Food Science of Animal Products

Review Article

Recent advances on applying for liquid nitrogen quick-freezing in aquatic animal products

Bochao Huang[1], Jiwang Chen[1,2] ✉, Jiahui Lu[1], Liuqing Wang[1], Chuyi Jiao[3], Hongyan Lu[1,2] ✉

[1] College of Food Science and Engineering, Wuhan Polytechnic University, Wuhan 430023, China
[2] Hubei Key Laboratory for Processing and Transformation of Agricultural Products, Wuhan Polytechnic University, Wuhan 430023, China
[3] Hubei He Yuan Gas Co., Ltd., Yichang 443000, China

✉Address correspondence to Jiwang Chen, jiwangchen@whpu.edu.cn; Hongyan Lu, luhongyan937@whpu.edu.cn

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Abstract: Aquatic animal products are rich in protein, lipids, and moisture and are often stored at frozen temperature. However, aquatic animal products are prone to deterioration caused by ice crystal formation, lipid oxidation and protein denaturation. Quick freezing is crucial for preserving the quality of aquatic animal products by preventing the formation of large ice crystals. Liquid nitrogen quick-freezing (LNF) provides a fast-freezing rate, minimal ice crystal formation, preservation of product texture and nutritional properties, shelf-life extension, energy efficiency, and quality and safety improving. This review comprehensively illustrates the mechanism of LNF, the impact of LNF on qualities of aquatic animal products including flavor, texture, color, and nutrition. Additionally, LNF devices applied on aquatic animal products are also discussed. Furthermore, future prospects and research directions are suggested, including optimizing freezing processes, understanding the impact on nutritional value and considering sustainability and energy consumption. However, challenges such as freezing damage, cost considerations, and quality control issues for LNF application need to be addressed.

Keywords: aquatic animal products; liquid nitrogen quick-freezing; ice crystals; lipid oxidation; protein denaturation; quality; device

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1 Introduction

Aquatic animal products refer to the animal products obtained from both freshwater and seawater, such as fish, shellfish and shrimp, etc. These products possess remarkable nutritional and economic significance, characterized by their high-quality protein content, essential fatty acids, as well as a wealth of vitamins, minerals, and other vital nutrients[1], which are important for human nutrition and global food supply[2]. Protein is an indispensable macronutrient vital for promoting tissue growth, facilitating repair processes, and maintaining overall tissue health, thereby contributing to an extended lifespan. Aquatic animal products have a higher protein content on an edible fresh weight basis (mean 17.3%) than most terrestrial meats (mean 13.8%)[3]. Meanwhile, aquatic animal products contain the highest concentration of long-chain omega-3 polyunsaturated fatty acids, including eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA)[4]. Omega-3 fatty acids exert cardioprotective effects by improving the lipid profile (increasing high-density lipoprotein cholesterol while decreasing levels of oxidized low-density lipoprotein cholesterol), modulating arachidonic acid metabolism to produce the vasodilator called production of prostaglandin I_3, and regulating blood pressure and heart rate[5]. The omega-3 fatty acids EPA and DHA derived from fish have positive effects on infant development, cardiovascular diseases, cancer and various mental illnesses[6]. Additionally, they have been linked to promising results in weight management and cognitive function in those with very mild Alzheimer's disease, and have shown potential in mitigating various mental illnesses such as depression, attention-deficit hyperactivity disorder and dementia[7]. The consumption of moderate quantities of fish has been associated with a decreased susceptibility to heart disease, which is evident in Japan's exceptional health benchmarks, including life expectancy and the prevalence of cardiovascular ailments[3]. These observations underscore the beneficial impact of aquatic animal products on enhancing human well-being.

Aquatic animal products serve as crucial export commodities, playing a significant role in fostering local economic prosperity and employment stability. In 2020, global aquatic animal production amounted to 177.8 million tonnes, slightly decreasing from the record-breaking 178.9 million tonnes in 2018 (Table 1). In addition, of global aquatic animal production, capture fisheries contributed 90.3 million tonnes (51%), while aquaculture production contributed 87.5 million tonnes (49%). Of the total production, 63% (111.9 million tonnes) originated from marine sources (70% from capture fisheries, 30% from aquaculture), while 37% (65.9 million tonnes) originated from inland waters (83% from aquaculture, 17% from capture fisheries). The estimated total first-sale value of global aquatic animal products reached 406 billion dollars in 2020, with capture fisheries contributing 141 billion dollars and aquaculture contributing 265 billion dollars. Besides aquatic animals, algae production in 2020 amounted to 36 million tonnes (wet weight), with 97% originating from aquaculture, predominantly in marine environments (Food and Agriculture Organization of the United Nations (FAO)).

However, the perishable nature of fresh aquatic animal products

Table 1 World fisheries and aquaculture production, utilization and trade (FAO 2022).

Production	1990s	2000s	2010s	2018	2019	2020
Fishing						
Inland (10^6 t)	7.1	9.3	11.3	12.0	12.1	11.5
Ocean (10^6 t)	81.9	81.6	79.8	84.5	80.1	78.8
Total catch (10^6 t)	88.9	90.9	91.0	96.5	92.2	90.3
Aquaculture						
Inland (10^6 t)	12.6	25.6	44.7	51.6	53.3	54.4
Ocean (10^6 t)	9.2	17.9	26.8	30.9	31.9	33.1
Total aquaculture (10^6 t)	21.8	43.4	71.5	82.5	85.2	87.5
Total world fisheries and aquaculture (10^6 t)	110.7	134.3	162.6	178.9	177.4	177.8
Utilization						
Human consumption (10^6 t)	81.6	109.3	143.2	156.8	158.1	167.4
Non-edible (10^6 t)	29.1	25.0	19.3	22.2	19.3	20.4
Population (10^9)	5.7	6.5	7.3	7.6	7.7	7.8
Apparent consumption per capita (kg)	14.3	16.8	19.5	20.5	20.5	20.2
Trade volume						
Export quantum (10^6 t)	39.6	51.6	61.4	66.8	66.6	59.8
Proprotion of exports to total output (%)	35.8	38.5	37.7	37.3	37.5	33.7
Exports (10^9 dollars)	46.6	76.4	141.8	165.3	161.8	150.5

Note: Data of 1990s, 2000s, and 2010s are annual averages; 10^6 t, fresh weight equivalent.

renders them vulnerable to spoilage within the supply chain, attributable to their inherent quality attributes[8]. Such susceptibility not only catalyzes the deterioration of product quality but also engenders potential food safety hazards. The reason is that the protein and lipid constituents inherent in fresh aquatic animal products are susceptible to enzymatic degradation and microbial proliferation, thereby precipitating their progressive deterioration throughout the course of storage and transportation within the supply chain. This easily results in the quality deterioration of fresh aquatic animal products[8].

Common freezing preservation is a technique employed to preserve aquatic animal products, using of cooling equipment to lower the core temperature of these products. Subsequently, the decline of the water within the product is frozen, followed by the reduction of the product's temperature to −18 °C or below[9]. Common freezing methods include air freezing and flat freezing[9]. Air freezing is a traditional freezing method where food is exposed to low-temperature air. In the process, the air moves by natural convection or with the help of low-power fans[10]. The temperature decline is achieved by the absorption of heat from the food surface by the surrounding air. In air freezing, the moisture on the food surface gradually evaporates, forming an ice layer, thereby achieving freezing. While utilizing natural or enhanced convection of cold air for food preservation, suffers from a low heat transfer coefficient[11]. Consequently, air freezing processes are often characterized by extended freezing times and high energy consumption[12]. Flat freezing is a common freezing method where food is placed on a flat surface. The mechanism of flat freezing relies on conduction and convection heat transfer to lower the temperature of the food. The cold air exchanges heat with the food surface, resulting in freezing[11].

During the common freezing process, the majority of free water undergoes transformation into ice crystals, effectively inhibiting chemical and enzymatic reactions as well as the growth of microorganisms by restricting the availability of free water. However, the formation of larger ice crystals can result in deterioration of muscle microstructure and alterations in protein characteristics, leading to a reduction in nutritional value and diminished sensory attributes[13]. Jiang et al.[12] observed that grass carp may undergo dehydration and structural changes in muscle tissue during freezing. In addition, frozen aquatic animal products may experience quality degradation during frozen storage, manifesting as discoloration, dehydration, texture hardening, loss of nutritional value, and altered taste. The primary factor contributing to quality deterioration is the low freezing rate. Conventional freezing methods characterized by slow freezing rates, promote the formation of large, irregularly shaped ice crystals within the intercellular space which leads to cellular damage, mechanical injury to muscle tissue, and undesirable chemical reactions such as lipid oxidation and protein denaturation[14]. Cai et al.[15] found that a slower freezing rate resulted in lower hardness of sea bass (*Lateolabrax japonica*) fillets. The second factor contributing to quality deterioration is temperature fluctuations. Fluctuations in temperature may lead to the thawing and refreezing of small ice crystals, causing them to aggregate into larger crystals, a phenomenon known as recrystallization[16]. This process can result in a gradual increase in the size of ice crystals over time during storage. Repeated freeze-thaw cycles lead to irreversible physicochemical changes, including structural damage, degradation of nutritional component and alterations in color[17]. Javadian et al.[18] found that frozen rainbow trout had a significant quality loss resulting from the freezing-thawing process. The third factor contributing to quality deterioration is the presence of microorganisms. Freezing aquatic animal products do not entirely eliminate bacteria and parasites, which growth was temporarily suppressed. However, Javadian et al.[18] found that a residual microbial population capable of surviving during frozen storage might proliferate upon thawing, potentially leading to microbial spoilage of the thawed rainbow trout. Inadequate hygiene practices and handling procedures during freezing and storage may allow these microorganisms to proliferate again, posing potential food safety concerns. Many researchers focused on these issues to develop novel technologies including liquid nitrogen quick-freezing (LNF), high pressure freezing[19], radio-frequency assisted freezing[20], and ultrasound-assisted freezing[21] to control crystallization, promote freezing efficiency, and improve the quality of frozen aquatic animal products.

Compared to traditional freezing methods, LNF technology offers several benefits, including efficient heat transfer, rapid freezing rate, formation of consistent and small ice crystals, preservation of high food quality, and environmental sustainability[22–24]. LNF employs specialized equipment to freeze foods, maintaining a temperature range typically between –50 and –110 °C. The freezing process is deemed completely upon achieving a core temperature of –18 °C within the foods[25]. The close contact between foods and liquid nitrogen during freezing facilitates the occurrence of partial moisture vitrification, as it reduces heat transfer resistance and lowers the temperature of the frozen foods. Additionally, as an inert substance, liquid nitrogen does not undergo chemical reactions with the food, thereby preserving its quality to a greater extent[26]. Some researchers reported that LNF could reduce water mobility and drip loss of catfish and obscure pufferfish during frozen storage[14,27]. LNF could also cause the least mechanical damage to the fresh balsa fish, and the freshness and quality were guaranteed[28]. These outcomes serve as a theoretical foundation for advancing modernized quick-freezing techniques in industrial production[28]. Diao et al.[29] found that LNF preserved the water-holding capacity (WHC) of grass carp muscles, and more smaller, regular intracellular ice crystals were observed, compared to air freezing. LNF treatment demonstrated a positive impact on preserving the freshness and retarding the spoilage process of red drum (*Sciaenops ocellatus*) fillets during frozen storage[30]. Teng et al.[31] indicated that LNF *Perca fluviatilis* fillets were closer to fresh fillets regarding texture. Microorganisms constitute a pivotal factor in the assessment of quality safety, playing a crucial role in ensuring the safety of aquatic animal products[32]. Crayfish (*Procambarus clarkia*) treated with LNF which exhibits a rapid cooling rate, enabling it to effectively eliminate a wide range of microorganisms, including psychrophiles that may remain viable in conventional freezing methods. Moreover, the intracellular substances present in microorganisms serve as a favorable medium for their growth, but the swift freezing process of LNF restricts their release, ultimately resulting in the demise of these microorganisms[26]. Therefore, it is more effective to use LNF to improve the quality of frozen aquatic animal products if technically and economically allowable.

2 Impact of LNF on the qualities of aquatic animal products

LNF has rapid freezing rate with its extremely low temperature, and enables rapid freezing of products, helping in preserving the texture, flavor, and nutritional value of aquatic animal products.

2.1 Effect of LNF on the physicochemical properties of aquatic animal products

2.1.1 Color

Color is one of the most important attributes of aquatic animal products, as it is directly related to consumer acceptance[33–34]. Yang et al.[35] delineated the sensitivity of the brightness value (L^*), a measure of lightness, in fish muscle tissue to varying conditions, establishing it as the most responsive parameter amongst the colorimetric indices evaluated. The study further elucidated that the modulation of freezing temperatures exerted a notable influence on the L^*, thereby affecting the perceived quality of fish muscle. Specifically, the implementation of medium and low liquid nitrogen temperature were found to enhance the L^* of golden pompano muscle, with the –95 °C LNF treatment exhibiting particularly beneficial effects. This finding suggests an optimization of the cryogenic treatment process could yield improvements in the quality retention of the muscle tissue. Additionally, the rapid freezing afforded by such treatments was observed to mitigate the degradation of key muscle constituents, including myoglobin and myofibrillar proteins. Contrarily, the investigation revealed no discernible difference in the redness value (a^*) between golden pompano subjected to freezing and those maintained in a fresh state. This outcome was corroborated by a parallel study examining the impact of varying freezing rates on the a^* of rainbow trout (*Oncorhynchus mykiss*) fillets, which similarly reported an absence of significant alterations. Collectively, these findings underscore the nuanced effects of cryogenic processing on fish muscle quality, highlighting the potential of tailored freezing protocols to optimize sensory attributes[36]. This is possibly caused by myoglobin restoring its natural conformation and color after thawing of the rainbow trout[37]. In general, changes in yellowness value (b^*) could be related to the oxidation of polyunsaturated fatty acids[8]. Fortunately, there was no significant change in the b^* of the LNF-treated rainbow trout, indicating that LNF treatment had little effect on fish fat oxidation[35].

2.1.2 Hardness

Hardness is an important quality parameter of fish, affecting its sensory and functional properties[38]. Hardness is closely related to the WHC, since water plays an important role in shaping muscle structure[39]. Yang et al.[35] discovered that the diminutive ice crystals and reduced internal pressure within golden pompano fish, processed within the suitable low-temperature spectrum, positively contributed to muscle texture preservation. However, the utilization of ultra-low liquid nitrogen temperature (–115 °C) resulted in an adverse impact on hardness. The swift alteration in cell volume due to the exceedingly rapid freezing rate engendered significant internal pressure, culminating in detrimental structural impairment and diminished hardness[35]. Yang et al.[27] found that LNF positively impacted the maintenance of pufferfish (*Takifugu obscurus*) fillets' microstructure and hardness, and LNF has also proven beneficial in maintaining the hardness of frozen Pacific oyster carapaces and adductor muscles[31]. Jiang et al.[12] found that LNF improved hardness of grass carp more effectively compared to air freezing, which could be due to their slight physical disruption of small ice crystals to proteins. Yan et al.[40] also found the hardness of *Litopenaeus vannamei* were better maintained after –95 °C LNF.

2.1.3 Shear force

Shear force is an indicator of muscle tenderness and is measured as the maximum peak force required to shear through aquatic animal products[27,41]. The presence of large irregular-shaped ice crystals can induce deleterious effects on muscle fiber integrity, precipitating a cascade of structural breakdown phenomena. This includes the compromise of physical architecture, attenuation of membrane resilience, and diminishment of shear strength alongside textural properties. Jia et al.[42] found that the LNF might result in a high initial shear force of pufferfish, but gradually decrease as the increase of storage time. Compared to air-blast freezing, ultrasound-assisted freezing, and radio-frequency assisted freezing, LNF has a slower reduction rate of shear force.

2.1.4 Moisture content

Moisture content represents a critical quality attribute in aquatic animal products and can be evaluated through various parameters, including drip/thaw loss, WHC, and total moisture content[43]. During the freezing, a vapor pressure differential between the aquatic animal products and the surrounding environment arises, leading to moisture loss via evaporation and ice sublimation. This phenomenon manifests as drip loss from the products[44]. Drip loss, defined as the reduction in weight or volume occurring before and immediately following freezing, can negatively impact both the textural and sensory attributes of aquatic animal products' muscle[45]. Hernández et al.[46] found that, a comparative analysis of drip loss in chicken halves subjected to different freezing methodologies revealed that the utilization of liquid nitrogen spraying for the freezing process resulted in significantly lower drip loss compared to those frozen via air-blast freezing at a temperature of −29 °C. WHC is a useful parameter for describing the quality in aquatic animal products[47]. It pertains to the capacity of aquatic animal products to retain both inherent and added moisture, influencing the subsequent processing, sensory attributes, and consumer acceptability of frozen products[39]. Yang et al.[35] found that the golden pompano fish treated with −95 °C LNF had the highest WHC among all frozen treatments including −35 °C air-refrigerator freezing, −35 °C LNF, −55 °C LNF, −75 °C LNF, −95 °C LNF, and −115 °C LNF because the formation of small ice crystals through rapid freezing reduced physical cell damage and chemical changes of proteins. Yang et al.[27] found that pufferfish (*Takifugu obscurus*) fillets treated with LNF had a higher WHC than air-refrigerator freezing. However, the ultra-low liquid nitrogen temperature may harm the WHC. This change may have been due to the considerable internal pressures produced by the rapid change in cell volume through the fast freezing rate, resulting in adverse structural damage and decreased WHC. Yan et al.[40] also found −95 °C LNF shrimps (*Litopenaeus vannamei*) were the best at maintaining WHC among all the frozen treatments including −35 °C air freezing, −35 °C LNF, −65 °C LNF, and −125 °C LNF.

2.1.5 Morphological characteristics

The morphology of the aquatic animal products assumes a pivotal role in determining its sensorial properties, and it directly correlates with enhancing consumer satisfaction and preferences[48]. The morphology of frozen aquatic animal products can be partially inferred by examining the size and distribution of crystals within the tissue[49–50]. Jia et al.[42] elucidated that the microstructural characteristics of aquatic animal products subjected to LNF treatment exhibited a proliferation of diminutive and homogeneous pores. This phenomenon is conjectured to arise from the prolific generation of smaller ice crystals facilitated by the rapid freezing rate. Throughout the duration of frozen storage, the microstructural morphology of LNF-treated frozen tissues exhibited marginal alterations. Espinoza Rodezno et al.[50] found that in the case of freshwater prawn (*Macrobrachium rosebergii*), frozen with liquid nitrogen has been shown to cause less damage to the tissue cell structure, characterized by the formation of smaller ice crystals, in comparison to air-blast freezing and refrigerator freezing methods. Moreover, the morphological characteristics of aquatic products encompasses the observation of the inter-bundle spacing within muscle fibers, facilitating a quantitative understanding of their structural characteristics[51–52]. Pan et al.[53] found that in the case of grass shrimp (*Penaeus monodon*), the inter-bundle spacing of muscle fibers was notably diminished in grass shrimps subjected to LNF at temperatures of −80, −100, and −120 °C, in comparison to those frozen via air-blasting at −35 °C. Oliveira et al.[51] also found that the cross-sectional analysis of muscle fiber bundle spacing in tilapia (*Oreochromis* sp.) consistently demonstrated that liquid nitrogen freezing methods preserved the structural integrity of muscle tissue more effectively than those utilizing air-blast freezing.

2.1.6 Sensory evaluation

Sensory evaluation is a scientific method used to evoke, measure, analyse and interpret those responses to the aquatic animal products as perceived through the senses of sight, hearing, touch, smell, and taste[54]. Teng et al.[31] found that the utilization of −80 °C LNF effectively mitigated protein and lipid degradation, thereby preserving the flavor compounds in oysters. Yang et al.[55] found that with the prolongation of storage time, the frozen swimming crab (*Portunus trituberculatus*) by liquid nitrogen spray freezing had relative lower decrease in sensory scores than fresh swimming crab during frozen storage. After 180 d of storage, the swimming crab with LNF had sensory score of 6.95 with good quality. However, LNF's susceptibility to inducing low-temperature fracture and product whitening of grass carp may negatively impact sensory quality[12].

2.2 Effect of LNF on the nutritional properties of aquatic animal products

2.2.1 Protein

Due to the exceedingly rapid freezing rate inherent to LNF, aquatic animal products may be expeditiously cryopreserved to subzero temperatures. This swift freezing modality contributes to the abatement of protein degradation (Figure 1) and denaturation (Figure 2), thereby safeguarding the structural integrity and stability of the proteinaceous framework. Gao et al.[56] and Zhang et al.[57] documented that the cryopreservation process has a discernible impact on protein conformation, engendering elevated surface hydrophobicity while concomitantly diminishing protein solubility. Meanwhile, traditional freezing has a slow freezing rate causing a deterioration in protein quality, primarily because slow freezing resulted in lower enthalpy than rapid freezing[58]. LNF can relieve changes in protein conformation compared to traditional freezing[42]. Gao et al.[56] found that the combination of soluble soybean polysaccharides (SSPS) and LNF is a promising method for freezing bighead carp surimi. LNF was useful in preventing protein denaturation of bighead carp surimi during frozen storage. SSPS-LNF surimi had the highest protein solubility. LNF and SSPS could also mitigate protein structure changes during frozen storage. Sulfhydryl groups in protein structure are the most reactive of all amino acid residues. So another parameter used to assess protein deterioration in aquatic animal muscles is the reduction of total sulfhydryl group content[59]. This phenomenon occurs due to the accelerated denaturation of myosin molecules, wherein the reactive sulfhydryl groups become susceptible to oxidation, leading to the depletion of sulfhydryl groups and an increase in disulfide bond content[60]. Lü et al.[9] indicated that on the 90th day of storage, the total sulfhydryl content of small yellow croaker from LNF was 0.37 mmol/g prot, which was significantly higher than the other five methods including refrigerator direct-freezing, saline solution impregnation freezing, flat freezing, tunnel type continuous freezing, and air-blast freezing, proving that LNF could effectively alleviate the denaturation of muscle fibrous proteins in small yellow croaker meat. The Ca^{2+}-ATPase activity was commonly used to measure the degree of protein denaturation during freezing and frozen storage due to its ATPase activity. Furthermore, the loss of Ca^{2+}-ATPase activity can also be attributed to protein-protein interactions and subsequent protein rearrangements[61]. The changes in total sulfhydryl content and Ca^{2+}-ATPase activity were observed, which can be used for the evaluation of protein oxidation[62]. Zhao et al.[30] indicated LNF could significantly delay the decline of Ca^{2+}-ATPase activity and effectively inhibit protein denaturation of red drum (*Sciaenops ocellatus*). Hu et al.[63] found that fresh hairtail frozen by liquid nitrogen had higher Ca^{2+}-ATPase activity than refrigerator. It was indicated that the LNF could decelerate the denaturation of protein in frozen fish muscles.

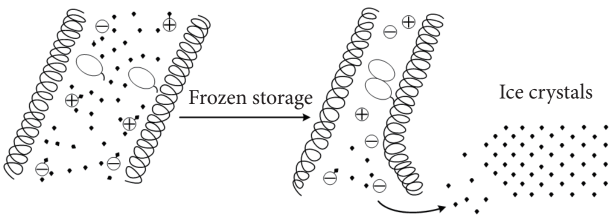

Figure 1 Model of protein degradation of freezing aggregation.

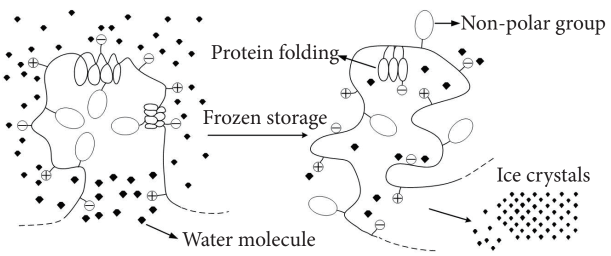

Figure 2 Model of protein denaturation of unfolding.

2.2.2 Lipids

The lipids from aquatic animal products are rich in hemeproteins such as hemoglobin and pro-oxidants such as transition metals, enzymes, and long-chain polyunsaturated fatty acids (PUFAs)[59,64], and PUFAs are highly susceptible to hydrolysis and oxidation. Lipid hydrolysis and oxidation change the appearance and nutritional value, produce off-odors and off-flavors, and shorten shelf-life of aquatic animal products. Lipid hydrolysis and oxidation can be caused by free radicals, ice crystals and enzymes during freezing and frozen storage (Figures 3 and 4)[65]. Assay of acid value, polar compounds contents, fatty acids composition, peroxide value (POV) and thiobarbituric acid reactive substances (TBARS) value is the accepted method of assessing the degree of lipid hydrolysis and oxidation[42,66]. During the 60-day short-term frozen storage, the LNF-treated frozen swimming crabs (*Portunus trituberculatus*) had lower TBARS value than the untreated frozen crabs, indicating that LNF could inhibit the primary lipid oxidation of the swimming crabs in the short term[55]. Mao et al.[67] also found that the TBARS value in large yellow croaker decreased with the decline of the freezing temperature from −60 to −120 °C, implying an inhibition of liquid nitrogen spray freezing on lipid oxidation of large yellow croaker. Yu et al.[68] found that after 20 weeks of frozen storage, compared with freezer freezing and air freezing, the TBARS value of giant freshwater prawn (*Macrobrachium rosenbergii*) frozen by liquid nitrogen was the lowest and had obvious significance, so LNF was an effective measure to inhibit the lipid oxidation of prawn.

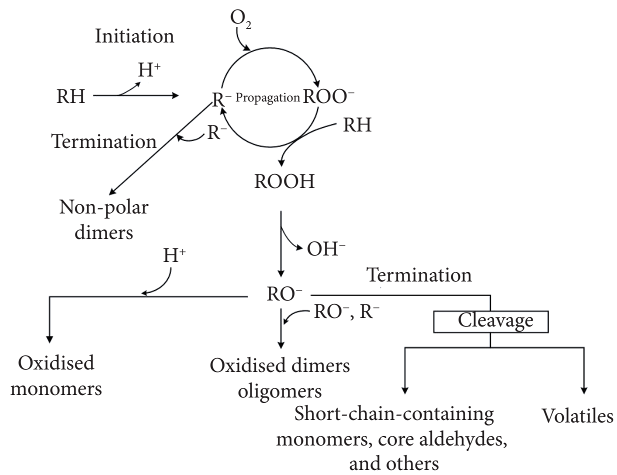

Figure 3 Simplified scheme of lipid oxidation.

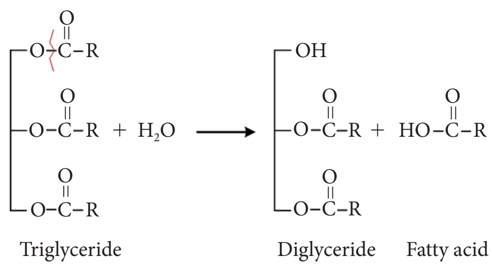

Figure 4 Formation of fatty acids and diacyl glycerols.

In general, LNF has a positive impact on the quality and nutrition of aquatic animal products (Table 2).

3 Mechanism of LNF

LNF has extremely fast freezing rate due to its low heat resistance. Consequently, the ice crystals are small and equally distributed[56]. The application of LNF has been observed to mitigate the nucleation of ice crystallites, thereby diminishing deleterious impacts upon the cytoarchitecture and preserving the integrity of aquatic animal products. This is attributable to the capacity of the LNF methodology to pass through the maximal crystallization zone (Figure 5), resulting in the formation of ice crystals that are diminutive in size, homogenous in distribution, and copious in number[42]. LNF exhibits an exceptionally elevated freezing rate. The heightened freezing rate characteristic of LNF expedites the phase transition of liquid nitrogen to its gaseous state, facilitating the swift removal of substantial heat from the foods. Consequently, this phenomenon accelerates the overall heat transfer process within the foods, leading to efficient preservation and quality retention[69]. Since the heat transfer rate is high, crystals are produced in smaller, more uniform sizes and greater numbers inside and outside the cell. In the freezing process of aquatic animal products, the formation of fine and well-proportioned ice crystals play a crucial role in minimizing mechanical damage to muscle tissue and reducing the loss of muscle juice[70]. Therefore, LNF may alleviate quality deterioration of aquatic animal products.

Table 2 The effect of LNF on the quality of aquatic animal products.

Aquatic animal specie	Effect	Reference
Catfish	Reduce water mobility and drip loss	[14,27]
Fresh balsa fish	Cause the least mechanical damage	[28]
Grass carp	Preserve water-holding capacity (WHC) Improve hardness effectively	[12,29]
Red drum (*Sciaenops ocellatus*)	A positive impact on preserving the freshness and retarding the spoilage process Decelerate the denaturation of protein	[30]
Perca fluviatilis	A positive impact on preserving the freshness regarding texture	[31]
Crayfish (*Procambarus clarkia*)	Enable it to effectively eliminate a wide range of microorganisms	[26]
Golden pompano	Enhance the L^* of golden pompano muscle, yield improvements in the quality retention of the muscle tissue, reduce its thawing loss, cooking loss, L^*, and has a negative impact on structural and hardness	[35]
Pufferfish (*Takifugu obscurus*)	A positive impact on microstructure and hardness, and could result in a high initial shear force and WHC of pufferfish	[27,42]
Pacific oyster carapace and adductor	A positive impact on maintaining the hardness	[31]
Shrimp (*Litopenaeus vannamei*)	A positive impact on maintaining the hardness and WHC	[40]
Freshwater prawn (*Macrobrachium rosebergii*)	Cause less damage to the tissue cell structure	[50]
Grass shrimp (*Penaeus monodon*)	Make the inter-bundle spacing of muscle fibers notably diminished	[53]
Tilapia (*Oreochromis* sp.)	Preserve the structural integrity of muscle tissue effectively	[51]
Oyster	Mitigates protein and lipid degradation effectively	[31]
Carp surimi	A positive impact on preventing protein denaturation and mitigating protein structure changes	[56]
Large yellow croaker	Inhibit lipid oxidation, and make it the lowest thawing loss	[67]
Snakehead (*Channa argus*)	Mitigate the detrimental effects on muscle tissue	[24]
Swimming crab (*Portunus trituberculatus*)	Make thick shells crack	[55]
Giant freshwater prawn (*Macrobrachium rosenbergii*)	Inhibit the lipid oxidation	[68]

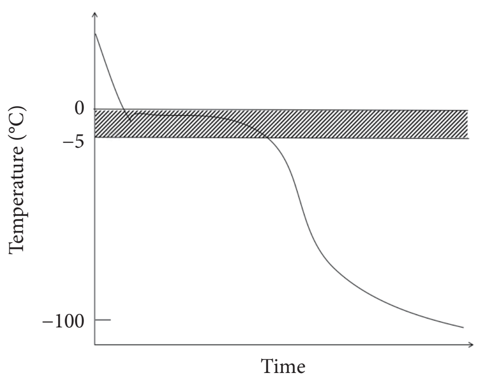

Figure 5 Freezing curve of aquatic animal products.

4 LNF methods in aquatic animal products preservation

At present, there are several LNF methods applied to aquatic animal products. Some of the commonly used ones include liquid nitrogen immersion freezing and cryogenic freezing with liquid nitrogen spray (LNSF).

Immersing aquatic animal products in liquid nitrogen at −196 °C freezes the outer product surface instantaneously[71]. Immersion quick freezing is an ideal for the products that are difficult to individually quick-freeze, since they have tendency to clump or stick to the belt during the freezing process. Immersion quick freezing using liquid nitrogen enables them to be frozen singly, thus keeping their individual form, texture and taste. The meat microstructure of aquatic animal products would have been affected by the freezing rate. The effect of immersion quick freezing is superior to that of traditional air freezing because the ice crystals formed during air freezing process mainly produce inside the muscle fibers, which generates relatively more compression to the muscle fibers[71]. In a comparative study of liquid immersion freezing at −60 °C versus air freezing at −20 °C, the ice crystal size exhibited a 95% reduction, while the mean diameter decreased by 77%. This significant reduction in ice crystal dimensions has the potential to substantially mitigate the detrimental effects of ice crystal formation on snakehead's muscle tissue[24].

LNSF has been regarded as a promising technology owing to the high freezing rate (Figure 6). The large amount of heat absorbed by liquid nitrogen as it evaporates and the low temperature of nitrogen makes LNSF capable to reduce the temperature of aquatic animal products rapidly[67]. Total volatile basic nitrogen (TVB-N) content was employed to assess the freshness of the flesh of fish. Mao et al.[67] found that the change in TVB-N content of LNSF large yellow croakers (*Larimichthys crocea*) varied linearly with the decrease of the freezing temperature and final temperature. The consequence may result from the inactivation of spoilage bacteria and endogenous enzymes involved in protein degradation by rapid freezing. The reduced oxygen concentration during LNSF and less structural destruction of cells might also be the reasons for the inhibition of protein degradation.

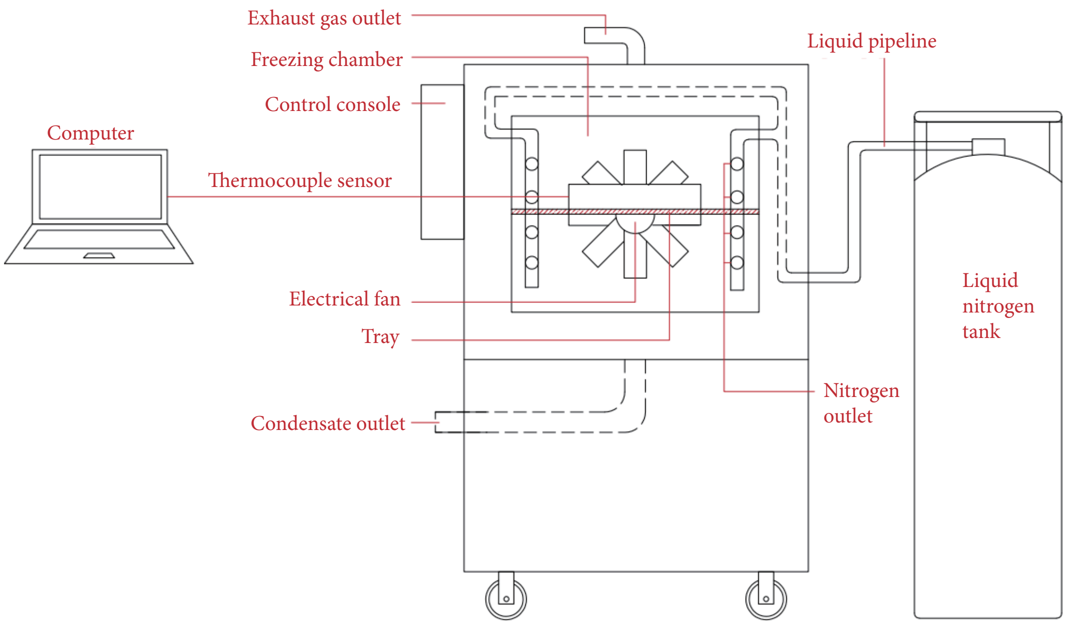

Figure 6 Schematic view of the LNSF system.

5 Limitations and challenges of LNF for aquatic animal products

Freezing methods and freezing conditions can effectively improve the quality of aquatic animal products (Figure 7). Although LNF is an efficient way of freezing which offers manifold benefits, its application in the preservation of aquatic animal products is not devoid of constraints and hurdles. Excessive rapidity in the freezing rate precipitates a notable disjunction in temperature gradients between the food's surface and its core. As the superficial water transitions to ice, this incongruity engenders a surge in expansion pressure, culminating in cellular rupture and structural compromise[30]. Kim et al.[72] indicated that the rapid freezing rate achieved through the use of liquid nitrogen was found to induce macroscopic cracks within the muscle tissue of fish. Consequently, these deleterious effects compromise the sensory attributes and

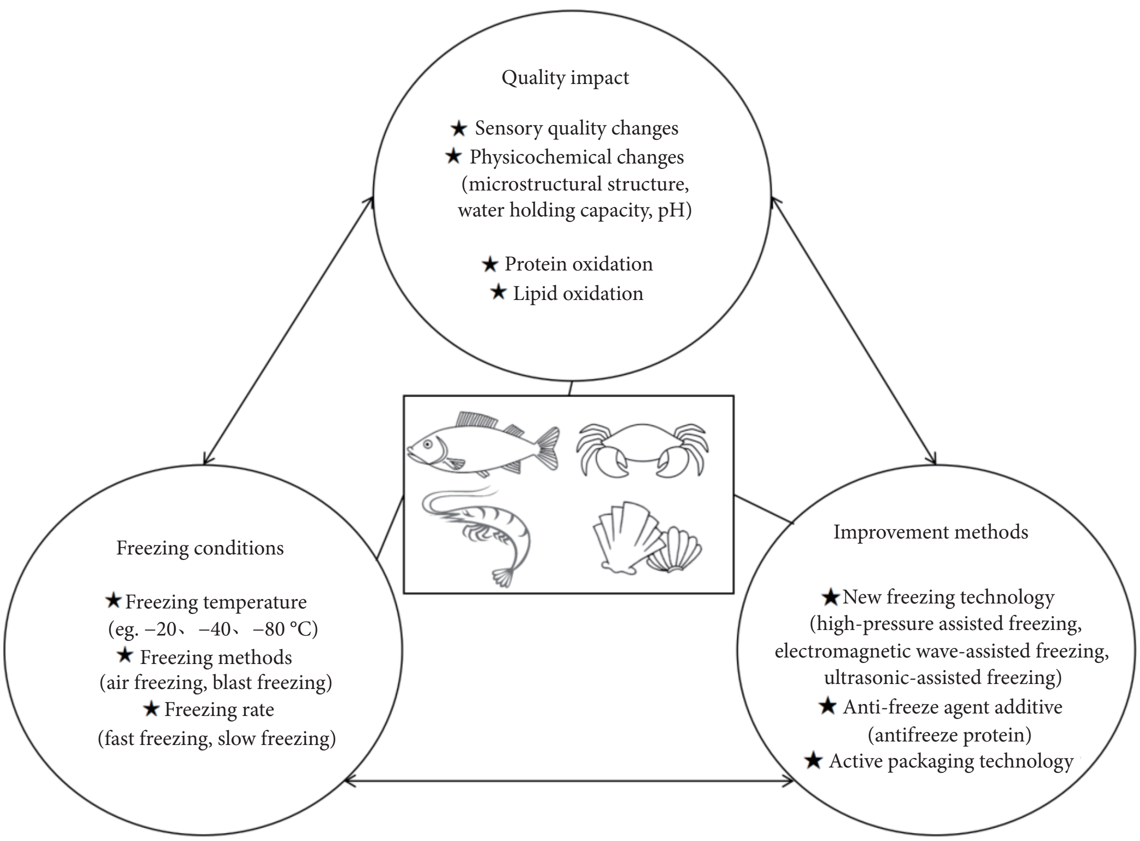

Figure 7 Changes in the quality of frozen aquatic animal products and improvement measures.

overall quality of aquatic animal products[73]. Yang et al.[55] found that swimming crabs (*Portunus trituberculatus*) with thick shells were found to be susceptible to cracking during liquid nitrogen flash freezing and frozen storage, posing risks of economic and quality losses. It is necessary to control the freezing conditions of liquid nitrogen reasonably to avoid the occurrence of freezing damage. Lopkulkiaert et al.[69] have demonstrated the ability of liquid nitrogen to expedite the freezing process. However, it has been observed that the optimal freezing temperature may differ among various food items. For example, −95 °C LNF is the most appropriate temperature for golden pompano which reduced its thawing loss, cooking loss, lightness values[35]. Also, Mao et al.[67] found that lowest thawing loss was obtained at the freezing temperature of −90 °C of large yellow croakers frozen by LNSF. This disparity could be attributed to variances in tissue structure and composition among different foods. Consequently, understanding and considering these distinctions becomes crucial in determining the appropriate freezing conditions for achieving optimal results in terms of preserving the quality and characteristics of specific aquatic animal products[35].

The relatively elevated expense associated with liquid nitrogen poses a potential impediment to its widespread adoption in certain segments of the aquatic animal products industry. Particularly for economically low-priced aquatic products, the financial feasibility of LNF methodologies may be deemed less competitive in comparison to alternative preservation techniques. Kuang et al.[24] reported that freezing 1 kg of food needed 0.8–2 kg liquid nitrogen and the consumption was not in cyclic utilization. Henceforth, LNF emerges as an unsuitable option for the cryopreservation of bulk commodities. Furthermore, prudent consideration must be allocated to the energy consumption entailed by LNF methodologies, particularly within the purview of large-scale manufacturing, where heightened energy expenditures could substantively escalate operational costs[74].

6 Conclusions and prospects

This paper provides a comprehensive review of the application of LNF in aquatic animal products. By comparing with traditional freezing methods, LNF has extremely fast freezing speed which effectively reduces the formation of large ice crystals. Furthermore, the impact of LNF on qualities of aquatic animal products such as color, hardness, shear force, moisture content, muscle morphological characteristics, sensory evaluation, as well as lipid oxidation and protein denaturation were also discussed. Subsequently, various LNF methods applying on aquatic animal products are reviewed. Finally, the limitations and shortcomings and the future research prospects of LNF were introduced. In summary, LNF represents a significant advancement in the preservation of aquatic animal products, offering many benefits in terms of quality. However, there are still many limitations and constraints. With continuous research and innovation, LNF has the potential to become a highly important freezing method in the aquatic animal industry.

Conflict of interest

The author declares no conflict of interests.

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