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Influence of frozen storage of fish on changes in lipids and fatty acids

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Abstract
The freezing point of food is a critical factor for the determination of many physical properties such as freezing time (Planck's equation), water activity, water distribution, amount of frozen water and thawing time. In fish muscle the freezing point is depressed below that of pure water because of small solutes present in the muscle water. The formation of ice crystals is proceeded by nucleation, which can be homo- or heterogeneous. Supercooling is the driving force for ice nucleation and is defined as the difference between the actual temperature and that of the solid-liquid equilibrium. Changes in lipids during frozen storage of fish can, directly or indirectly, lead to quality deterioration. Fish and other seafood have a high content of PUFA, which are very susceptible to oxidation during frozen storage, and lipid oxidation is the main reason for quality deterioration in frozen stored fatty fish. Furthermore whole lipids, free fatty acids (FFA) and oxidised lipids or their products can interact with proteins, in some cases resulting in quality deterioration of especially lean species.

Keywords: crystal nucleation, point depression, Storage, Modified atmosphere

Introduction

The role of fish oil in human health

The role of fish oil in human health promotion and disease risk reduction with respect to the vascular system has been well studied (Shahidi, Alasalvar, 2011) [42]. Omega-3 fatty acids are not synthesized in the human body, thus the inclusion of fish oil rich in those fatty acids in food products is essential (Jabeen, Chaudhry, 2011) [14, 15,]. Due to the decline of wild fish stocks as a result of over-fishing and habitat alternations, the consumption of cultured fish could provide or even more omega-3 essential fatty acids such as EPA and DHA than wild fish for the human body (Cahu *et al*., 2004) [42].

Freezing preservation

Freezing preservation of fish has been used for thousands of years because of high product quality Persson, Londahl (1993) [31]. The concept of frozen storage relies on the lowering of the products temperature to slow down spoilage so that the thawed fish can retain the freshness (Kolbe *et al.* 2004) [19].

Ice crystal nucleation and formation

The formation of ice crystals is proceeded by nucleation, which can be homo- or heterogeneous. Supercooling is the driving force for ice nucleation and is defined as the mdifference between the actual temperature and that of the solid-liquid equilibrium. In a supercooled liquid, homogenous nucleation only occurs if the diffusing molecules spontaneously form a nucleus with a similar structure as ice and with a critical size making it energetically favourable for other water molecules to join. In foods, heterogeneous nucleation is most likely to occur, as a nucleus can form around suspended particles or a cell wall during supercooling. The number of nuclei formed in homo- as well as heterogeneous nucleation increases with increasing degree of supercooling and is crucial for the number and size of ice crystals formed. Apart from the degree of supercooling, the probability of nucleation also depends on the size or volume of the samples because of the statistical nature of the process (Love, 1970; Martino *et al.* 1998; Wolfe, Bryant, 2001) [50].

Freezing point depression

The freezing point of food is a critical factor for the determination of many physical properties such as freezing time (Planck's equation), water activity, water distribution, amount of frozen water and thawing time (Rahman and Driscoll, 1994) [33]. In fish muscle the freezing point is depressed below that of pure water because of small solutes present in the muscle water. The extent of this depression is approximately proportional to the osmotic pressure of the solution and results in a freezing point depression of about one degree Celsius in bulk muscle water (Ross, 1978; Roos, 1986; Wolfe *et al.* 2002) [51]. The freezing point is often referred to as 'the equilibrium freezing point', and can be defined as the temperature at which a minute ice crystal is about to dissolve in melting (Sei and Gonda, 2006) [41]. Others use the term 'initial freezing point (James *et al.* 2005) [16]. which is the temperature at which ice crystallisation begins. The ice crystallisation temperature is always below the equilibrium freezing point because supercooling is the driving force for nucleation and ice crystallisation. As described in 4.5 ice crystallisation is followed by the release of latent heat resulting in a rise in temperature to the equilibrium freezing point (Rahman and Driscoll, 1994; Fernandez *et al.* 2008) [33, 8,]. The equilibrium freezing point is often estimated from DSC thermograms using either the inflexion point at the left part of the endothermic melting peak (Sablani *et al.*, 2007) [39]. or the so-called 'onset temperature' which is the intercept between the tangent at this inflexion point and the baseline. The cooling/freezing curve method is also used to determine the equilibrium freezing point (Rahman, 1995; Kasapis *et al.* 2000; Sablani *et al.*, 2004) [34, 17, 38,]. Reported equilibrium freezing points of fish muscle and seafood are: -0.68 °C for king fish (Sablani *et al.* 2007) [39], -1.4 °C for tuna (Rahman *et al.*, 2003), -0.9 °C for abalone (Sablani *et. al.*, 2004) [38]. values between -0.5 and -2.1 °C for squid, calamari, scallop,

cuttle, mussel, octopus, and king prawn (Rahman and Driscoll, 1994) [33]. -0.83, -0.91, -0.83 °C for haddock, cod and sea perch respectively (Fikiin, 1998) and -5 °C for tuna (Agustini *et al.* 2001).

Changes in lipids and fatty acids

Changes in lipids during frozen storage of fish can, directly or indirectly, lead to quality deterioration. Fish and other seafood have a high content of PUFA, which are very susceptible to oxidation during frozen storage, and lipid oxidation is the main reason for quality deterioration in frozen stored fatty fish. Furthermore whole lipids, free fatty acids (FFA) and oxidised lipids or their products can interact with proteins, in some cases resulting in quality deterioration of especially lean species (Shenouda, 1980; Hultin, 1992; Mackie, 1993) [43, 13, 24,]. Due to lipid hydrolysis, FFA accumulate in the tissue during frozen storage, especially at high temperatures around -10 to -20 °C (Aubourg, 1999; Aubourg *et al.*, 2004; Rodriguez *et al.*, 2007) [1]. Slow freezing rates or fluctuating storage temperatures may result in the lysis of lysosomes and thereby increased activity of some endogenous lipases resulting in increased rates of FFA accumulation (Geromel and Montgomery, 1980) [2, 10,]. Accumulation of FFA does not in itself affect quality attributes of the product but have been shown to interrelate with lipid oxidation and have been proposed to have a pro-oxidant effect on lipids (Miyashita and Takagi, 1986; Han and Liston, 1987; Yoshida *et al.* 1992; Aubourg and Medina, 1997; Rodriguez *et al.*, 2007) [29, 52,]. Furthermore accumulation of FFA may lead to reactions between FFA and proteins resulting in decreased protein extractability. The exact mechanism of this interaction has not been shown, but is likely to be through electrostatic, Van der Waals, hydrogen or hydrophobic forces rather than covalent binding (Mackie, 1993) [24]. The role of whole lipids on the stability of proteins is unclear as they have been suggested to have a protective as well as a detrimental effect (Mackie, 1993) [24]. Oxidation of unsaturated fatty acids or triglycerides in fish results in the formation of free radicals produced through decomposition of lipid hydroperoxides via a free-radical mechanism. Free radicals can react with other molecules to form secondary products such as aldehydes, ketones, alcohols, short-chain fatty acids and hydrocarbons. Volatile carbonyl compounds are thought to be responsible for off-flavours and odours in oxidised seafood (Khayat and Schwall, 1983; Sikorski, 1994). Phospholipids undergo faster hydrolysis and oxidation than neutral lipids and though lean species only contain up to 2 % lipids, most of these are phospholipids, making them prone to oxidation despite the low lipid content (Han and Liston, 1987). Free radicals can also contribute to protein denaturation and aggregation. Radicals may extract hydrogen from protein side chains such as SH groups resulting in protein radicals, which can react with other proteins or lipids to form aggregates. Malonaldehyde, propanal, and hexanal, which are the end products of lipid oxidation, may also react covalently with side chain groups of proteins (Mackie, 1993) [24]. Whether lipid and protein oxidation are concomitant processes or if one precedes the other is still unclear, though (Baron *et al.*, 2007).

Storage time

However, fish and fishery products can undergo undesirable changes during storage and deterioration may limit the storage time. These undesirable changes result from protein denaturation (Fijuwara *et al.* 1998; Benjakul *et al.* 2005) [3]. and lipid oxidation (Sarma *et al.* 2000; Richards, 2002) [40]. The muscle proteins undergo a number of changes (causing insolubility and formation of aggregates) which modify their structural and functional properties Badii and Howell (2002).

Lipid oxidation

Degradation of PUFA by lipid oxidation during storage leads to formation of volatiles associated with rancidity (Pazos *et al.* 2005) [30]. The high degree of unsaturated lipids makes fish tissues highly susceptible to peroxidation and rapid deterioration. Oxidative changes are mainly related to taste and texture of the fish. In later stages of lipid peroxidation, changes in color and nutritional value are observed Dragoev *et al.* (1998) [5].

Fish transportation

Fresh fish fillets have a short shelf life even at refrigeration temperatures. The limited shelf life is a large hurdle for the export of fresh fillets from Iceland to mainland Europe or USA. Transport by sea to major cities in Europe takes about 4-6 days and even longer to the States. For this reason the transport of choice has been air freight. Recent work has shown that storage of superchilled fillets can extend the freshness period (Martinsdóttir *et al.* 2005). Further, combined use of modified atmosphere packaging (MAP) and superchilling can provide further freshness and shelf life extension for both bulk (Lauzon and Martinsdóttir, 2005) and retail (Wang *et al.*, 2008) cod products. These findings may contribute to changes required for fish transportation to foreign markets as lower costs, increased stability of the cold chain, environmentally-friendly packaging and shipping bmethods are among the main driving forces for improvement in the field of logistics. It is also anticipated that these changes may lead to decreased losses of fresh food products.

Modified atmosphere (MA)

The use of modified atmosphere (MA) to affect the shelf life of fresh fish is well documented (Tiffney & Mills, 1982; Farber, 1991, Lampila, 1991; Reddy *et al.*, 1992; Davis, 1993) [47, 20, 35,]. Most of the research has focused on MAP of fish products for the retail market. Considerable research has also been carried out on MA storage of whole white fish (Stansby & Griffiths, 1935; Villemure *et al.* 1986; Einarsson & Valdimarsson, 1990) [46]. and salmon (Veranth & Robe, 1979; Barnett *et al.* 1982; Trondsen, 1989; Sörensen *et al.*, 1990; Bergslien & Meling, 1991) [2, 48, 45,]. Retail and bulk packaging ("bag in box" system) of fish fillets in modified atmosphere was the subject of several trials at the Icelandic Fisheries Laboratories (IFL) and Matís since 1980.

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