SUPERCHILLING – INNOVATIVE PROCESSING OF FRESH FOOD

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ABSTRACT
Superchilling of food will give the food industry increased profitability and new commercial possibilities. The technology will give logistical advantages, both internal (processing/intermediate storage) and external, as well as extended shelf life of superchilled products. There will be less use of freezing/thawing, which normally lead to severe product weight losses and decreased profit.

The aim of the work summarized in this paper has been to investigate whether superchilling can be applied to improve shelf life of roast pork legs, whilst maintaining the processability, and without loosing the fresh properties and reducing the eating quality of the final product.

The results show that it is possible to more than double shelf-life of roast pork leg by superchilling. Airtight packaging, temperature control and stability during storage is critical factors in order to take advantage of all the benefits of superchilling and successfully implement the process in the food industry.

1. INTRODUCTION
The terms “superchilling” and “partial freezing” are used to describe a process where parts of the food products are frozen or partial frozen. During superchilling, the temperature of the foodstuff is lowered, often 1-2 °C, below the initial freezing point of the product. The process of superchilling was described as early as 1920 by Le Danois [1], even though he did not indeed use the words superchilling or partial freezing.

With superchilling technology, refrigeration capacity is stored within the products. The necessary lead time through the chilling equipment can be reduced as the ice formed in the surface areas absorbs heat from the interior of the products. The products will, when there is still some ice content after equilibrium, have a reservoir of cold to absorb heat from the surroundings without altering the product temperature much. Both these advantages are used in industrial applications today, furthermore several cutting processes in the food producing industry depend on a partial frozen surface in order to get clean cuts and stable reliable processes. It has also been shown that [2,3] the amount and distribution of ice in the product prior to processing greatly affects the process capacity and yield, and suggest that an optimum ice content and distribution exists.

At superchilling temperatures, most microbial activity terminates. Chemical and physical changes may however still take place, and in some cases accelerate. In literature, superchilling has mainly been applied to fish and poultry [4-22]. It is reported that the shelf life of superchilled food increases at least 1.5-4 times [23]. Ice crystallization can cause microstructural changes to tissue...
foods during freezing, such as extensive cell dehydration, drip loss and tissue shrinkage during thawing. Food characteristics such as pH, ionic strength, concentration of dissolved gases, viscosity, oxidation-reduction potential and surface tension could also be changed and lead to changes in enzymatic activity and protein denaturation [24-26].

As mentioned above one of the possible disadvantages of superchilling is increased drip loss. The drip loss is both product and process dependent; in order to comply with the demand for short processing times, the temperature of the superchilling medium might induce product-surface quality damages. There will also be uneven ice distribution during superchilling of geometrical complex food products.

Most food is a complex matrix of water, protein, carbohydrates, fats etc., where water molecules are chemically bound to proteins and salts. As a result, the water solution in food has a depressed freezing point and the freezing takes place over a temperature region (see Figure 1).

![Figure 1: Relations between energy- and ice content in salmon fillet.](image)

As shown in Figure 1, the phase changes will give a discontinuity in the enthalpy curve. Especially for the superchilling process, where small changes in temperatures give large changes in enthalpy and specific heat (C_p \rightarrow \infty at the initial freezing temperature), computer simulations and measurements are complex. The well-known Planck's equation for freezing calculations [27] and other equations cannot be used. Measurements during processing will not give any accurate answers due to the fact that the process is not a steady state, and the steep relationship between enthalpy and temperature in the latent zone (from initial freezing point down to approximately -5°C for Salmon). In this zone temperature is not a good parameter to base comparisons between different processes. The amount and distribution of ice inside the product, and possible also the characteristics of the ice crystals will constitute a better scientific basis for comparison. For heavily superchilled products, that is products where more than 50% is frozen ice – temperature measurements can again be used for comparisons (see Figure 1).

Superchilling conditions can be obtained by, air/gas blast freezers, hydrofluidisation units, and regular brine submersion systems or by use of CO₂ pellets. For flat or brick shaped products plate freezers can also be used. Regardless of method; the amount of ice in the product is probably the most important parameter to control when food products are superchilled. Small changes in product...
temperature or processing time can give huge changes in the amount of ice in the products. In industrial superchilling process for food, the heat removal should be rapid and cost effective. At the same time one should avoid local deep cooling that might reduce the food quality. Understanding and quantifying thermo-physical processes at and inside the food surface is therefore of utmost value for optimal design of cooling equipment and packing system for different food products.

The goal of the work summarized in this paper has been to investigate whether superchilling can be applied to improve shelf life of roast pork legs, whilst maintaining the processability, and without losing the fresh properties and reducing the eating quality of the final product.

2. CHALLENGES

Superchilling can give several positive effects as described in the previous chapter, but there are still several challenges when it comes to systematically use and documentation of superchilling as a commercial process in the food industry. Dedicated, flexible and robust superchilling units do not exist presently.

First the challenge is to define the degree of superchilling, that will improve the shelf life sufficiently and fulfil the demands regarding processability and quality attributes. Furthermore, it is necessary to design a superchilling process that is effective and flexible (variations in product shape and size) enough to be commercially interesting, and at the same time preserve the premium quality of the product. The kind of media that is used in order to achieve the superchilling will affect the possibilities for implementing it in an industrial process.

Another challenge is to change from “traditional technologies” such as chilling, freezing, thawing to the more complex superchilling technology. Superchilling demands more accurate information on product variation and flow. Special care prior and after the superchilling process itself needs to be taken. Neither of most equipment producers have the required energy- and thermodynamic competence to design and control the superchilling processes. The researchers need to advice the industries and to transfer the necessary process knowledge. An important part of this technology transfer will be to develop basic data for calculation by graphs etc, of chilling time and temperature, air flow, refrigeration load. This will also include principles for Control-Regulate-Monitor (CRM) systems for the superchilling process and the refrigeration system.

3. MATERIALS and METHODS

Based on extensive preliminary screenings – the desired degree of superchilling were estimated to approximately 10%. For the anticipated composition of the roast pork leg – this degree of superchilling corresponds to an equilibrium temperature of -1,1°C. The screening also showed us that the quality of the superchilled product is at least as good as the good fresh quality. Based on this and the fact that the fresh product is considered to have good quality in 10 to 14 days after slaughtering, reference samples for the “new” experiments were only carried out in the beginning the storage period. Frozen product is known to have at least 10% drip loss prior to processing.

3.1. Raw Materials and Preparation

Roast legs of pork of approximately 1000g was produced (cut, netted and vacuum packed in plastic bags, 9 randomly picked roast legs in each package) one day after slaughtering. pH and product weight were measured before packaging. Only roast legs with pH between 5,7 and 6,3 were used in the further experiments. Slaughtering day was set as day 0. In order to find a process that gave around 10% ice in these products, batches of roast legs were, at day 2, superchilled in an standard air blast freezing tunnel (-30°C, ca 2m/s, two packages in each batch) for 30, 60 and 70 minutes. The fraction of ice were measured in the roast legs immediately after superchilling, and after 6 days of storage at -1,1°C. Roast legs were superchilled in equivalent conditions for 65 minutes at day 3. These products were after superchilling stored at -1,1°C in up to 32 days. Microbiological-, chemi-
cal- and sensory-quality were analyzed three times during the storage period (day 15, 22 and 35). At day 3, the quality of fresh references was analyzed. In order to illustrate the growth of ice during superchilling, packages with roast legs were superchilled in equivalent conditions for 40, 60 and 80 minutes. The superchilled products were cross-sectioned and photographed with an IR-camera (± 2°C).

3.2. Calorimetric quantification of ice
A simple calorimeter, based on an insulated and waterproof storage chamber, instrumented with thermocouples to measure exact product- and water temperatures, was used for ice fraction measurements. The superchilled products were submerged in the center of the chamber with a defined volume of water. Product- and water temperatures were measured continuously as the products were tempered and the water was cooled. The temperature changes were, together with information about the products thermal and physical properties, used to estimate the amount of ice in the products.

3.3. Sensory analysis
The sensory quality of 6 roast legs from one package were analyzed by a trained panel after a standard quality control test, were points between 1 and 9 is given (9 is best). Product with score between 7 and 9 were classified as good.

3.4. Microbiological analysis
The microbiological quality of superchilled roast legs of pork was analyzed after 15, 22 and 35 days. Similar analysis of chilled roast leg of pork at day 3 was used as reference. 6 roasts from each bag were analysed each of the days. 20-25g were aseptic sliced from and end of each roast and placed in a sterile bag (BagPage®). Total plate count was analysed according to the method NMKL146 [28]. Occurrence of psychotropic bacteria’s was determined according to the method NMKL74 [28].

3.5. Chemical analysis
pH, water binding capacity (WBC) and product weight were analysed for superchilled roast leg of pork after 15, 22 and 35 days. Similar analysis of chilled roast leg of pork at day 3 was used as reference. 6 roasts from each bag were analysed each of the days. pH was determined three places directly in each roast with a Metron 80 pH-measurer with insert electrode. WBC was decided by pressing a cylinder shaped piece (~4g) between two layers of two filter-papers (Schleicher & Schuell 597 Roundfilter, 90mm) for 60 seconds. A ceramic tile and a weight of 1008.7 gram were placed on top of the filter-papers during pressing.

![Figure 2: The ice fraction as a function of superchilling times, n=2-5 [29]](image-url)
4. RESULTS and DISCUSSION

The superchilling were carried out at equivalent conditions as in the preliminary screening with similar products. The ice fraction as a function of superchilling times between 0.5 and 4 hours (freezing tunnel, -30°C, ca 2 m/s) is given in Figure 2.

Based on ice fractions and thermodynamic estimates, the superchilling process giving 10% ice in the products after superchilling and storage were chosen to be: 65 minutes, -30°C and 2 m/s. IR pictures showed the ice distribution in the products after ended superchilling and were used as complementary information. The ice distribution in an assortment of the roast legs after different superchilling times is shown in Figure 3.

As mentioned in the introduction, scientific analyses can be based upon direct temperature measurements for heavily superchilled products. For these products – the ice fraction calculations will be too uncertain. Furthermore, the experimental setup and variations in product size also introduce errors. One element that especially influences the results is whether the vacuum is maintained throughout the entire superchilling process (chilling and storing) or not. These elements explain the slight discontinuity in Figure 2.

Figure 3: IR –pictures of superchilled roast pork legs vacuum packed in plastic bags. (a), (b) and (c) is examples of bags that has been superchilled in 40, 60 and 80 minutes respectively at -30°C and 2 m/s
In Figure 3 the ice distributions in product placed in the centre of the packages are compared with the ice distribution in products in the corner of the packages. In the centres, the ice build up mainly from the top and the bottom of the product as there is no contact with either chilling medium or bloody liquid between the products. Superchilling of large packages with food, gives uneven ice distribution after superchilling. During storage, the ice becomes evenly distributed in the products. However, this process takes time (in the packages used in these experiments – up to 36 hours). The temperature differences in the products, between the products and between products and surrounding are very small. With an ice fraction of around 34%, it takes around 90 hours before the product temperature raises from -2°C to approximately 4°C, when stored at 4°C [29]. This illustrates the effect of product internal refrigeration capacity - without superchilling the products would reach approximately 4°C within a few hours

The pH and WBC of superchilled roast legs during storage is shown in Figure 4. The sensory quality and the drip loss during storage of the roast legs are shown in Figure 5. Microbiological quality of superchilled roast legs during storage is shown in Figure 6.

The WBC of the roast legs was somewhat lower in superchilled products than in the reference products (day 3). However, the difference was small and could also have been caused by advanced storage. In a similar experiment, the WBC of superchilled products has been significant higher than of frozen reference products [30]. The muscle proteins ability to bind water is affected by amino acid composition, their shape, conformation and surface characteristics in addition to other factors like pH, temperature and concentrations of salts and ions [31]. The WBC of the roast legs did not seem to be affected of the small pH changes in the products due to storage time and/or superchilling. The pH of the superchilled products changed similarly during storage as in other surveys with similar products [32]. Figure 5 shows that the sensory quality of the superchilled products was good, even after 35 days of storage. The drip loss increased somewhat during storage but did not affect the sensory quality of the products. The drip loss of fresh and frozen references were at day 14 4.0±0.3 (n=9) and 7.4±3.0 (n=9).

Figure 4: The development of pH and WBC of superchilled roast legs during storage n=18
Figure 5: The sensory quality (n=6) and the drip loss (n=3) during storage of the roast legs
Figure 6 shows that growth of mesophilic and psychrotrophic bacteria increased somewhat during storage but were acceptable during the whole storage period. Normal acceptable limit of mesophilic bacterial growth is for roast legs $1.0 \times 10^6$ cfu/g.

The results show that it is possible to increase the shelf-life of the roast pork leg to at least 35 days by superchilling. The product also responds ideal to brine injection direct from superchilled status (Results not shown in this paper). The experiments also stated that airtight packaging is crucial for the result. Temperature control and stability during storage is one critical factor in order to take advantage of all the benefits of superchilling and successfully implement it in industry.

5. CONCLUSION

It is possible to more than double the shelf-life (chemical, microbiological and sensorial) of the roast pork leg by superchilling. The product also responded ideal to brine injection direct from superchilled status (results not shown in this paper). The experiments also stated that airtight packaging is crucial for the result. If superchilling is going to be the preferred process to use for the food industry, some factors have to be met.

Superchilling can give advantages in both internal (processing/intermediate storage) and external (improved temperature control), as well as extended shelf life of their products. There will, due to increased shelf life of the products, be less use of freezing/thawing for production buffers, which normally lead to severe product weight losses and decreased profit. Additionally, the ice stored in the superchilled products will to some extent protect from or reduce temperature rise in the poor cold chains.

There is a large need for help with implementation of superchilling in the industrial process plants and routines. The main challenge has been how to control the process and equipment for chilling in a continuous processing line. Normally, the industry uses temperature control during their processing steps. However, as seen from Figure 1, the enthalpy or ice content changes very rapid in the superchilling region. Small changes in the temperature results in large changes in ice fraction, which again can lead to unfortunate quality changes in the products. Very accurate temperature measurements will therefore be necessary and will be a great challenge. Besides, in industrial processes, differences in product size, geometry, airflow in equipment etc., will often give changes in temperatures and variations within the product, which make measurements challenging.

Since temperature control is very difficult and often inadequate, a new basic principle for measurement and control of ice fraction is needed. Due to the complexity of mathematical and computing
technology, the new methods will be of great value. In a longer perspective, some of these methods can be developed for industrial application.

ACKNOWLEDGEMENTS

Gilde Bøndernes Salgslag, Norsk Kjøtt, and The Norwegian Research Council

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