Experimental substantiation of the storage temperature regime ensuring the stable supercooled state of meat and meat products

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Abstract. One of the ways to ensure safety, preserve quality and increase the shelf life of meat with minimum technological processing of raw materials is the use of supercooling and storage technologies at sub-cryoscopic temperatures. Supercooling is a process of refrigeration processing, which provides the meat temperature decrease (by 1-2°C) below the cryoscopic temperature without phase conversion of water into ice (supercooling) or with partial ice formation (freezing). Subcooling ensures better quality preservation and longer shelf life of raw meat and finished meat products compared to cooling. Phase transformation of water into ice during freezing and freezing of food products causes irreversible changes in them as a result of crystal formation in muscle fibers and denaturation of sarcoplasmic and myofibrillar proteins. The article presents the results of research to justify the temperature regime of storage, which provides a stable hypothermal state of meat and meat products. It is shown that the limit temperature of subcooling is a fixed individual characteristic of the beginning of ice formation in meat and certain types of meat products and can be used as an indicator to justify the temperature of the cooling medium, providing the stability of products in the subcooled state.

1. Introduction

The priority directions of solving the problem of preserving the quality and increasing the shelf life of chilled meat are the use of additional auxiliary technological means to the cold, such as vacuum packaging, packaging in a controlled gas environment, the use of physical, chemical and biological preservatives.

A serious problem in expanding chilled meat production is the limited shelf life of chilled meat. It is known that at 0 °C the growth rate of microorganisms causing deterioration of meat is half the rate of growth at 5 °C. Development of methods for storage of chilled meat at temperatures below 0 °C without phase transition of water into ice could significantly increase the shelf life of meat compared to storage at 0 °C.

According to the International Institute of Refrigeration (IIR), a temperature drop of 1 °C to minus 1 °C doubles the shelf life of meat [1], and according to research by the Federal Center for Meat (Kulmbach, Germany) in the field of temperature reduction from 0 °C to minus 1.5 °C,
respectively, by 30% [2], which indicates the dominant value of the temperature of the cooling medium to increase the shelf life of meat in the chilled state.

One of the ways to preserve quality, ensure safety and increase the shelf life of meat with minimum technological processing of raw materials is the use of supercooling and storage technologies at sub-cryoscopic temperatures.

Supercooling is a refrigeration process that reduces the temperature of meat (by 1-2°C) below the cryoscopic temperature without phase conversion of water into ice (supercooling) or with partial ice formation (freezing). Subcooling provides better quality preservation and longer shelf life of most food products (meat, poultry, fish, fruits and vegetables) in comparison with cooling [6-10] and is used in production of some food products - ice cream [11] and cryoconcentrated fruit juices and blood of cattle [12-13].

Earlier studies in refrigeration technology when freezing foodstuffs attributed subcooling a decisive role in formation of ice crystals and their distribution, but this assumption was not confirmed [3]. Under normal technical conditions of foodstuff freezing their subcooling is not significant for two reasons.

Firstly, under practical conditions of freezing from cold air, frosting crystals get to the surface of the product, and the crystals grow deep into the product.

Secondly, the cooling medium temperature is usually below the limit temperature of subcooling and this leads to crystallization on the product surface. Vibration, stirring and other mechanical influences stimulate crystallization of subcooled water. The more significant the subcooling temperature is, the closer it gets to the limit subcooling temperature.

The desire to extend the possible shelf life of products during cold storage, avoiding damage caused by freezing, was a reason for creating the refrigeration process called subcooling.

Studies conducted by N.A. Golovkin et al. [4] showed that in supercooled meat the autolytic processes are 1.5÷2 times slower than in chilled meat and in some quality parameters are superior to chilled meat. The disadvantage of the technology for storing subcooled meat is that the state of subcooling is easily disturbed if the meat is subjected to any mechanical action.

Vacuum packaging is important to ensure the durability of storage of animal and plant products in a chilled state. The high barrier properties of the packaging reduce the oxygen permeability coefficient and increase the shelf life of the products.

In a study by Japanese authors from Osaka University on cooling and storage of lettuce in the subcooled state with the use of vacuum-packing, it has been proven that subcooling is efficient to preserve the quality and extend the shelf life, compared to the traditional method of storage in the chilled state [5]. Mass loss for samples stored under conventional cooling conditions was 8% by the end of the third week, while for samples stored under hypothermal conditions at minus 2.6 °C - 3%, and the number of microorganisms after three weeks of storage increased to 105.1 DOE in the case of hypothermal conditions and to 106.2 DOE after conventional cooling.

To ensure the stable subcooled state of the products at sub-cryoscopic temperature, it is important to study the influence of various factors on the nucletation temperature of the product, to determine the exact level and stable maintenance of the cooling medium temperature.

The aim of the work is to determine the cooling medium temperature, which provides a stable subcooled state of boneless vacuum packed meat (BVM) of different quality groups and meat products on the example of sausages.

2. Materials and methods of the research
The object of the study was the meat of cattle (steers 1.5 years, Longissimus Dorsi muscles with a weight of 0.2-0.3 kg) of two quality groups of meat (NOR and DFD) and sausages "Dairy" produced by JSC "Klinsky Meat Processing Plant" (GOST R 52196-2011). Sorting of cattle meat by qualitative groups was carried out by values of active acidity of environment (pH) and cryoscopic temperature.

During the research we determined the values of parameters of cooling processes, storage and quality indicators of beef of the first category using modern instruments and research methods.
Research methods: thermometric, physical and chemical (pH, cryoscopic temperature, limit temperature of supercooling, mass fraction of moisture).

The active acidity of the medium was determined by its direct measurement in the thickness of L. Dorsi with the use of pH-meter Testo-205, entered in the State Register of Measuring Instruments of the Russian Federation under № 30759-05. The combination of a penetrating pH sensor and a temperature probe ensures high accuracy of determination and fast temperature compensation, regardless of the environmental conditions.

Mass fraction of moisture was determined using the moisture analyzer "Eulas-2M". Error of humidity measurement results depending on the analyzed material is from ±0.2 to ±1.5%, State Register No. 22077-12.

The temperature of air, meat and meat products was determined using the precision temperature meter MIT-8.10M. Maximum permissible basic error of the device, °C ± (0.015+10 -5 *t)°C, State Register of the Russian Federation No. 19736-11.

Cryoscopic temperature was determined by thermographic analysis of the stabilization temperature on the freezing curve, typical for phase transformation of water into ice, using a precision meat temperature meter MIT-8.10M and the meter of the recorder IS-203.2, State Register number 30414-11.

Relative air humidity was determined with the help of humidity meter and temperature converter DV2TSM-R. The limit of the basic absolute permissible error of relative humidity measurement is ±2%, State Register of the Russian Federation No. 25948-05.

Cooling and supercooling of boneless beef samples was carried out in laboratory conditions of refrigeration technology of animal products by a slow step method of lowering the temperature of the medium in the dry-air thermostat TSV-02 (Russia).

3. Results and discussion
One of the main factors affecting the shelf life of chilled meat is the initial state of the meat (Table 1).

| №/№ | Beef NOR | Beef DFD |
|------|----------|----------|
| 1    | 5.60     | 6.77     |
| 2    | 5.58     | 6.72     |
| 3    | 5.60     | 6.91     |
| 4    | 5.58     | 6.80     |
| 5    | 6.03     | 6.83     |
| x    | 5.68     | 6.81     |
| ±s   | 0.20     | 0.07     |

| №/№ | Beef NOR | Beef DFD |
|------|----------|----------|
| 1    | 73.98    | 75.39    |
| 2    | 73.29    | 77.99    |
| 3    | 74.64    | 74.57    |
| 4    | 75.91    | 76.34    |
| 5    | 76.03    | 75.87    |
| x    | 74.77    | 76.03    |
| ±s   | 1.20     | 1.28     |

| №/№ | Beef NOR | Beef DFD |
|------|----------|----------|
| 1    | -1.17    | -0.90    |
| 2    | -1.08    | -0.81    |
| 3    | -1.09    | -0.79    |
| 4    | -1.10    | -0.86    |
| 5    | -1.01    | -0.87    |
| x    | -1.09    | -0.85    |
| ±s   | 0.06     | 0.05     |

Considering the availability of different quality groups on the meat market, the main physical and chemical indicators (mass fraction of moisture, active acidity of the environment (pH) and color) of NOR and DFD of meat have been determined.

It follows from the data obtained that the most significant difference between normal and DFD meat is observed in the point estimation of meat color and the value of active acidity of the medium (pH). The difference in mass fraction of moisture was 1.26%, and in cryoscopic temperature - 0.24°C.

Experimental studies to determine the cryoscopic temperature and the limit temperature of subcooling were carried out on meat of different quality groups, distilled water was taken as a standard
for comparison (Figures 1, 2). It was found out that the cryoscopic temperature of distilled water is equal to 0 °С (which confirms the reliability of the chosen measurement method), for meat NOR - minus 1.0 °С, and DFD - minus 0.85 °С.

It is shown that the occurrence of supercooling in distilled water depends on heat dissipation conditions (Figure 1). The value of subcooling limit temperature during slow cooling of distilled water reaches minus 6.0 °C, and for NOR meat - minus 3.2±3.5 °C, DFD - minus 2.3 °C (Figure 2).

![Figure 1. Effect of cooling conditions on the cryoscopic temperature and the overcooling limit of distilled waters](image1)

**Figure 1.** Effect of cooling conditions on the cryoscopic temperature and the overcooling limit of distilled waters

![Figure 2. Influence of different quality groups of meat on cryoscopic temperature and hypothermal limit, (1-DFD; 2,3-NOR, 4-air temperature).](image2)

**Figure 2.** Influence of different quality groups of meat on cryoscopic temperature and hypothermal limit, (1-DFD; 2,3-NOR, 4-air temperature).

The subcooling required to initiate germination in food is much lower than for pure water because the food contains dissolved substances that act as germ-forming agents.

Analysis of data on temperature changes in BWM during slow step cooling (Figure 3) shows that in the temperature range from 0 to minus 3.0 °C meat can exist in three thermal states:

- chilled (at near-cryoscopic temperature minus 0.5°C);
- supercooled (at sub-cryoscopic temperature minus 2.0°C without phase transition of water to ice);
- frozen (at sub-cryoscopic temperature minus 2.0°C with phase transition of water to ice up to 50%).
Figure 3. Changing the temperature of meat in the process of step cooling (step 2.0 °C/24 h) while maintaining the air temperature with an accuracy of ± 0.1 °C

Comparative data on temperature changes during step cooling of BWM and meat products (sausages) are shown in Fig. 2. 4. Analysis of data on cryoscopic temperature and nucleation temperature shows that the cryoscopic temperature of meat was minus 1.0 °C and the temperature at the beginning of nucleation was minus 3.0 °C, while for “Dairy” and “Hannover” sausages these values are minus 3.0 °C and minus 7.0 ÷ 8.0 °C, respectively.

Figure 4. Dependence between cryoscopic temperature and the beginning of ice formation of meat and meat products at sub-cryoscopic temperatures (1 - 3 - meat samples, 4 - 5 - sausage samples, 6 - air temperature).

The received data testify to a considerable difference between cryoscopic temperature and the limit temperature of meat and meat products subcooling and necessity of differentiating modes of meat and meat products storage in subcooled condition.

4. Conclusion
It has been established that the limit temperature of subcooling is a fixed individual indicator of the beginning of ice formation for meat and certain types of meat products and can be used in combination with the cryoscopic temperature as a criterion to justify the cooling medium temperature, which ensures the stability of products in the subcooled state.
In pure water, there is more subcooling for homogeneous germ formation. The degree of subcooling required to initiate germination in the meat is much lower because the product contains solids and dissolved substances that act as germ-formers.

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