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The Effects of Freezing on the Nutritional Composition of Fish

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ABSTRACT

The degradation of fish in the storage condition of the freezer is influenced by several factors which include the fishing species, the rate at which the fish is frozen, the temperature at which it is stored, the duration of storage, the type of freezing applied, and enzymatic processes. The freezing and frozen storage lead to macro- and microscale changes of fish muscles, with major changes being lipid oxidation inducing rancidity, protein denaturation and aggregation causing toughness, red color fading and freezer burn. The process of freezing involves transforming water to ice which in turn results into an increase in the concentration of dissolved substances, adjusting the acid-base balance. It can lead to pH changes of up to 1 unit, often towards acidity and in some cases up to 10 units due to salt and other compounds precipitation. The described changes permanently alter the properties of the physical-chemical nature of frozen fish including the convenience and storage conditions of the food, thereby directing attention to the necessity of new approaches in technologies.

Keywords: Frozen storage, fish degradation, nutritional composition, enzymatic processes, freezing effects.

INTRODUCTION

Fish and fishery products are subject to different cooking method to increase their hygienic quality through destroying pathogenic microorganism and elevating their flavor and taste [1]. In the course of cooking, some chemical and physical changes take place which can either be favorable or unfavorable for the nutritional value of the food. For example, protein denaturation during cooking contributes to increased digestibility; it usually results in the decreased content of thermolabile compounds, fat-soluble vitamins or polyunsaturated fatty acids [1, 2, 3]. Fish frying through the traditional means of food preparation improves the sensory values of the food by giving off aroma compounds, tempting color, crust and taste [2]. On the other hand, the modern customers are paying more attention to health risks connected with high oil consumption for example, obesity and heart diseases. These considerations can diminish the marketability of coated products, which can take on quite a large amount of cooking oil during the flash-frying process, up to 30% of their weight according to [4]. Furthermore, the repeated use and overheating of oil during frying can generate various lipid degradation compounds that may then negatively impact human health [4].

Microwave ovens transform regular electricity into high-frequency microwaves that water, fat, and sugar can absorb, thus water molecules vibrating lead to food heating [5]. The martensite transformation, advocated in the patents by [6, 7], succeeded in increasing the toughness to 85 of the hot rolled Zr steel produced by pure rolling. The change is wrought by the triggering of partial recrystallization by plastic deformation, with partial rather than complete recrystallization for food heating and food preservation several types of electromagnetic waves have been reported by different researchers. Microwave heating has been well studied but infrared heating is somewhat still unexplored [8]. Infrared radiation has many benefits over conventional heating methods such as shorter heating time, small equipment size, faster processing, flavor retention, vitamin retention and minimal migration of solvent from the core to outer region [9]. Freezing is used more frequently for fish and fish products as it as better preservation properties than other storage temperatures, in regard to taste and nutritional essence. What is more, the cryogenic treatment reduces the microbial or enzymatic activity, thus increasing the lifespan of the preserved objects [10]. Commonly used frozen

fish products like fish cutlets, fish fingers, and fish burgers provide constant, predictable quality, easy transportation, and are close to fresh counterparts [11]. Eating fish also increases meal consumption aside from the nutritional quality it provides to the body. As such, fish products in forms such as 'ready to cook' and 'ready to eat' have great potential as condiments [12]. Fish fingers, fish cutlets, and fish burgers are the products which can bring different varieties of healthy foods and to increase per capita consumption [11]. Further studies are necessary for producing novel aquatic products which by the mean time are accepted by local consumers and storing life is prolonged.

Principles of Freezing

Freezing is a process that lowers the temperature below the freezing point, allowing most of the water to turn into ice. The freezing point depends on the substances dissolved in the tissue fluid, with fish containing 75–80% water [13, 4]. During freezing, latent heat is removed during the phase transition of water from liquid to solid, along with sensible heat reduction as the temperature decreases.

The presence of dissolved and colloidal materials in the tissue fluid decreases the freezing point below 0°C. Each food must be cooled down to its specific cryohydric point to freeze completely. Seafood typically starts freezing at temperatures between −1°C and −3°C. The freezing process involves the concentration of organic and inorganic salts, which depress the freezing point. Most water (90–95%) is frozen at −25°C, with the critical zone for ice formation occurring between −1°C and −5°C to avoid the formation of large ice crystals that can disrupt cell walls.

The freezing process of fish occurs in three stages. First, the product's temperature decreases just below 0°C, removing sensible heat. Second, the temperature remains constant at around −1°C during the 'thermal arrest period,' where latent heat is removed. It's crucial for the fish to pass through this period quickly to ensure a high-quality frozen product. In the last stage, the temperature sharply decreases, allowing for freezing of the remaining water, followed by further cooling to the desired subfreezing temperature to remove the sensible heat of the frozen food [4, 13].

Chemical and nutritional changes from freezing on Fish Quality

Fish muscle comprises dark and light muscles, with dark muscle predominantly used for sustained activity, particularly in swimmers like tuna and mackerel, which have higher amounts of dark muscle compared to other fish species. Light muscle is present in all fish species. Sarcoplasmic proteins, abundant in pelagic fish, include enzymes and oxygen carriers. Myosin, actin, tropomyosin, and troponin are myofibrillar proteins responsible for muscle contraction.

Frozen storage leads to freezing denaturation of fish proteins, particularly myofibrillar proteins. This denaturation results in the formation of protein-protein bonds and the development of high-molecular-weight polymers that become unextractable in salt solutions. The increase in salt concentration in the unfrozen phase contributes to protein denaturation alongside physicochemical changes during frozen storage. Protein insolubility poses a more significant challenge than lipid oxidation in lean fish. The extent of protein denaturation depends on various factors such as fish species, nutritional status, rigor stage, pretreatments, freezing velocity, lipid oxidation, and storage temperature. Protein denaturation is less pronounced when freezing occurs in the pre-rigor stage compared to the post-rigor stage of fish. Denatured proteins also lose their enzymatic activity.

Secondary reactions occur between proteins and various reactants, leading to lower extractability and reduced functionality of myofibrillar proteins during frozen storage [14]. Marine animal muscles are reported to be more susceptible to protein denaturation by freezing compared to mammalian muscle [15]. Changes in the functional properties of frozen fish muscle are attributed to conformational transitions of muscle proteins, resulting in protein aggregation involving hydrophobic interactions, hydrogen bonding, and the formation of covalent, non-disulfide bonds. Additionally, alterations in the structure of water and/or protein-water interactions, along with the transfer of water to larger spatial domains, contribute to these changes [16]. Protein denaturation during freezing or frozen storage is considered to be influenced by salt concentration and denaturing due to the freezing out of water molecules, which alter the conformation of proteins. Furthermore, free fatty acids formed during freezing affect the stability of myofibrillar proteins [17].

Functional properties of proteins, including solubility and extractability of the myofibrillar fraction, are related to many functional properties. Freezing, particularly at a slow rate, initially results in a noticeable decrease in myosin-actin affinity due to myosin head denaturation, followed by a continued decrease in ATPase activity and denaturation of the myosin tail [18]. Frozen storage leads to conformational changes in protein molecules, resulting in a loss of functionality such as water holding capacity, viscosity, gel-forming ability, and lipid emulsifying capacity. Undesirable characteristics such as odor, consistency, hardness,

and stickiness are observed in frozen products due to protein denaturation.

The enzyme responsible for trimethylamine oxide (TMAO) breakdown to dimethylamine (DMA) and formaldehyde (FA) remains active down to temperatures as low as −8°C. Formaldehyde levels in fish muscle serve as an index of frozen storage deterioration. In species where formaldehyde is produced, such as gadoids, muscle texture and functionality deteriorate faster during frozen storage due to DMA and FA formation, accompanied by a decrease in myofibrillar protein extractability [19]. FA reacts with different functional groups of protein side chains to form intra- and intermolecular methylene bridges, leading to protein denaturation and aggregation [20]. FA accumulation is higher in dark muscles of fish, resulting in a dry and cottony texture upon chewing. Additionally, FA participates in the formation of interaction compounds with fluorescent properties [21]. The proportion of disulfide and non-disulfide covalent bonds with proteins also increases with frozen storage time, contributing to protein denaturation and aggregation [20].

[20] reported a continuous decrease in sulphydryl groups with a concomitant increase in disulfide bond formation in lizardfish, croaker, threadfin bream, and bigeye snapper during extended frozen storage. Proteins are susceptible to oxidative reactions, where exposure to oxygen leads to the destruction of amino acids and the formation of protein-lipid bonds. This results in the formation of protein-centered radicals due to structured aggregates between carbonyl groups of oxidized lipids and protein molecules [22].

Oxidation of proteins leads to modification of amino acid residue side chains, formation of protein carbonyls, cleavage of peptide bonds, formation of covalent intermolecular cross-linked derivatives, and loss of sulfhydryl groups, impacting muscle quality by altering solubility, protein functionality, essential amino acid content, and digestibility [23]. During frozen storage of fish, lipid hydrolysis and oxidation occur, influencing protein denaturation, texture changes, functionality loss, and fluorescence development. Lipid oxidation compounds react with proteins, peptides, free amino acids, and phospholipids [21].

The hydrophobic effect of free fatty acids on proteins and the interaction of oxidized lipids with cysteine-SH, the epsilon-NH3 group of lysine, and N-terminus groups of aspartic acid, tyrosine, methionine, and arginine in fish proteins influence the solubility of myofibrillar and sarcoplasmic proteins [24]. Highly unsaturated fatty acids, abundant in fish lipids, are prone to lipid oxidation. These polyunsaturated fatty acids are oxidized to hydroperoxides in the presence of oxygen and pro-oxidant molecules such as heme pigments and trace elements. The rate of oxidation increases with the amount of unsaturation and double bonds of fatty acids, as well as temperature and light exposure. Further oxidation leads to the decomposition of hydroperoxides into multiple compounds.

Non-volatile and volatile compounds, varying in molecular weight and polarity and bearing different oxygenated functions such as hydroperoxy, hydroxy, aldehyde, epoxy, and ketone functions, are formed during frozen storage of fish [25]. Aldehydes can cross-link with proteins, leading to muscle tissue hardening. Malondialdehyde and gluteraldehyde, end-products of lipid oxidation, interact with other compounds such as amines, nucleosides, nucleic acids, proteins, amino acids, and phospholipids to form polymers, resulting in structural damage and changes in functionality [26]. Maintaining the storage temperature of frozen fish as low as possible is essential to inhibit oxidation of highly unsaturated lipids, directly related to the production of off-flavors. Lipid oxidation leads to undesirable changes in taste, odor, texture, muscle functionality, and a reduction in nutritional quality. Fatty fish has a shelf life of 4–6 months at −18°C, while lean fish can be preserved for 7 to 12 months [27].

Endogenous fish enzymes may remain active during frozen storage, even at −20°C, leading to lysosomal enzyme leakage as the lipid peroxidation enzyme system remains active at temperatures below the freezing point of fish tissue. Phospholipase may be activated by freezing, initiating phospholipid hydrolysis in frozen fish muscle. Lipases and phospholipases play significant roles in lipid hydrolysis, leading to the formation of free fatty acids. Both fatty and lean fish species exhibit significant lipid hydrolysis during frozen storage, resulting in rancid flavor and deleterious effects on ATPase activity. Free fatty acids interact with proteins, contributing to texture deterioration and lipid oxidation, forming higher-molecular-weight lipids (triglycerides and phospholipids) more rapidly [21, 18, 28].

Frozen storage can disrupt muscle cells, releasing mitochondrial and lysosomal enzymes into the sarcoplasm, leading to the loss of water-soluble proteins, vitamins, and minerals during thawing, with increased leakage of expressible fluid as the proportion of denatured proteins increases. Lipid oxidation affects the nutritional value of frozen food by triggering oxidative interactions with sulfur-containing proteins, resulting in nutritional losses. Additionally, protein oxidation leads to the loss of essential amino acids and decreases product digestibility [29].

CONCLUSION

The freezing process effectively retards biochemical and physical changes in foods, but it cannot entirely eliminate undesirable alterations. Deterioration of fish during frozen storage is influenced by various factors, including fish species, freezing rate, temperature, duration of storage, freezing method, and enzymatic degradation. Chemical and structural changes occur in fish muscle during freezing and frozen storage, including oxidation of lipids leading to rancid odor and flavor, toughening due to protein denaturation and aggregation, discoloration primarily due to oxidation reactions, and freezer burn. The conversion of water to ice during freezing increases the concentration of dissolved materials, leading to changes in acid-base equilibrium. This can result in pH shifts of up to 1 unit, usually towards acidity, and in some cases, drastic pH changes up to 2 units due to the precipitation of salts and other compounds such as phosphate. These changes irreversibly affect the physicochemical properties of food systems, emphasizing the need for enhanced technologies to improve the quality of frozen fish.

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