EFFECT OF CRYOPROTECTANTS ON THE FUNCTIONAL AND ORGANOLEPTIC PROPERTIES OF FROZEN STORED GROUND PORK

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SUMMARY

Possible application of cryoprotectants to avoid freeze induced damage of meat proteins was examined in ground pork.

Standard quality, lean, ground pork ham (without sinews) was treated with and without 2 % sodium chloride and 3 different type of cryoprotectants, respectively. Protein denaturation during 8 months of frozen storage (18°C) was investigated by Differential Scanning Calorimetry (DSC), determination of soluble protein content, cooking loss and pH. Thiobarbituric acid (TBA)-number as regarding the extent of rancidity was also measured.

It was found, that ground pork with added salt can not be recommended to store, frozen, because sodium chloride deteriorates the functional and organoleptic properties of fresh meat, and among the cryoprotectants used the mixture of sucrose-sorbitol could prevent the denaturation of proteins most effectively.

Introduction

Freezing slows down the speed of chemical, biochemical and microbiological processes, therefore it can be used for the storage of fresh meat. Freezing and frozen storage in spite of their apparently optimal technology could cause disadvantegous alterations, which negatively affect the technological properties of meat. The ongoing processes promote the denaturation of meat protein, which acts in decreasing protein solubility, worsening gelling, water retention and water holding capacity, therefore cooking yield is increasing, and oxidative products (chemicals) originated from rancidification will deteriorate organoleptic properties (off odour, off flavour).

Miller et al. (1980) and Awad et al.(1968) found, that protein solubility decreased during frozen storage at temperature -17,8°C in pork, but also in beef.
Lipid oxidation during frozen storage has to be judged also from the point of view of organoleptic properties. Ramsbottom (1947) established, that lipids in frozen meat are susceptible to oxidative deterioration. Indicators for this changes are peroxide number and Thiobarbituric acid (TBA)-number.

During freezing "free water" changes into icecrystals, which - depending on their size - differently damage the cellmembrane. Miller et al. (1980) and Verma et al. (1985) found, that functional properties of fish, mammalian and poultry meat deteriorates when frozen stored at -18°C.

Disadvantages of freezing are to be eliminated, which is possible not only by improving technology but using cryoprotectants, as well.

Among cryoprotectants most of the mono- and disaccharides, many polyols, some aminoacids and carboxylic acids, some carbohydrates and some esthers could be mentioned. From these compounds sucrose and sorbitol are used generally and successfully in surimi production added to myofibrillar fish protein for eliminating the disadvantegous effect of freezing (Macdonald and Lanier, 1991). Researchers prefer low molecular weight (low-MW) carbohydrates because they have favourable price, their purchase is easier and they are not susceptible to undergo Maillard reaction.

Theories with respect to the mechanism of stabilization effect of this molecules are different. Nevertheless there is a general difference between the mechanism of stabilization effect of low-MW and high-MW (high molecular weight) carbohydrates . According to Arakawa and Timashev (1982) low-MW carbohydrates as stabilizing solute molecules are excluded from the surface of the protein molecule, thus "preferentially hydrating" the protein. With respect to the other theory, in contradiction to the previous one, sugars form a

"coating" around protein molecules (Matsumoto, 1979), so preventing their dehidration. Effect of low-MW sugars could be really explained by changing thermodynamical properties of the protein - solute molecules system, therefore favouring the native state of protein.

High-MW carbohydrates have a so-called cryostabilization effect which means these molecules increase the glass transition temperature (Tg') of protein - aqueous solutions, and therefore the speed of the, in this glassy state ongoing chemical and biochemical reactions slows down because of the extremely high viscosity (10^{14} Pa·s).

In Hungary pork meat has the highest share in meat consumption. Aim of our investigations was to determine how to maintain the meat quality by added cryoprotectants during long time frozen storage.

Material and methods

In our experiments standard quality (pH=5.95), lean (without fat and sinews), pork hams (water content: 75.57 %, fat content: 3.51 %, protein content: 19.56 %) with (II.) and without (I) 2 % sodium chloride added were blended with three types of cryoprotectants making the following combinations:

1/ no cryoprotectants added
2/ 5 % sucrose-sorbitol added (in ratio 1:1)
3/ 5 % glucose-sorbitol-citric acid added (in ratio 89:1 :1)
4/ 5 % glycerol added

Samples were vacuum packed into PA/EVA (polyamide/ethylene-vinylalcohol) bags flattened to 1 cm of thickness, then frozen to -18°C and stored frozen at this temperature for 8 months. pH-value, soluble protein content, content of total protein, TBA-number and cooking loss were determined from samples taken after 0,2,4,6, and 8 months of storage respectively, as well as Differential Scanning Calorimetry (DSC), Filterpaper Pressing method by Grau-Hamm and sensory evaluation were carried out.

pH of the fresh ground meat and of the samples was measured by an OP-106 type pH-meter.

Extent of protein denaturation was determined by a SETARAM Differential Scanning Calorimeter. Samples (approx. 300 mg) were heated by a heating rate of 1°C/minute from 25°C to 90°C, and heat flow was registered using distilled water as reference. Peak maximum temperature (T_{max}) were used to describe denaturation temperatures of proteins.

Soluble protein content of the samples was determined by a 1.1 M KI (potassium-iodide)-phosphate buffer extraction (Helander, 1957), and total protein content was measured according to the Hungarian Standard (MSz 5874/8-1978) using Kjeldahl destruction in Contiflo analyzer).

TBA-number determination was carried out by the photometric method of Newburg and Concon (1980).

Cooking loss was determined from ham-type models, which were produced as follows: to the thawed samples (within 24 hours at +5°C) 50 % water, 0,4 % diphosphate and 2,5 % sodium chloride were added, then homogenised. Different samples of known weight were filled into cans of approx. 150 g of capacity, which were sealed and then stored in refrigerator at +5°C for 24 hours. Next day the cans were heated at 80°C for 60 minutes in a water bath, then cooled by running water, and stored for overnight in refrigerator (at +5°C). Cooking loss was determined based on weight measurement (Mihályi et al., 1989).

Sensory evaluation (colour, flavour and texture) was carried out from these samples by a 3-member's panel, giving scores and description to individual samples. Results were evaluated by analysis of variance.

Results and discussion

It was not possible to reach a definite conclusion from pH, because pH of the samples were fluctuating during storage.

Analysis of variance of soluble protein content of samples is shown in Table 1.

Sucrose-sorbitol mixture had significantly better cryoprotective ($p<0,05$) effect on soluble protein of the samples (means higher values) than all other mixtures and that of the control. Soluble protein content significantly changed depending on storage time.

Considering the interactions it can be concluded that regardless of storage time effect of cryoprotectants is weakened when salt is added, with the exception of sucrose-sorbitol mixture.

TBA-number (indicating the extent of rancidity) of stored samples can be seen in Table 2. According to the results salt has a prooxidative effect. Glucose-sorbitol-citric acid mixture could most effectively prevent rancidity. This influence was significantly different from that of other cryoprotectants (it can be seen in Table

3.). Although there are statistical differencies between TBA-numbers of samples, from functional point of view TBA-values are not extremely high.

Protein denaturation during frozen storage can be described by the change of temperature belonging to endotherm peaks and alteration of under-peak area (i.e. enthalpy needed for denaturation). This is possible when using a Differential Scanning Calorimeter. Thermograms of the fresh and up to six month frozen stored samples are seen in Figure 1. and 2. Thermograms of samples without added salt (I) show fundamentally three endotherm peaks. Based on literature data the first one (with 53-54°C temperature) is related to denaturation of myosine, the peak at 60-61°C to that of collagene and sarcoplasmic proteins and the peak at 74-75°C is connected with the transformation of actin. Thermograms of samples with added salt (II) were considerably different from that of without sodium chloride (I). Smallest "peak-temperature" was approximately 2°C lower than that of myosine peak of samples without added salt, furthermore the highest "peak-temperature" was 65-66°C, thus it was approximately 8-10°C lower than that of the "actin-peak" of samples without added salt. Samples with added salt suffered more evident denaturation during frozen storage than samples without sodium chloride. This is showded by the disappearance of "myosine-peak" at 50-51°C, which could not be prevented by the cryoprotectants either. Enthalpy of protein denaturation decreased when salt was added to the samples. Glucose-sorbitol-citric acid as cryoprotectant reduced enthalpy to the largest extent. The analysis of variance of peak-temperatures related to the denaturation of actin is included in Table 4.

Analysis of ham-type models

Cooking loss

Water holding capacity of different, frozen stored pork meat samples was characterized by cooking loss of ham-type models. Analysis of variance of cooking loss data is seen in Table 5.

According to the results added salt increased cooking loss of the samples. Models containing sucrose-sorbitol mixture had a significantly lower cooking loss than the control one (without cryoprotectant) and other cryoprotectant containing samples.

Sensory evaluation

As far the organoleptic properties of heat-treated models it has been found that the mixture of sucrose-sorbitol effectively improved colour. However, added salt had an important deteriorative effect on colour See Table 6.). Texture of models containing the mixture of sucrose-sorbitol was the firmest, but also the most elastic. Added salt caused texture damage during storage. Increase in cooking loss is accompanied by deterioration of texture (it becomes crumbly and disintegrating) (see also Table 7.). The models with added cryoprotectant had a sweety taste, with a strange off-flavour in case of the sample with glycerol. Samples containing sodium chloride and some type of cryoprotectant also had a sweety flavour (see Table 8.).

Conclusions

According to the results it could be concluded:

- Cryoprotectants used can generally and the mixture of sucrose-sorbitol can prevent protein denaturation as well as improve water holding capacity of samples. Without added salt the quality is maintained up to 8 months of frozen storage, and with added salt deterioration (cooking loss) is about half as much as that of control sample (without any cryoprotectants) during the same period of storage.
- Ground pork with added salt is not recommended to frozen storage, because sodium chloride deteriorates water-holding capacity of samples (increasing cooking loss, decreasing soluble protein content), promotes rancidification processes, worsens the texture of heat-treated model samples and also it alters colour.
- Based on DSC-thermograms through the displacement of heat-induced denaturation peaks the effect of different cryoprotectants could be easily followed during frozen storage.

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