

Review Article

Quality of Aquatic Products via Cryogenic Freezing

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Abstract

The quality of perishable nutritious aquatic products can be sustained by the technique of cryogenic freezing. In this paper, physicochemical changes that aquatic products experienced in the cryogenic freezing process were reviewed. Due to the rapid freezing rates, cryogenic freezing resulted in the lower drip loss, higher water holding capacity and smaller ice crystals. The technique can obviate the protein denaturation of fish muscle, inhibit the formation of thiobarbituric acid reactive substances and reduce the lipid oxidation. The pH values, firstly decreased and then increased in the storage duration after cryogenic freezing. Texture of cryogenic aquatic products experienced the significant differences in different parameters. Few studies about color and sensory attributes of cryogenic aquatic products were investigated. Besides, quality drawbacks of cryogenic technique were still existed in defective morphology, thawing loss and other enzymatic changes

of food products. Moreover, some methods applied recently to assist cryogenic freezing had been presented.

Keywords: Freezing rate; Water content; Protein denaturation; Lipid oxidation; Morphology; Assisted freezing methods

1. Introduction

Aquatic products are highly perishable and nutritious [1]. They are rich sources of high-quality protein, lipid, minerals, and other nutrients [2]. However, aquatic products are easily spoiled and undergo autolysis, microbial activity, chemical oxidations, and enzymatic reactions after death [3, 4]. Proper technique is essential to prevent the spoilage and extend the shelf life of aquatic products [3]. Freezing is one of the most common preservation techniques for food products [5]. Although freezing can slow down the biochemical and

physicochemical reactions within the tissue of food products, but it cannot stop the undesirable changes in foods [6]. Quality changes of frozen fish products depend on many factors, including fish species, freezing rate, temperature, methods, and frozen storage time [6]. To sustain the quality of food, cryogenic freezing was initially conducted in 1942-45 with the usage of nitrous oxide, and well established in the early 1960's with several commercial liquid nitrogen freezers available [7, 8]. In food industry, the most popular cryogenic substances are gaseous or liquid forms of nitrogen, and liquid or solid forms of carbon dioxide [8-10]. Due to the rapid freezing rate, cryogenic freezing can minimize the moisture loss, reduce the dehydration and drip loss, and preserve the texture of food products [9, 11]. However, the technique cannot conceal its drawbacks in the cracking morphology [12, 13], harsh thawing loss and other enzymatic changes of food products [14] compared to other freezing techniques. The aim of this paper is to review both the positive and negative effects of cryogenic freezing on the quality of aquatic food

products, and address the recent techniques assisted to sustain the food products' quality.

2. Effects of Cryogenic Freezing on Seafood Quality

Physicochemical attributes can reflect the quality of seafood intuitively [15]. The physicochemical changes of food products in the freezing and frozen storage process are strongly related to the freezing rate/temperature used [16, 17], ice crystals formation/distribution [18] and interior characteristics of seafood products [19]. Table 1 presents some publications about the applications of cryogenic freezing in aquatic products and its major physicochemical changes. Considering the similarities of some biochemical and physiological aspects between aquatic and land animals, some cryogenic freezing studies with poultry and cattle have been included in this review to assist understanding the involved technology.

Product	Scientific name	Cryogenic treatment	Reference
Common goldfish pieces (thickness 5 mm)	<i>Carassus auratus</i>	submerged 30 s in Freon 12 bath which was precooled with LN ₂	[20]
Grass shrimp	<i>Penaeus Monodon</i>	Liquid nitrogen freezer at -80, -100, -120°C for 7.12, 5.8, and 3.75 min, respectively	[12]
Tilapia chunks (40 × 100 mm and 9.5 - 14.5 mm)	<i>Oreochromis sp</i>	Liquid nitrogen freezer at -87, -128°C for 4.3 and 2.0 min, respectively	[21]
Whiteleg shrimp	<i>Litopenaeus vannamei</i>	Submerged in liquid nitrogen for 40s	[22]
Tiger shrimp	<i>Penaeus monodon</i>	Cryo-test liquid nitrogen chamber at -70, -80, -90, -100°C for 214, 191, 154, and 116 s, respectively	[23]
Channel catfish fillets (85 - 100 g/ piece)	<i>Ictalurus punctatus</i>	Cryogenic freezer employing liquid CO ₂ at -59.06°C for 19.3 min	[24]
Northern snakehead	<i>Channa argus</i>	Immersed in liquid nitrogen; the core temperature reached -73°C after 20.5 min	[14]
Bighead carp fillets	<i>Aristichthys nobilis</i>	Cryogenic cabinet freezer at -50°C for 10 min,	[25]

(thickness 0.12 mm)		ethanol (95%) as a coolant	
Hairtail blocks (length 6.0 cm)	<i>Trichirus lepturus</i>	Immersed in liquid nitrogen at -196°C for 0.3 min	[26]
Red swamp crayfish	<i>Procambarus clarkii</i>	Immersed in liquid nitrogen for 4h	[27]
Freshwater prawn	<i>Macrobrachium rosebergii</i>	Immersed in Liquid nitrogen container, 1 kg of prawn used 1 L liquid nitrogen	[28]

Table 1: Description of the process of cryogenic freezing in aquatic products.

2.1 Water content

Moisture is an important characteristic in meat quality during freezing and thawing process, which can be calculated as drip/freezing loss, water holding capacity and total moisture content [29]. During the freezing process, the pressure difference between the product and the environment leads to the evaporation of water and ice sublimation, which causes the drip loss of the product [30]. Drip loss, the shrinkage or weight loss of products before freezing and immediately after freezing, can affect the textural and sensory quality of fish muscles [31]. Drip loss of chicken halves frozen by spraying liquid nitrogen (<-100°C) was lower than those of air blast frozen halves operated at -29°C [32]. Weight loss during freezing of two cryogenic methods (liquid nitrogen and carbon dioxide, controlled at -74°C) for beef patties are lower than mechanically frozen patties (at -29°C) [33]. Similarly, the catfish fillets frozen by liquid carbon-dioxide at -59°C had the lower drip loss than those of air-blast freezing at -25°C after six months of storage at -20°C [24].

Water holding capacity (WHC) is a useful tool for describing the quality in muscle foods post-mortem, and a low WHC has been often described as an effect of post-mortem structural changes in the muscle [34]. The water holding capacity exhibited an increased order for hairtail (*Trichirus lepturus*) samples frozen by conventional air freezing at -20°C, refrigerator cryogenic freezing at -80°C and liquid nitrogen

immersion freezing at -196°C (86.8, 87.4, 89.2%, respectively) [26].

In term of moisture content and relative moisture loss, there were no significant differences for air-blast and cryogenic freezing after 6 months of storage at -20°C [24].

2.2 Protein denaturation

Protein denaturation can be manifested mainly by the decrease in solubility or extractability of myofibrillar fraction, particularly the decrease of salt soluble protein extractability. Interestingly, it was observed that cryogenic freezing obviates the denaturation of protein in fish muscle. For instance, cryogenic freezing can be recognized by the higher value of protein extractability compared to other freezing methods in some cases [14, 25]. The content of salt-soluble proteins of northern snakehead (*Channa argus*) frozen by liquid nitrogen and stored at -20°C for 14 days was not significantly different from that of the fresh one [14]. Whilst another freezing treatment with ultra-low temperature freezer -80°C decreased the salt-soluble protein contents of northern snakehead after 14 days of storage at -20°C [14]. Another example occurred on frozen bighead carp (*Aristichthys nobilis*), as the cryogenic immersion freezing reduced the salt extractible protein contents in a smaller degree than those of the air-blast freezing during the frozen storage at -18°C of 180 days [25]. However, salt soluble protein extractability is not a good index for evaluation of the effects of freezing methods in shrimp.

Since there was no significant difference in solubility of muscle protein of grass shrimp (*Penaeus monodon*) frozen by air-blast freezer at -35°C and liquid nitrogen freezer at -80 , -100 and -120°C , and then stored at -20°C for 4 weeks [12]. Similarly, the decrease in salt-soluble protein was only affected by the increased numbers of freeze-thaw cycles of tiger shrimp (*Penaeus monodon*), but the differences of salt-soluble protein values between the cryogenic and air-blast freezing was not discussed [23].

Additional indicator of protein oxidation is the decrease of total sulfhydryl group content in fish muscles [35]. The accelerated denaturation of myosin molecules happened as the reactive sulfhydryl groups are exposed to oxidation, which results in the disappearance of the sulfhydryl group and the increase of disulfide bond content [36]. Moreover, the rearrangement of proteins via protein-protein interactions are also contributed to the loss of Ca^{2+} -ATPase activity [37]. The assessment of protein oxidation in bighead carp (*Aristichthys nobilis*) frozen by cryogenic immersion freezing and air-blast freezing were observed by the changes in total sulfhydryl group content and Ca^{2+} -ATPase activity [25]. The values of these two indices were significantly higher in cryogenic immersion freezing than those of air-blast freezing samples during the frozen storage of 180 days. It was indicated that the cryogenic freezing could decelerate the denaturation of protein in frozen fish muscles. Similarly, red swamp crayfish (*Procambarus clarkii*) immersed in liquid nitrogen for 4h exhibited higher Ca^{2+} -ATPase activity at 1-12 weeks than other freezing treatments with freezer at -80 , -30 and -18°C [27].

2.3 Lipid oxidation

Fish are highly susceptible to oxidation due to the intrinsic factors that fish are rich in polyunsaturated fatty acids, hemoproteins such as hemoglobin, and pro-

oxidants such as transition metals and enzymes [35]. Some external factors influence the lipid oxidation in seafood included pre-slaughter and slaughter stress, heat, pH-changes, pressure, modified-atmosphere packaging, and edible coatings treatments [38]. Moreover, the differences in freezing rate also affect the lipid oxidation of fish muscles through the studies about cryogenic and air-blast freezing during the frozen storage duration [23, 24, 33].

The thiobarbituric acid reactive substances (TBARS) method was also used to determine the secondary lipid oxidation products in these studies [39]. Generally, the TBARS value of fresh meat was significantly lower than frozen meat during the frozen storage (90 days frozen at -20°C) [40]. The TBARS value of cryogenic freezing was lower than air-blast freezing after 6 months storage of catfish fillets [24]. In addition, For both air-blast and cryogenic freezing, the TBA value of frozen tiger shrimp (*Penaeus monodon*) increased during the freeze-thaw cycles indicating an increase in lipid oxidation; however, the cryogenic freezing obtained slightly lower TBA values than those of air-blast freezing [23]. Earlier in the food industry, mechanically frozen beef patties obtained significantly higher TBA value at 90 and 120 days of storage than those of cryogenic frozen patties [33].

2.4 pH

During the frozen storage, fish products subjected to cryogenic freezing firstly experienced a slight decrease of pH (0.2-0.5 units) within 14-30 days [14] or 0-40 days [25] and a gradual increase of pH (0.2-0.6 units) from 60 days and the following storage duration [14, 25]. This phenomenon was observed in cryogenic freezing of northern snakehead (*Channa argus*) [14] and bighead carp (*Aristichthys nobilis*) [25]. Especially, for northern snakehead, the pH value in the first 14 days of frozen storage was not significantly different from that

of the fresh meat, which was conceived that the liquid nitrogen freezing could postpone the onset of rigor mortis [14].

The initial reduction of pH has possibly been associated with the glycogenolysis that occurs after death in fish with the production of lactate [41-43]. The increase of pH after 60 days of frozen storage may due to the decomposition of amino compounds, caused primarily by microbial activity [41, 43]. Some authors have associated the increase of pH and the increase of volatile basic components and solute concentration [25, 42]. In addition, the enzymatic activities cannot be depleted [42, 44] and the protein degradation still takes place [45] in freezing and frozen storage, which attribute to the increase of pH.

2.5 Color

Color is one of the key sensory characteristics for accessing the freshness of fish muscles, with great impact on the consumer's perception and acceptability [46, 47]. For color measurement, the Commission Internationale de l'Eclairage (CIELAB) system is widely used with three-dimensional diagram composed of L^* (lightness, scale from 0 (black) to 100 (white)), a^* (redness, scale from $-a$ (green) to $+a$ (red)), and b^* (yellowness, scale from $-b$ (blue) to $+b$ (yellow)) [35]. Total color difference $\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$ is used to compare the differences in perception capacity.

Up to date, there is little information about the effect of cryogenic freezing on the color analysis of fish muscles. Rodezno, et al. [24] were the authors who published the comparison on color measurements of cryogenic and air-blast freezing of catfish fillets stored at -20°C for 6 months. The color analysis was determined after catfish fillets thawing. There were no significant differences in L^* , a^* , b^* and ΔE^* values among the cryogenic, air-blast

freezing and fresh samples at the first month of storage. At 3-month and 6-month, there was a decrease in the L^* and a^* values and an increase in ΔE^* in both cryogenic and air-blast freezing samples, where L^* value of cryogenic freezing sample was higher than that of air-blast freezing. Meanwhile, there were no significant differences in a^* , b^* and ΔE^* values between these two freezing treatments at 3-month and 6-month. From the results, it is conceived that the most sensitive value is lightness, which decreases throughout the storage duration, can be the remark of color difference of fish fillets in cryogenic and air-blast freezing.

The color differences (after thawing) existed at three and six months of frozen storage of cryogenic fish samples [24] could be the results of variety of factors, as pigments degradation [35], hemo-protein denaturation [47] and ice crystals acceleration [48]. However, during the freezing process the freezing temperature and freezing rate, but not the pigments concentration, would result in the temporary color loss of fish muscles [48, 49]. Nevertheless, it can not be excluded that the long duration of frozen storage would contribute to the degradation of astaxanthin, canthaxanthin, and beta carotene in fish muscles. In addition, cryogenic freezing with smaller ice crystals size and aggregation, and reduced lipid oxidation hopefully may result in the little color difference of frozen fish muscles after a frozen storage duration. In brief, the mechanisms leading to color changes of fish muscles after cryogenic freezing and storing at low temperature should be wholly inquired in the future.

2.6 Texture

Texture can basically influence seafood quality since it can be used as supportive data to physicochemical, microbiological and sensory attributes [41, 50]. Fish muscle texture depends on the intrinsic biological factors that are related to fish species and muscle fiber

density [41]. During the frozen storage, the unfrozen water is still available for chemical reactions and lipid oxidation [51]. A number of substances that cause the off-odors and flavors can form covalent bonds with muscular proteins contributing to the textural changes

[41]. Instrumental texture in cryogenic freezing fish can be measured by shear force and compression test with variety of different testing instruments and parameters (hardness, springiness, chewiness, resilience and elasticity, etc.) (Table 2).

Products	Treatment	Sample	Method	Main effects	Reference
Northern snakehead	Immersed in liquid nitrogen for 20.5 min	1 × 1 × 0.5 cm	determined by a Texture Analyzer; compressed twice perpendicular, speed of 1 mm/ s; deformation rate 60%	Hardness showed no significant changes within 30 days of storage and then decreased gradually with extended storage time. Small effects on springiness and cohesiveness. Chewiness and resilience were affected by freezing methods	[14]
Bighead carp fillets	Cryogenic cabinet freezer at -50°C for 10 min, ethanol (95%) as a coolant	3.0 × 2.0 × 1.0 cm	texture analyzer with a TMS 5 mm steel probe; deformation rate 50%; initial test force 0.01 N; time internal, 5 s.	Hardness and elasticity values decreased dramatically over time.	[25]
Red swamp crayfish	Immersed in liquid nitrogen for 4h	20 × 20 × (10-15) mm	TA-XT2 Texture Analyzer; compression force axially at 50% strain with a P/36R probe; pretest speed 0.5 mm/s	Springiness increased at week 4 and then decreased as storage time increased.	[27]

Table 2: Results of research with cryogenic freezing on the texture of aquatic products.

Hardness obtained in the compression test is one of the primary parameters, with a decrease observed in immersion cryogenic freezing treated fish [14, 25, 27]. The immersion liquid nitrogen resulted in the lower hardness values of red swamp crayfish (*Procambarus*

calrkii) stored at -18°C from 4 weeks and over, compared to -80°C and -30°C freezer at the relevant storage temperature and time [27]. Similarly, the northern snakehead frozen by immersion in liquid nitrogen and stored at -18°C also produced the lower

hardness values at 14-150 days than those of ultra-low temperature freezer at -80°C [14]. From these results, we suggested that immersion cryogenic freezing could negatively affect the texture of fish. In contrast, the bighead carp frozen by a cryogenic cabinet quick freezer with circulation temperature of -50°C obtained the higher hardness values than those of the air-blast freezing at -25°C all over the storage duration of 180 days at -18°C [25].

Other parameters in the compression test investigated the effect of cryogenic freezing on springiness, chewiness, resilience and elasticity [14, 25, 27]. The springiness values of crayfish frozen by immersion liquid nitrogen and stored at -18°C increased at week 4 and decreased as the storage duration increased until week 24 [27]. The same trend happened for the springiness values of northern snakehead frozen by immersion liquid nitrogen and stored at -20°C , as the springiness value increased at 14 days and decreased over the storage duration of 150 days [14]. In the same study about northern snakehead, the authors reported that the immersion cryogenic freezing obtained the lower values of chewiness compared to other freezing treatments with ultra-low temperature freezer at -80°C to the core temperature of fish reached -60 and -18°C [14]. Also in the same study, there were no significant differences in the resilience values of different freezing treatments of northern snakehead [14]. For the elasticity values of bighead carp frozen by cryogenic and air-blast freezing, the higher values of elasticity parameter was reported for cryogenic freezing during the storage duration of 180 days at -18°C [25].

Furthermore, fillet texture can be partly attributed to the acid lysosomal cathepsins in intact fish muscle cells [52]. Cathepsin D is one of the important lysosomal proteases involved in breakdown of fish muscle structure [53]. Its proportion is high in the soluble

fraction in early post mortem; however, it can be decreased by the release of α -actinin in postmortem proteolysis [54]. In grass shrimp (*Penaeus monodon*), Pan and Yeh [12] showed that unfrozen shrimp had a higher value of cathepsin D-like activity than those of frozen shrimp. In addition, frozen shrimp subjected to cryogenic freezing had little damage to muscle cell due to the higher value of cathepsin D-like activity in the intact lysosomes, compared to air-blast freezing [12].

2.7 Morphological characteristics

Morphology in frozen foods plays the key role in sensorial properties and perception of consumers [55]. The size and distribution of crystals in tissue can partially reflect the morphology of frozen food products [20, 28]. At or below the freezing point of fish muscle, the ice nucleation grows in the extracellular spaces and enlarge the extracellular ice crystals upon freezing and frozen storage [56]. The freezing temperature [16] and freezing rate [57] can affect the location, shape, size and quantity of ice crystals formed during the freezing and frozen storage. Particularly, quick freezing rate of liquid nitrogen resulted in large amount of small ice crystals in goldfish skeletal muscle, compared to slow freezing rate of a refrigerator, which produced an irregular distortion of tissue ultrastructural components [20]. In addition, freezing by liquid nitrogen could result in less damage to tissue cell structure with smaller ice crystals compared to air-blast freezing and refrigerator freezing in freshwater prawn (*Macrobrachium rosebergii*) [28].

Furthermore, morphological analysis in aquatic products can also be observed by the spacing between muscle fiber bundles [12, 21, 58]. For grass shrimp (*Penaeus monodon*), the spacing between muscle fiber bundles was smaller (6.0 ± 0.6 to $8.8 \pm 1.1 \mu\text{m}$) in liquid nitrogen freezing samples at -80 , -100 and -120°C than in air-blast freezing samples at -35°C ($21.3 \pm 5.7 \mu\text{m}$) [12]. After 4 weeks of frozen storage at -20°C , the fiber

spacing in air-blast freezing samples increased to $64.8 \pm 14.3 \mu\text{m}$, while those of liquid nitrogen freezing samples increased to the range between $13.6 \pm 1.5 - 19.0 \pm 3.1 \mu\text{m}$ [12]. The cross-section spacing between muscle fiber bundles of tilapia (*Oreochromis sp*) also proved that liquid nitrogen freezing maintains better integrity of muscle structure than air-blast freezing [21].

In an attempt to combine the operative effects of cryogenic freezing and vacuum packaging, Qian, et al. [25] studied the morphology of vacuum-packaged bighead carp (*Aristichthys nobilis*) with immersion cryogenic freezing and air-blast freezing. The results showed that cryogenic freezing samples had no significant deterioration at 2 months of frozen storage at -18°C , whereas the air-blast freezing samples showed twisty muscle fiber structure and gradual damage as the frozen storage time increased. Scanning electron microscopy was used to study the ice crystals formation and muscle fiber microstructure of poly-ethylene packaged hairtail (*Trichirus lepturus*) frozen by three different freezing treatments [33]. The muscle fibers of liquid nitrogen immersion freezing samples were tightly attached and few detachments were observed; while, the refrigerator cryogenic freezing samples demonstrated small loss of integrity between muscle fiber; and the conventional air freezing samples showed the muscle fiber deformation and myofibrillar breakages.

2.8 Sensory attributes

Few studies has been investigated on sensory attributes of seafood frozen by cryogenic freezing. On the contrary, sensory evaluations towards other cryogenic frozen food products, such as poultry and cattle, had been conducted. The early study about cooked chicken thighs frozen by liquid nitrogen spray or sharp freezing reported no significant difference in sensory scores [57]. Similarly, taste panel test with cooked chicken halves frozen with liquid nitrogen spray system was not

significantly lower than the air-blast frozen halves [29]. Those results could be attributed in the part to the lower scores in sensory panels of tenderness and juiciness of liquid nitrogen frozen chicken halves in comparison to the unfrozen halves samples [29]. In addition, Sebranek, Sang, Rust, Topel and Kraft [25] evaluated the consumer panel score for flavor, juiciness and overall desirability for ground beef patties frozen by liquid nitrogen or liquid carbon dioxide in a cryogenic tunnel at -74°C or mechanical freezer at -29°C for 120 days. The results showed that there were no significant differences in flavor, juiciness and overall desirability score for two cryogenic freezing treatments. The mechanical treatment, on the other hand, was scored significantly lower at all evaluation time. Future studies on sensory attributes of cryogenic fish products are therefore recommended.

2.9 Quality drawbacks in cryogenic freezing technique

Although cryogenic freezing is considered as one effective freezing treatment, it still has some major drawbacks to the morphology, thawing loss and other enzymatic changes of food products. Firstly, the rapid freezing rate of liquid nitrogen induced macroscopic cracks in fish muscle [12, 13]. In addition, the immersion cryogenic freezing produced no superiority in justifying the microstructure of northern snakehead (*Channa argus*) fillets than the ultra-low temperature freezing at -80°C to the core temperature of -18°C [14]. Larger extracellular spacing and disorganized myofibrils were observed in immersion cryogenic freezing since 30 days of frozen storage, while the ultra-low temperature freezing samples showed the disorganization at 90 days of storage at -20°C [14]. Secondly, changes in thawing loss showed the weak characteristics of cryogenic freezing of northern snakehead (*Channa argus*) fillets [14]. Fish samples were frozen in 3 groups by ultra-low temperature

freezer (-80°C) to the core temperature of -60°C (T1) or -18°C (T2), and immersion in liquid nitrogen (T3). Upon freezing, fish were stored at -20°C for five months. Unfortunately, the results showed that thawing loss of cryogenic freezing group (T3) obtained the higher values than T1 and T2 from 30 days of storage as well as the following storage days [14].

Last but not least, the shortcomings of cryogenic freezing had been recognized by the increase of lysosomal enzymatic activities in fillets tissue [14]. As widely known, enzymatic activities in frozen and thawed products can be indexed by the α -glucoside and β -N-acetyl-glucosaminidase of fish muscle [22, 23]. Significantly higher levels of α -glucoside and β -N-acetyl-glucosaminidase activities were found in fillets tissue of frozen northern snakehead by immersion liquid nitrogen freezer than those of ultra-low temperature freezer after 60 days of storage [14]. Taken together, these findings support further research to account for quality attributes of fish products frozen by cryogenic freezing technique.

3. Methods Assisted Cryogenic Freezing

Some methods assisted cryogenic freezing have been conducted to improve the quality attributes of seafood products. Some of the methods are included edible films and coatings, or the combination of cryogenic with other assisted freezing methods.

Edible films and coatings are widely used as the addition bioactive compounds and additives that contribute to preserve the quality, safety and sensory properties of foods [60]. Phosphate and sodium bicarbonate have been used on meat, poultry, fish, and seafood products to promote water-holding capacity, reduce cooking loss and improve color and organoleptic properties of food [61-63]. It has been demonstrated that the effects of cryogenic freezing on yield and water

retention of white shrimps (*Panaeus vannamei*) can be improved [64]. Indeed, the sodium bicarbonate containing traces of citric acid at 4 g/100 ml with sodium chloride at 3 g/100 ml had increased the yield by 6.83, 7.7, and 10.28 g/100 g fresh shrimp for uncooked products as frozen by cryogenic freezing at -35, -40, and -60°C. In addition, Solval, et al. [65] examined chitosan nanoparticles as glazing material for cryogenically frozen shrimp (*Litopenaeus setiferus*). The results showed that solutions with chitosan (CH) and sodium tripolyphosphate (TPP) (0.25 g/100 mL CH + 0.083 g/100 mL TPP; or 0.5 g/100 mL CH + 0.167 g/100 mL TPP) could reduce the lipid oxidation, total aerobic counts, yeast and molds without affecting the color and texture attributes during 30 days of storage at -20°C. Similarly, cryogenically frozen shrimp (*Litopenaeus setiferus*) vacuum tumbled and treated with chitosan-sodium tripolyphosphate (CH-TPP) nanoparticle solutions showed the significantly improved in its quality characteristics [66]. CH-TPP vacuum tumbled shrimp reduced the aerobic plate counts and lipid oxidation, retained the color, texture, and moisture contents during 120 days of storage at -20°C. Overall, there seems to be some evidence to indicate that the quality of cryogenically frozen food can be improved by the addition of edible films and coatings.

Recent attention has focused on the combination of cryogenic and assisted freezing methods with respect to mass loss, quality attributes and thermal conductivity of foods [11, 67]. A key study investigated in radiofrequency assisted freezing is that of Anese, et al. [67], in which a pilot-scale radiofrequency equipment was modified to a cryogenic fluid flowed chamber to freeze pork meat. The results showed that low voltage pulses of 2 kV radiofrequency cryogenic frozen meat could reduce the thawing loss and ice crystal size and cell disruption of pork meat. The work also viewed

cryogenic fluid (air) instead of the expensive liquid nitrogen. In addition, a mathematical model was performed to determine the best combination of cryogenic freezing and conventional freezing to reduce the operating cost [11]. There were some conclusions drawn from that study: (1) nitrogen gas at very low temperature can reduce the freezing time and mass loss of food products, (2) the properties of food products depends on its thermophysical attributes and its geometry/size, (3) there is a linear relationship between the cryogenic freezing time and the energy consumption. From those results, the authors aimed to figure out the best configuration to reduce costs inherent of liquid nitrogen.

4. Conclusions

Although cryogenic freezing is a feasible commercial technology to preserve the properties of fresh aquatic products, the technique is defective in morphology, thawing loss and other enzymatic changes of food products. However, future investigations in understanding the assisted methods, combined with the use of mathematical models could be helpful to achieve better quality attributes for the cryogenic freezing products.

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Conflicts of Interest

The authors declare no conflicts of interest.

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