezing process	°C	-28	-30	-31
4.	Temperature in the thermal center of the product, at the end of the freezing process	°C	-15	-15	-15
5.	Total freezing time	s	498	965	603
6.	Average linear freezing rate for an operating cycle	cm/h	6.32	6.29	1.62
7.	Liquid nitrogen consumption for an operating cycle	kg	6.90	7.05	7.20

Total freezing time registered a minimum value for blueberries and a maximum for strawberries.

The average linear freezing rate registered values corresponding to a very fast freezing process for blueberries and strawberries, and corresponding value for a fast freezing process in the case of raspberries.

Liquid nitrogen consumption registered a minimum value for blueberries and a maximum for raspberries. The fact that the consumption of liquid nitrogen does not vary proportionally with the total freezing times for the three species of berries taken into account, may be a confirmation that the heat transfer from the product to the atmosphere inside the quick freezing room does not take place identically for all the three species and it depends on the composition and structure of the respective tissues, for some of them the thermal transfer is faster and for others slower, depending on the thermophysical characteristics of the respective product.

Aspect of the samples before and after freezing are presented in table 3.

Table 3

Aspect of the samples before and after freezing

Description	Samples aspect during the experimentation		
	Blueberries	Strawberries	Raspberries
Before freezing			
After freezing			

In the case of blueberries, following the visual analysis of the state of frozen products' outer surface, it was found that fissures and cracks appeared in fruit epidermis and pulp during freezing. Strawberry and Raspberry fruits reacted better, with no deterioration of the outer surface condition. *Allan-Wojtas et al. (1999)* stated that although rapid freezing was related to a better internal microstructure of individual berries, it may also cause a fissure on the berry skin as a result of thermal shock.

Although fast freezing is considered to be the best method to maintain the texture of frozen products, *Chassagne-Berces et al. (2009, 2010)* suggested that very fast freezing rates may lead to loss of firmness due to freeze cracking.

CONCLUSIONS

When artificial cold (refrigeration, freezing) is used to preserve horticultural products, unlike other methods, the best results are obtained in keeping the attributes and quality at a level as close as possible to that of the fresh product.

Among the existing freezing methods, freezing with cryogenic agents allows obtaining average linear freezing rates superior to the other methods.

The fastest procedure for cooling food products involves the use of liquid nitrogen, which comes into direct contact with the surface of the food product that needs to be frozen.

Although fast freezing is considered to be the best method to maintain the texture of frozen products, very fast freezing rates may lead to loss of firmness due to freeze cracking., as a result of thermal shock.

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