CRYOGENIC FISH FREEZING: SCIENCE, TECHNOLOGY & ECONOMICS

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Abstract Application of cryogenic liquids such as liquid nitrogen has tremendous potential in retaining the quality of the fish as fresh as the original one or near to it through ultra fast cryogenic freezing. While freezing the fish, it is the rate of freezing which dictates the quality of the fish that would be obtained after thawing fish. The smaller the size of the ice crystals during freezing the lesser is the cellular deterioration resulting to minimum changes in fish's texture and appearance and negligible drip loss upon thawing. Cryogenic freezing is capable of creating this environment along with retaining flavour, colour and nutritive value of fish, reducing oxidative, chemical, and microbial changes of fish. Several aspects of liquid nitrogen freezing vis-à-vis quality of the frozen fish have been reviewed in this paper. There are several ways of freezing fish with liquid nitrogen, viz., immersion freezing, spray freezing and high velocity gas freezing. Though immersion freezing has not gained popularity owing to its uncontrolled cooling rate, efficient design in terms of retention of quality of fish using liquid nitrogen can bring it in the fray. Liquid nitrogen spray freezing has gained popularity through out the world for last several decades. Gaseous nitrogen at a very low temperature obtained from liquid nitrogen can be circulated at a very high rate in a freezing chamber. However, individual quick freezing (IQF) through spray freezing in tunnels with liquid nitrogen have gained commercial acceptance among food processors. The present study aims at narrating the factors responsible in designing the liquid nitrogen freezer along with appropriate examples. In this paper a cost comparison has been made between the liquid nitrogen freezing and conventional freezing systems. Though theoretically, 1.2 kg of liquid nitrogen per kg of fish frozen dictates the operating cost of liquid nitrogen, the efficiency of the design of the freezer ultimately governs the operating cost of liquid nitrogen freezing system. Besides, the availability and price structure of liquid nitrogen supply also maneuvers the operating cost of the liquid nitrogen freezing system. The fixed cost of the freezer is has been found to be much cheaper compared to any mechanical freezing system. It can be concluded that a proper design of the freezer along with uninterrupted supply of liquid nitrogen at a reasonable price has a tremendous potential to serve the fish freezing industry when quality of the fish becomes the dictum for freezing fish.

INTRODUCTION

There are several ways of freezing food products. Several freezing techniques are being commercially used all over the world. This paper has an objective to critically analyze the different aspects of freezing food products with liquid nitrogen (LN₂). The word IQF, i.e., Individually Quick Freezing is self-explanatory. IQF has several advantages over bulk, packed or unpacked freezing of foodstuffs. Though the word IQF relates to either conventional or cryogenic freezing, this paper aims at dealing IQF with liquid nitrogen.

FREEZING METHODS

The freezing methods may be divided into different categories based on the achieved rate of freezing. The rate of freezing may be defined as the velocity of ice

front in cm/hr moving from the surface to the core of the food product. If the rate of freezing is between 0.05 to 5 cm/hr, the freezing method is known as slow freezing. If the rate is between 5 to 10 cm/ hr. the method is called rapid freezing or quick-freezing and if the rate is 100 cm/hr or more, the method is called ultra rapid freezing. Examples of slow freezing are: food products frozen in pallets, cabinets and shelf in cold storage rooms; bulk, packed or unpacked food products frozen in trays & trolleys through cold air blast; thin flat packages of food products frozen through contact of two refrigerated plates etc. Examples of rapid or quick freezing are: small solid foods of fairly uniform size & shape frozen by fluidized freezer; irregular small products frozen in agitated, sprayed and flowing brines like CaCl₂ & NaCl solutions and propylene glycol in tanks through immersions. Freezing with liquefied gases like liquid nitrogen, liquid carbon di-oxide, and food grade refrigerant 12 constitute examples of ultra

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fast or rapid freezing. Freezing rates of 0.54 cm/h, 1.08 cm/h, and 1.8 cm/h can be obtained with forced convection of air at -30 °C, at -50 °C, and forced convection of liquid nitrogen vapours at -80 °C respectively. The effectiveness of these methods of freezing have been studied by several researchers. The physical and chemical changes occurring in the food product during freezing and subsequent storage are indices of the performance of the freezing methods. The physical property such as weight losses of the food product, which is expressed as a percentage of the initial unfrozen food product's weight, and chemical properties such as colour, texture, odour, flavour, tenderness etc. are of importance. Researchers have observed that the faster the method of freezing better is the retention of quality. Hence, it is desirable that depending on the food product, its size, shape, the method of freezing should be selected.

LIQUID NITROGEN AS A REFRIGERANT

Some of the salient properties of liquid nitrogen has been summarized below:

- 1. It is colourless, odourless, light (sp. gr. = 0.8) and very mobile liquid.
- 2. It is chemically inert, sterile, and does not impart any taste, colour and flavour.
- 3. It is extremely less soluble in all liquids.
- 4. One volume of it produces about 700 volume of gaseous nitrogen.

The above features of liquid nitrogen show that liquid nitrogen has high potentiality to serve as a refrigerant for food products.

SALIENT FEATURES OF THE ADVANTAGES OF INDUSTRIAL INTEREST

By analyzing the advantages and with the help of frozen shrimp export data (MPEDA, 1992) it can be revealed that

- A 10% saving in dehydration loss amounts to about Rs. 10,000 lakhs or more equivalent foreign exchange earning annually from export of shrimp only.
- (2) A 10% saving in freezing time amounts to about 7600 tonnes of more prawn freezing with the same capacity of LN_2 freezer over the year.
- (3) A better retention of quality in IQF bags about Rs. 501/- per kg more than that in

conventionally frozen materials as per the international trade dealings.

- (4) The simplicity of the equipment removes involvement of more number of trained personnel. This may encourage small entrepreneurs to go for IQF with LN₂.
- (5) The capital investment being low, small and medium size entrepreneurs may get funding from banks easily.

The disadvantages associated with LN₂ freezer are:

- Inefficient cooling process arising out of lack of design concepts which causes more consumption of liquid nitrogen than necessary resulting in high operational cost.
- High temperature differential may cause blisters on some of the product owing to the poor conductivity of the food product. The optimization of the cooldown process of the freezer as well as the product may eliminate this problem.

These disadvantages can be eliminated or reduced to a great extent with proper considerations in design.

Quick Frozen Foods

A group of experts on quick frozen foods described it as the product subjected to a freezing process in appropriate equipment and complying with certain conditions during the freezing process, storage, transport and distribution. In this definition temperature plays a major role.

There is general acceptance of the regulation that the temperature of a frozen food at the end of the freezing process and during storage must be -18 °C or below. In practice storage temperatures are even much lower for many products, for technologic and economical reasons and because of these lower temperatures, there will be more temperature reserve in the handling, transport and distribution stage.

Liquid Nitrogen Food Freezers

There are three types of liquid nitrogen freezers available other than liquid nitrogen <u>immersion freezers</u>, viz.;

1. Total evaporation spray freezer or tunnel freezer

- 2. Cascade freezer with liquid recirculation.
- 3. High velocity gas freezer using liquid nitrogen.

Among these three LN_2 freezers, tunnel freezers have gained commercial application widely in many food industries.

In the first case liquid nitrogen is sprayed directly onto the food and evaporates completely and the resultant cold gas is recirculated to effect further cooling. The second system is similar to the first one having a difference in the fact that an excess of liquid nitrogen is sprayed over the food and is recirculated. In the third method liquid nitrogen does not come directly in contact with the food material, but is used to cool down one or more chambers in which the temperature is thermostatically controlled.

LIQUID NITROGEN TUNNEL FREEZERS

Fig. 1 shows a typical liquid nitrogen tunnel freezer. The freezer of this type is divided into three zones, viz.; precooling or chilling zone, freezing or spraying zone, and equilibration zone. The food to be frozen is bedded on a variable speed conveyor belt, which traverses the length of an insulated open-ended tunnel. The belt is made of stainless steel. The belt is loaded upto 70% of its capacity. Speed of the belt depends on the product thickness, desired temperature and throughput. The major portion of the tunnel consists of a precooling or chilling zone. In this zone, cold gaseous nitrogen, vaporized by contact of the food at the far end of the tunnel, is made to pass countercurrently with the food. This zone reduces possible thermal stress, if any. Approximately about one half of the total load is met by the nitrogen gas in the precooling zone. In freezing zone, the vaporization of liquid nitrogen is done by spraying LN₂ directly onto the food materials. The surface temperature of the food approaches the liquid nitrogen temperature, i.e., -196 °C. The food then passes into an equilibration zone in which the outer surface of the food material equilibrates thermally against the warmer interior, permitting the food to exit the freezer at the desired temperature. In equilibration zone, about 1 percent of the vapour obtained from the freezing zone is circulated to prevent infiltration of ambient air into the exit of the tunnel. Otherwise, moist air would cause a serious internal frost buildup. The food product is in the precooling zone for about 5/7th and in the freezing zone for about 1/7th of the total time. With the increase of the thickness of the product for a given initial and final temperature, the length of the precooling zone should decrease, increasing the length of the freezing zone. This indicates that for an efficient LN₂ freezing tunnel there should be some provision for adjusting or selecting the length of the precooling and freezing zones.

IMMERSION FREEZERS

The freezing of products such as fish, by simply immersing them in liquid nitrogen has been widely used for many years. Equipment such as "CRYODIP" manufactured by Air Products PLC has found wide acceptance in the freezing of sea foods and fruits and has replaced the CFC immersion process in Europe.

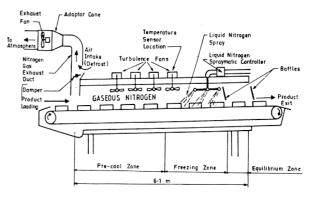


Fig. 1 Tunnel Operating Details (1.0.L., Calcutta)

Fig. 2 shows a schematic liquid nitrogen immersion freezer. It is essentially an efficient insulated box.

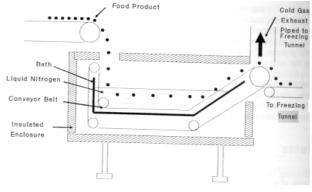


Fig. 2 Schematic view of LN₂ immersion freezer

Food products are conveyed through a bath of liquid nitrogen at -196 °C, maintained at a constant level. A conveyer lifts the individually crust frozen products from the liquid nitrogen. Irregular and complex shapes of food products can be dealt with as the liquid nitrogen accesses all the surfaces of the product. Control of residence time is important to prevent over-freezing and, with some food products, cracking from thermal shock. (Bald, 1991).

Goswami et. al. (2001) have shown the experimental time temperature relationships of shrimp while dipping in a bath of liquid nitrogen and reported the retention of its quality in terms of chemical and biochemical properties of the frozen shrimp.

ENGINEERING CONSIDERATIONS FOR THE DESIGN OF TUNNEL FREEZER

Main engineering considerations, which are required in the design and development of tunnel freezer, are:

* The exposure time of the food product in the gaseous and LN_2 zone should be accurately proportioned such that optimum utilization of the total available refrigeration occurs. Power requirement to attain maximum heat transfer between the liquid and gaseous nitrogen and the food product should be minimum.

* Cooldown losses should be minimum by keeping machine size and structural masses minimum.

* Appropriate insulation should be used such that losses to the ambient are minimum. Structural components should be arranged for quick disassembly and ease of cleaning.

HEAT TRANSFER IN LN2 TUNNEL

For an efficient LN₂ freezing tunnel it is essential that as much heat as possible should be removed from the food material by the cold gaseous nitrogen. In order to obtain high freezing rate it is necessary that the LN₂ evaporates on the food material to be frozen, because a very high heat transfer coefficient will be obtained when heat transfer takes place from the surface to liquid boiling on the same surface. For the best utilization of the cold being at disposal in the nitrogen, it is necessary that LN₂ evaporates on the food to be frozen and the cold nitrogen gas be heated up as much as possible at the expense of the cooling of the food. The attainable heat transfer coefficients between food and gas, or rather between food and gasified liquid determine the ratio of the length of the freezing zone to that of the chilling zone.

Heat transfer coefficients in the gas cooling zones are very much dependent upon the gas velocity, i.e., the energy input into the system in relation to the capacity of the fans. The gaseous heat transfer coefficient can be calculated as:

 $h = 0.176(2.05 + (0.3048v)^{0.75})$ where, h = film heat transfer coefficient, W/m² K v = velocity, m/sec

Generally, gaseous heat transfer coefficient is of the order of 40 - 60 W/m^{2 °}C. For direct LN₂ spray heat transfer coefficient is about 100 - 150 W/m^{2 °}C (Bald, 1991).

The low heat transfer coefficient in the gaseous zone can be somewhat compensated by the high temperature differential available from the nitrogen gas. However, Liquid nitrogen spray system has the highest heat transfer coefficient amongst the available freezing media.

It is not quite so easy to determine the exact heat transfer coefficient between gas and food surface. However, relating to a medium temperature differential for the whole tunnel, there is a medium heat transfer coefficient of about 58 W/m² °C, whereby in the precooling zone heat transfer coefficient varies between 17 to 23 W/m² °C and in the spraying zone heat transfer coefficient is about 174 W/m² °C. Nevertheless, heat transfer is considerably higher directly below the spray nozzle than between the two nozzles. The ratio between the precooling zone and the freezing zone can be approximated to 7: 1.

In general heat transfer coefficient available in LN_2 freezing is very high compared to that available in conventional freezing systems.

FREEZING TIME

The time required for freezing with liquid nitrogen depends upon several thermophysical and geometrical factors of the food product, initial and final temperatures of the product, heat transfer coefficients between the cooling medium and the surface of the food product etc. The time required for freezing of food product with LN_2 can be calculated based on modification of PLank's basic formula for calculating freezing time as:

$$t_{f} = \left[1 + \frac{5C_{1}(T_{1} - T_{F})}{8L_{F}}\right] \frac{\rho_{s} q d}{T_{F} - T_{g}} \left(\frac{1}{h_{c}} + \frac{B d}{k}\right)$$

where,

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q = heat transferred from food per unit mass = $C_1 (T_1 - T_F) + L_f + C_2 (T_F - T_2)$

- C₁= specific heat of food product above freezing temperature
- C₂= specific heat of food product below freezing temperature
- $L_f =$ latent heat of fusion of food product
- T_l= initial temperature of food product
- T_2 = final temperature of food product
- T_{F} = freezing temperature of food product
- T_g= refrigerant temperature
- $\rho_s =$ density of ice
- d = product half thickness (or radius for cylindrical or spherical products)
- h_c = covectional heat transfer coefficient k= thermal conductivity of the food material
- B= constants that depends on the geometry of the food product.

Table 1 shows a comparison of freezing time vis-a-vis weight loss of four different food products using four different freezing equipment. Depending on food product a reduction of 1/3rd to 1/10th in freezing time and 1/2 to 1/6th in weight loss have been observed in liquid nitrogen spraying compared to conventional freezing methods. There are many other models and charts by which freezing time can be predicted. Some of these are: Neumann model, Tao's chart, Cleland and Earle model etc. Goswami et al (1985) have showed that for freezing a 3 cm cube of shrimp, the theoretical freezing time using modified Plank's equation in the case of LN_2 freezing came to be 1/10th of that in the case of air blast freezing. The lowering of temperature from a certain limit does not lead to any essential reduction in the freezing time, meaning that the freezing process at -140 $^{\rm O}{\rm C}$ and at -180 $^{\rm O}{\rm C}$ can be carried out at practically the same rate. This means that if the tunnel is properly designed, the consumption of liquid nitrogen can be reduced to some extent.

Quality of food product frozen with ln₂

One very important factor in the consumer's selection of a frozen food item is the quality of the product. The quality of the product is directly related to the amount of cell damage incurred in the freezing process. Out of the two theories in vogue for cellular break down, one proposes that the concentration of acids in the cellular solution increases as the ice crystals form within the cell. The resulting higher acid concentration either damages or decomposes the cell walls. The other theory proposes that the cellular walls are ruptured by the penetration of long, thin needles of ice. Upon thawing of the food products, the contents of the cells are lost owing to the rupture of the cellular walls. The quality of the food product in terms of flavour, aroma, texture, nutritive value, and appearance are directly related to the amount of cell damage incurred in the The smaller the freezing time, freezing process. smaller is the crystal & LN₂ freezing produces a high freezing rate thereby produces very small ice crystals causing negligible damage to the cells.

The extent of dehydration of a food product caused during freezing can be attributed to two principal factors, viz., (1) differences in vapour pressure between the food product and the freezing medium, & (2) the length of time that the food product is subjected to the freezing medium. The differential vapour pressure between the food product, fish in particular, and the freezing medium is such that dehydration loss is less than 0.01%.

It has been found that for the case of fresh lean and fatty fish LN_2 freezing system extended the storage life considerably compared to conventional method of freezing.

CURRENT STATUS OF CRYOGENIC FREEZING SYSTEMS

The introduction of quick freezing methods was in the late 1930's and 1940's. The first liquid nitrogen tunnel freezer came into existence in as early as 1950. At present, in U.K. there are over 200 cryogenic freezers, mainly using LN₂. In U.S.A. several hundreds of cryogenic food freezers are in vogue of which LN₂ freezers dominate the cryogenic freezing systems. In Eurpoe, Australia, Canada, Japan, China, LN₂ freezing has gained formidable popularity among the food processors and the consumers. It has been reported that in India, there are about 80 IQF system available presently. Surprisingly, out of these 80 odd IQF system, there is only one LN₂ freezing system working in India. When rest of the world is using liquid nitrogen freezers commercially in large numbers and obtaining one of the best quality frozen foods out of it, in India, use of liquid nitrogen freezers has not gained its popularity till now. The reason may be the high operating cost of LN₂. For high valued products the high operating cost is offset by the saving in

dehydration losses and by other advantages. It is now high time that LN_2 freezing techniques should be explored vigorously in developing countries like India, Bangladesh, to capitalize the advantages available out of it.

Pioneer organizations of $LN_{\rm 2}$ freezer manufacturers in all over the world

There are several manufacturers of LN_2 freezers all over the world. New and New manufacturers are coming up day by day. Selling protocol of these freezers are different for different manufacturers. Some of the leading manufacturers of LN_2 freezers are: Air Products and Chemicals, Inc., USA; British Oxygen Limited (B.O.C.); Integral Process Systems, Inc. USA; American Cryo- Chem. Division, USA; AIRCO Cryogenics, USA; National Rnterprise FEROX in Decin, CSSR, Czechoslovakia etc.

Consumption of LN₂

Consumption of liquid nitrogen depends on several factors such as moisture content, inlet and outlet temperatures, thermophysical properties of the food product; freezing equipment, belt loading ratio, residence (or freezing) time, cool down losses, exhaust gas temperature, production rate, length of production etc. Table 2 indicates representative consumption ratios of LN_2 consumption. Depending on the food product, theoretical consumption of liquid nitrogen varies in the ratio of LN_2 to food product between 0.5 to 1.3. Factors causing high cryogen consumption due to faulty tunnels are: low belt coverage, drawing of too much air into the tunnel, blocked spray header nozzles, loss of insulation due to water penetration etc.

COST OF FREEZING WITH LN₂

The operating cost of freezing tunnel is generally high. This primarily depends on the cost of liquid nitrogen. It should be kept in mind that the high operating cost of liquid nitrogen freezing can easily be compensated by the saving in dehydration loss and improved quality of the frozen food. When in the international market of frozen marine products, the position of developing countries like India, Bangladesh is not satisfactory, medium end big entrepreneurs of frozen foods should come forward to explore the freezing technique with liquid nitrogen. It is also true that unless there is a uniform pricing and availability of LN_2 in all over the country, the implementation of LN_2 freezing systems in countries like India, Bangladesh is difficult. Only some odd individual entrepreneurs may come forward to utilize LN₂ freezing systems.

Since there is no available data on the cost of LN_2 freezing in our currency, it is not possible to analyze cost in our currency. However, a number of researchers have analyzed LN_2 system of freezing. Owing to cost factor, almost all the food processors in our country being inclined presently in conventional

freezing systems, a comparative cost has been shown in Table 3. The values have been converted with a multiplication factor of 70 for Pound to Rupee conversion and of .4536 for lb to kg conversion. It is clear that apart from the operating cost of LN_2 , the LN_2 freezing system is much cheaper compared to the conventional freezing systems.

CONCLUSION

 LN_2 freezing systems have definite advantages in its use. Of course every system has its own merits and demerits. One has to choose system depending on one's requirement. In general, considering the high cost of liquid nitrogen in our country, LN_2 freezing systems can be effectively used for high valued food products, mainly for export purpose. This freezing being efficiently operating in all the developed countries can also be implemented in our country. The big and medium frozen food industries should take up the challenge of implementation of freezing with liquid nitrogen in our country.

Table-1: Freezing time and weight loss for four types of Food freezing equipment

Food	Fr. System	Fr. Time, m	Wt. loss,
			%
	SBF	35	0.7
Beef	LFF	4	0.1
	LNF	8	0.5
	CBT	180	1.3

SBF-Spiral belt freezer, LFF-Liquid freon freezer, LNF- Liquid nitrogen freezer, CBT- Cold air-blast Freezer

Table-2: Representative consumption of LN₂ Food product's initial temperature = 15.5 °C, Final temperature = -17.7 °C

Frozen item	Ratio, kg LN ₂ / kg Food
Fish and sea food	1.0 - 1.3
Meat and Meat Products	0.7 - 0.8
Poultry	1.1 - 1.3
Pizza	0.4 - 0.5

Table-3: Comparison of cost between air-blast and LN_2 freezing

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S1.	Item		LN_2 fr.	Air-blast
No.				fr.
1.	Prod./Annum (kg)		576108	621831
2.	Cap.	Plant	134400	287360
	Cost	BLdg.	48160	100800
	(Rs.)			
3.	Electricity (Rs.)		5184	206432
4.	LN_2 (Rs.)		1307040	-
5.	Maintenance (Rs.)		-	208000
6.	Tank Rental (Rs.)		291200	-
7.	Labour (Rs.)		1043200	1881600
8.	Depriciat	Plant	192000	410560

	-ion (Rs.) Bldg.	17184	36000
9.	Total (Rs.)	3038368	3130752
10.	Dehydration (Rs.)	140192	822496
11.	Final Total (Rs.)	3178560	3953248
	Cost per kg	Rs. 5.62	Rs. 6.36

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