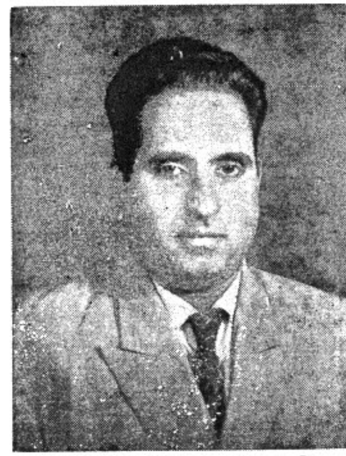
Freeze Drying and its Application in Fish Preservation



T. K. GOVINDAN

What is freeze drying?

It is a method of drying or dehydration or removal of water from a material. The purpose is to preserve the material for long periods which is achieved by creating such low conditions of humidity in the material that micro organisms responsible for causing the spoilage reactions do not get conducive atmosphere for growth and proliferation. In olden days, natural agents like sun and wind used to perform this task for human beings. But as civilization progressed, artificial means were employed and the term 'dehydration' is at present used to denote removal of water by artificial means under carefully controlled conditions. An ideal method of dehydration must remove water reversibly, i.e., when the expelled water is supplied back to the dried material, it should yield a product as near in qualities to the starting material as possible, if not of the *same* properties, as regards appearance, odour, flavour, texture and nutritive value. With this end in view, modifications started to be applied to the process until it emerged into the latest and most ideal method so far achieved by science, i.e., freeze drying, which, as the name itself implies, consists in removal of water under frozen condition.

When invented?

The principle of freeze drying was known to scientists for at least one and a half centuries and the first ever attempt to freeze dry a material dates back to the first decade of the present century. In this epoch-making experiment, the researcher concerned froze some biological tissues and fluid by immersion in a freezing mixture of ice and salt and kept the frozen material in a vacuum desicator over concentrated sulphuric acid which absorbed the water vapour released by it. Drying was slow in this experiment but effective, thus establishing the practical feasibility of the method. Further modifications were incorporated in the method by later workers which included substitution of the desiccant (sulphuric acid) by continuous vacuumisation with the help of a vacuum pump, application of heat energy to hasten the process etc. Quantities of serum were preserved by this method in U.S.A. and U. K. prior to the outbreak of the second world war. The war, however, necessitated the wide scale application of this method to preserve blood plasma so vitally required for transfusion to wounded soldiers. Soon, other materials like vaccines, semen (for artificial insemination) etc. started to be preserved by this novel method, yielding highly porous solids with great affinity for water. This latter property of the product has earned the name 'lyophilisation' to the process at the laboratories of the French scientists. Researches on application of this method for preservation of food started some three decades back and commercial production of freeze dried foods commenced in the middle 1950's. Among the agencies responsible for this development may be mentioned the British Ministry of Food and Agriculture Experimental Station, Aberdeen, U. K. and the U. S. Quarter-Master Food and Container Institute for Armed Forces, Chicago, U. S. A.

Principle involved

The principle involved in this method is sublimation of ice. What is sublimation? If a lump of camphor is exposed to atmosphere for sufficiently long time, the whole thing disappears. We never notice any liquid being formed from the lump and what actually happens here is that the solid camphor gets directly converted into vapour without passing through the intermediate state of liquid. This process of a solid getting directly vapourised is called sublimation. If we heat ice at atmospheric pressure, it first melts into liquid (water) and then evaporates. But if ice is kept under a sufficiently low vacuum and heat is supplied, it sublimes. The principle can be explained in another manner. If some water is kept in a vessel exposed to the atmosphere, molecules of water escape from the surface into the atmosphere, the quantity of which depends upon the temperature and pressure to which it is subjected. In case the pressure above the water is reduced, more and more water molecules escape and when the pressure becomes reduced to saturation vapour pressure of water, it starts boiling. The energy required for this process of vapourisation is absorbed from the water itself which consequently gets cooled. If the vacuumisation is continued, boiling of the water also continues accompanied by consequent cooling and at one particular stage the water starts freezing. At this point water simultaneously freezes and vapourises (boils), i.e., ice, water and vapour co-exist and the temperature and pressure of the system at this stage are + 0.0075°C and 4.58 mm of Hg. respectively. If the pressure is lowered due to further vaporisation and then, only ice and vapour are encountered in the system, that is to say, if ice is subjected to temperatures and pressures below the above said limits, it sublimes, of course, at rates consistent with the energy it is able to acquire for the purpose. In case energy in the form of heat, ultra violet radiations, infra red rays, ultra high frequency dielectric heating etc. is supplied, the process of sublimation can be accelerated.

The process of freeze drying

The material to be dried is frozen and loaded into a chamber which is then evacuated. This is called the pre-freezing technique. On the other hand, the fresh material can be charged as such into the chamber and vacuum pulled down quickly when the free water on the surface of the material evaporates absorbing the latent heat of vapourisation from the material which consequently gets frozen. This is called evaporative freezing technique. In both cases, when the vacuum in the chamber falls down to about 1.0 mm of Hg or less and the temperatures recorded are —15 to —20°C, heat is supplied when the water in the material (remaining as ice under these conditions) sublimes. Input of heat is so adjusted that at no time excess energy than what is utilized for the sublimation process is made available. In other words, the whole success of the freeze drying process depends upon the dexterous adjustment of the heat input so that at no point in the process, the material gets a chance to thaw to the least extent. Sublimation is allowed to proceed in this manner keeging the temperature of the material at subzero levels until almost 90% of the water is removed. The sublimed water vapour is either condensed on a refrigerated coil and with-held as ice until the drying is over or driven out by means of steam jet ejectors. A combination of these two is employed in most of the commercial plants. The temperature of the material is allowed to rise slowly towards the final stages of drying to drive away the last traces of moisture and drying is completed at 30 to 50°C according to the nature (heat sensitivity) of the material. Temperatures of the material at different points and the heating plates are measured by means of thermocouples introduced at the appropriate places and indicated on a self recording instrument.

Pre-freezing v/s evaporative freezing techniques

When a pre-frozen material is freeze dried, the ice sublimes from the surface and slowly the ice front recedes into the material leaving the cell structure unaffected. The vapours sublimed from the ice layer inside pass unhindered through the dry cell structure and escape. This phenomenon is illustrated in figure 1.

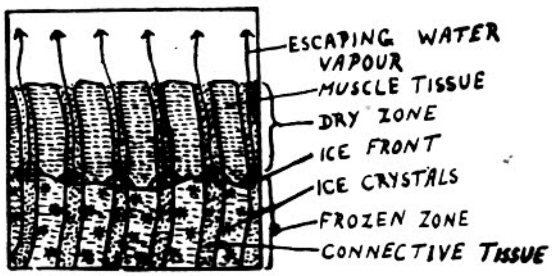


Fig. 1. *Diagramatic representation of solid phase drying.*

On other hand, if the same material is evaporatively frozen, the free adhering water from the surface evaporates first. What remains in the material is not pure water but a solution of different solutes like proteins, non-proteins, carbohydrates, mineral salts etc., the composition of which is decided by the material itself. When water in such solutions vapourises, they leave behind the dissolved solutes on the surface of the material which not only causes hindrahce to the free movement of water vapour; but also retards reconstitution when the dried material is put in water. This is illustrated in figure 2.

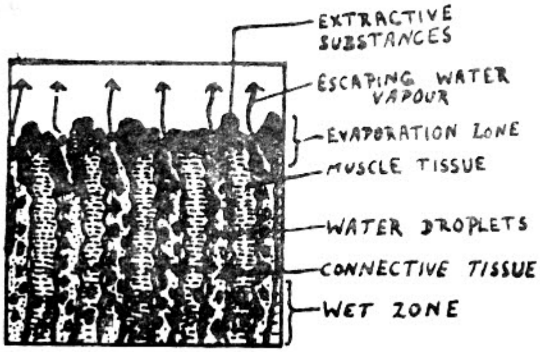


Fig. 2 *Diagramatic representation of liquid phase drying. Note the shrinkage in muscle tissues and deposition of solids on the surface.*

This phenomenon proceeds until the material gets frozen and thereafter normal freeze drying follows. In the conventional liquid phase drying, the whole drying process takes place in the manner shown in figure 2, droplets of solution moving to the surface and evaporating from there leaving the solutes on the surface. This is also accompanied by strong shrinkage of the tissues which is a further hindrance to the absorption of water during reconstitution. In normal freeze drying there is no movement of matter inside the material excepting the sublimed vapours. Hence in products freeze dried by the evaporative freezing technique, the properties of the final Product are affected to the extent to which liquid phase evaporation has occured at the beginning stages. But two points on which this method can claim advantage over the pre-freezing technique are : 1) 15 to 20% of the original moisture in the material is driven out in the evaporative freezing process resulting in shorter overall drying periods and consequent reduction in processing expenditure and 2) separate freezing plant and frozen storage required in the pre-freezing technique can be avoided rendering capital and operating expenses to be proportionately less. However, when quality of the product is the point of prime importance, we have necessarily to stick to the pre-freezing technique, though comparatively costlier.

Packaging

After the drying is over, the vacuum in the chamber is broken by sending in some dry inert gss like nitrogen or carbondioxide. The dried material is highly porous and hygroscopic. Hence, if the vacuum is broken with air, the moisture in the air is absorbed by the material besides the air filling the pores inside it. The oxygen of the air causes quick oxidative deterioration of the fats and other oxidisable compounds in the material. For the same reasons, the processed material has to be packed in air-tight containers like tin cans or laminated polythene bags, also under an inert atmosphere. Sturdy containers like tins are preferable because the freeze dried material is generally very brittle and any considerable external pressure crumbles it.

Materials amenable to freeze drying

Almost any food material can be dried by this method, exceptions being those containing excessive amounts of fat and sugar. In the case of fatty materials, the fat offers resistance to the free movement of water vapour and at the temperatures obtaining towards the final stages of drying. it melts and fills the pores left behind by the ice, so that at the time of reconstitution absorption of water is highly retarded. Too much of dissolved solutes like sugar in the water depresses its freezing point so much that it is extremely difficult to maintain the material in the frozen conditions during the freeze drying process. Precooked materials freeze dry more efficiently than raw ones. Freeze dried materials already in the market include shrimp, crab, meat. beef, chicken, eggs, ham, mushrooms, strawberries, peaches, blueberries, coffee and tea. Potato. onion, mutton and ready-to-serve food materials like ice-cream, salads and soups in the freeze dried form are now available in the American and European markets.

Advantages of freeze drying

Freeze dried foods offer several advantages over conventionally dried ones, or for that matter, over foods preserved by any of the older methods of processing. The materials do not shrink, but retain original volume and shape in freeze drying, whereas they shrink to one-fourth or one-fifth the original volume and get distorted in shape in the other methods of drying. Complete drying takes place in as short a time as eight hours from solid phase leaving final moisture contents of 1 to 3% in the new process while long drying periods of 15 to 36 hours, dehydration taking place from liquid phase with final moisture contents of 16 to 45% depending upon the method employed and encoutered in the conventional processes. Whereas freeze dried materials are highly porous and brittle, reabsorbing upto 95% of their original water contents in minutes and having long shelf lives counted in years, materials dried by the older methods are shrunk and hard to break, reabsorbing only 25 to 35% of their original moisture contents even after two to three hours of soaking in water and offer only comparatively short shelf lives counted in weeks of months at the most. Heat damage and loss of nutrients are almost nil in freeze dried foods and they require only minimum preparation for the table, while both heat damage and loss of nutrients occur and the products require elaborate soaking and preparation in the case of conventionally dried materials. In contrast to frozen foods, freeze dried materials are very light and hence cost less handling and freight charges and when once packed properly in air-tight containers, they no longer require low temporature storage, transportation and distribution, usually referred to as 'cold chain', which is absolutely unavoidable in the case of the former and which contribute to their higher consumer prices.

Freeze drying for fish preservation

As already pointed out elsewhere, researches on application of this method of preservation to food materials commenced in full swing about three decades back and fish, one of the most important protein foods was not excempted from these studies. Some points to be remembered while freeze drying fish are: 1) Teleost fishes must be beheaded, eviscerated and cut into slices or fillets with a maximum thickness of 2 cm, ie, only the edible meat should be taken for freeze drying. Shell fishes like prawns, crabs and lobsters must be deshelled. These preliminary preparations assist in quickening the process, increasing the payload of the dryer by avoiding waste materials and in easy preparation for the table of the freeze dried product. 2) The skin of raw fish and shells of crustaceans are impermeable to water vapour and hence while freeze drying such materials, the skin has to be either removed or prickad with some sharp needles and shells peeled off to allow water vapour to pass readily during the drying process. 3) Drying is easier from cut surfaces, especially if the cut is at right angles to the muscle fibre direction. Hence fish steaks or slices cut at right angles to the back bone freeze dry most readily among whole fish, steaks and fillets. 4) Pre-cooked fish and shell fish freeze dry more efficiently than raw ones, probably because the heat denaturation of the proteins facilitate vapour removal during drying.

Some of the earlier findings

Some of the conclusions arrived at by Russian workers in the early 1950's on freeze dried fish products were: 1) A partial denaturation of the proteins especially of the salt soluble fraction took place during freeze drying of fish. 2) Basic changes taking place during storage of freeze dried fish were yellowing and protein ageing manifested by decrease in hygroscopicity. 3) Depending upon the storage conditions, deterioration in organoleptic qualities like hardening of texture and loss of juiciness occurred. 4) Moistening of the freeze dried fish during storage caused faster yellowing and other protein changes necessitating special moisture-proof packing materials for the product. Oxygen was not found to have any effect on the yellowing of the dried fish. 5) Freeze dried fish can be stored for three to four months in air free from moisture and in carbondioxide without considerable change, for two months in polythene bags under room conditions and for one month in plywood box lined with wax paper.

Japanese workers observed in the early 1960's that when the pH value of the fish muscle was kept on the alkaline side, increases in rate of rehydration and water holding capacity of the rehydrated muscle occurred and that addition of poly phosphates to the muscle before drying, increased the rehydration rates considerably. However, the present auther has not been able to get this result in his studies. Scientists in Japan have also observed that in a few species of fish subjected to freeze drying extractability of myosin fraction was not so much lowered as in ordinary drying process and that sometimes the extractability was even higher than that before drying. The present author's findings also confirm this fact. Viscosity of myosin fraction decreased during freeze drying. Fish paste cake prepared from freeze dried meat had elasticity as large as the one from fresh meat; but the water content expressible from the former product was larger than that from the latter.

These workers also report that greater part of the actomyosin of the fish muscle was not rendered insoluble by freeze drying and that little difference between the amount of actomyosin of fresh and freeze dried muscle was seen, showing that various myosins are not denatured during freeze drying. Denaturation of actomyosin increased with incroase of temperature and length of storage. Rehydratability of the product also decreased with increase in the above factors. A relationship was noted between the water content in the dried muscle and denaturation during storage.

According to an American scientist, there is good evidence that the sarcoplasmic proteins survive freeze drying virtually in tact as shown by the electrophoretic and ultracentrifuge properties of extracts of this group of proteins from freeze dried cod which were very similar to those from frozen controls, thereby proving that damage to proteins caused by freeze drying is much less than believed. A large proportion of the important myofibrillar protein fractions survive the process and with suitable modifications damage to texture could be eliminated and freeze dried materials produced which when reconstituted would be indistinguishable from the fresh/frozen controls.

Work in India

Researches on freeze drying of fish in India were initiated for the first time in the year 1966 on a laboratory model freeze drying unit gifted to the Government of India by the Food and Agriculture Organisation under the United Nation's Development Programme, under the supervision of a foreign expert, also deputed by the F. A. O. Similar researches on other food materials were also started in India almost simultaneously or a bit earlier at the Central Food Technological Research Institute, Mysore and the Accelerated Freeze Drying Unit (Ministry of Defence) at Delhi, also on laboratory model units. It is gratifying to note that we are at present having one commercial size freeze drying plant in India which can freeze dry five tonnes of frozen material per day. Of course, the plant is owned by the public sector under the Ministry of Defence and is not at present available for civilian purposes.

Chief findings

Lean fishes and shell fishes like Cullawah (*Serranus* sp.), tuna, shark,

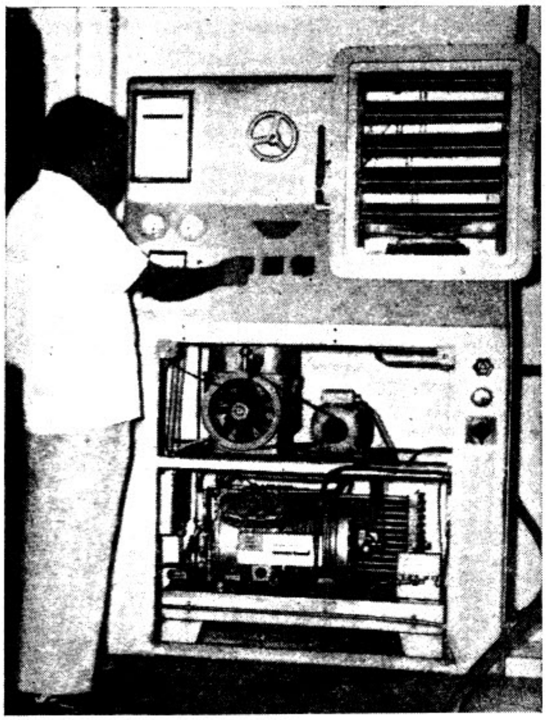


Fig. 3 *Author carrying out research on freeze drying of fishery products with a laboratory model freeze drying unit.*

kilimin (*Synagris* sp.) and prawns lend themselves well to the freeze drying process, with comparatively shorter drying cycles and yielding products with good reconstitution properties. Fatty fishes like sardine. mackerel and mullets require longer drying cycles, their fat contents retarding free vapour movements and yield products with poor reconstitution ratios. Pre-cooked fish products like blanched peeled and deveined prawns, cooked and flaked Cullawah, jew fish and sardines freeze dry more efficiently than their raw counterparts. Ready-to-eat foods like fish salads, fish soup mixes and fish cakes are well amenable to freeze drying preservation. In the case of fish freeze dried in the raw condition, a good fraction of the water in the reconstituted product can be squeezed out by pressing between fingers, showing that some of the reabsorbed water is only mechanically held in the pores of the dried product.

Raw and cooked fish and shell fish

In the case of fresh peeled and deveined prawns, the drying rate (kg of water lost / 100 kg dry matter / hour) remained constant for the first two hours of the drying cycle and then fell rapidly. Weight loss (kg water lost / 100 kg dry matter) and drying rate are low in the case of oil sardine (fat content: 36.1% DWB) compared to those of kilimin (fat content: 2.4% DWB). When there is higher fat content' the amount of water to be driven out is proportionately less on gross waight basis, giving a lower weight loss and drying rate than with a low fat material. Similar observations were made with Cullawah (lean) and mullet (fatty). In the case of cooked prawns freeze dried by the pre-freezing and evaporative freezing techniques, a rapid fall in drying rate occurred in the first few minutes in the latter technique, whereas the reverse was the case in the former. Cooked and flaked jew fish also behaved in a similar way while freeze drying by the above techniques.

Reconstitution ratios (as % of original water reabsorbed on reconstitution) varied in the case of various products. Cooked prawns and lean fishes rehydrated better than raw prawns and fatty fishes. At the end of the drying cycle, when the vacuum is broken, the fat (in the case of fatty fishes) is in the liquid form and tends to flow into the cavities left in the dry tissue from which water has evaporated, retarding rehydration. Rehydration is higher for pre-frozen material than for evaporatively frozen, because of the liguid phase drying occurring during the process of evaporative freezing. It therefore follows that liquid phase dehydration should be avoided as far as possible for getting a product with better reconstitution properties.

Fish salads

One of the major advantages offered by this novel method is that foods can be dehydrated successfully in the pre-cooked, ready-to-eat form, eliminating the need for any further preparation at the time of eating, other than mixing with the required amount of water. However, the freeze dried material has to be packed in air-tight containers in an inert atmosphers. Such foods are especially important for army combat rations as well as for space travellers who lack facilities for cooking their foods. In the United States, high calorie salad preparations have been developed from tuna, solmen, chicken and potato by mixing the pre-cooked material with mayonnaise and other flavouring agents and preserved by freeze drying for supply to defence personnel, with whom they are very popular. Such foods have become a necessity in our country also taking into consideration the needs of our border security forces working in high altitudes.

The present author has successfully developed similar products from cooked peeled and flaked seer, tuna and Cullawah which were mixed with salt and a fine emulsion of pre-cooked starch, refined groundnut oil, tomato, onion and pepper powder, freeze dried and packed in tin cans under nitrogen. The products were crisp, tasty and quite wholesome and were highly acceptable to whomsoever they were offered for consumer preference studies. The fat did not separate in the products.

Other products

Instant soup mixes were developed from two common varieties of Indian fishes, viz; seer and Cullawah, by precooking their cleaned chunks under pressure, separating the edible flesh and homogenising the same with onion, vanaspati, refined salt, maida, pepper powder and monosodium glutamate. A prawn-potato cake was also developed by grinding together canned prawns, cooked and peeled potato, vanaspati, refined salt, pepper powder, citric acid and monosodium glutamate. Both the products lent themselves well to freeze drying. A 5% suspension of the soup mix in water gave a fine soup on boiling for a few minutes. The prawn cake in the form of thin noodles could be fried for a few seconds in oil and taken, or wetted with water, shaped into cutlets and fried with a suitable coating. All the products were highly acceptable.

Economics

One serious disadvantage with this method of food preservation at present is that both the capital and operating costs are high compared to other method of dehydration, which in turn enhances the cost of the final product. The smaller the capacity of the plant, the higher the contributions of capital and operating costs towards the cost of the finished product. Expert opinion has put the minimum capacity of a freeze drying plant to be five tonnes of frozen material in three shifts per day for running it economically. On such a plant, taking the raw material to be fish and its cost to be Rs. 2/- per kg. and the plant works 250 days in the year, the cost of the finished product will be Rs. 37/- per kg. including packing and distribution charges at the existing labour and other utility charges in our country. This cannot be said to be exorbitantly high, because one kg. of freeze dried fish is equivalent to five kg. of frozen fish, which in turn is equivalent to ten kg. of fish as landed. Hence the actual cost works out to only Rs. 3–70 per kg. of fresh fish when it reaches the consumer in the interior markets in the freeze dried form. The comparatively higher cost of production of the freeze dried material will be compensated to some extent by their lower handling, transportation and distribution charges.

Conclusion

Freeze drying appears to be a promising method of food preservation for our country whose economy is essentially agro-based. Agricultural, farm and fishery products are by far the most important national products which have to be preserved and utilised in the best way possible to achieve prosperity for the nation in general. Farm products like meat and eggs, vegetables, fruits and fish which are the most perishable of the food materials deserve utmost care and attention from the point of view of proper preservation and distribution. These materials, especially the marine fish products have to be transported over long distances to make them available to people inhabiting the interior parts of the country. The best method for this will be to leave behind the water in these products (which constitutes anything from 70 to 90% of the material and which is a commodity universally available) at the places of their production and transport only the solids in them, so that they can be reconstituted at the place of actual consumption. This will not only prolong the storage life of such products, but will also reduce the costs of transportation and distribution, otherwise contributed by their water contents. Freeze drying is the best solution to this problem. Coffee and tea which are two of our important export commodities are sure to capture much more markets in case they are freeze dried and exported.

Fishery products are in a better position than all the others to be preserved by this method under the conditions obtaining at present in our country. Freezing plants and frozen storages, much in excess of the required capacity, have already been put up in all good centres of production of marine fish in our country now. These being essential adjuncts to a freeze drying plant, capital expenditure as far as these are concerned can be saved in case the freeze drying plants for such products are put up alongside already existing freezing plants. By judicious adjustments of the processing steps, the overall capital costs contributing to the higher cost of production of freeze dried products can be reduced to some extent. Let us hope that our food processing industry will catch up with the modern trends in processing technology and take to freeze drying in a big way both for internal purposes as well as for exports.