

Vitamin oils are stored in rust free, well washed and dried air tight drums. The head space should be kept minimum to avoid oxidation. It is advisable to fill the head space with inert gas such as nitrogen. If properly processed and stored, the oil will remain in satisfactory condition without the use of preservative. Exposure to air and sunlight will cause oxidation, discoloration and loss of vitamin potency. Small amounts of anti-oxidants BHA, tocopherol, NDGA etc. can be used to preserve the oil for longer periods.

Fish ensilage

When fish is available which cannot be used for direct consumption, for several reasons, is normally used for production of fish meal which has got ready market as an animal feed. If material is available at a place where there is no fish meal plant and no reasonable transport to the nearest plant or there may be severe restrictions on fish meal production because of fish odours one has to look for alternate processes. When the animal farms are very near to landing centres it is worthwhile to go for silage production. Fish silage can be defined as a product made from whole fish or parts of the fish to which no other material has been added other than an acid and in which liquefaction of the fish is brought about by enzymes already present in the fish. The product is a stable liquid with a malty odour which has very good storage characteristics and contains all the water present in the original material. It is a simple process and it requires little capital equipment particularly if nonoily fish are used. The use of oily fish usually requires oil separation. This involves expensive equipment and is only suited to a fairly large-scale operation.

Almost any species of fish can be used to make fish silage though cartilagenous species like shark and rays liquefy slowly. The production of fish silage involves preferably organic acid like formic acid (35 kg/1 tonne of fish) to preserve the fish and then allow the enzymes already present in the fish to liquefy the protein. Wooden or bitumen coated iron or concrete acid resistant tanks can be used for the process. Formic is favoured as it preserves the fish with out a very low pH and so the silage can be directly fed to animal without further neutralization. When 3.5% formic acid (85% conc.) is added to the fish the pH will be nearly 4. Mineral acid like sulphuric acid can also be used for this purpose instead of formic acid. But in this case pH would be about 2.5 which requires neutralization before feeding.

When the minced fish is mixed with the acid the fish tends to stiffen initially and liquefaction will proceed and the rate at which liquefaction takes place depends upon the temperature of the mixture. Fatty fish liquefy more rapidly than white fish and fresh fish liquefy more rapidly than stale fish and previously chilled or frozen fish. The warmer the mixture faster this process. At 25°C the process needs 2 days for liquefaction whereas at 15°C it needs 5 to 10 days and more at lower temperature. Temperature above 40°C should be avoided as the enzymes may get deactivated. Periodic agitation will help liquefaction.

There are no problems in storage of fish silage if the correct acidity is maintained. There are Changes during storage the protein becomes more soluble and there is an increase in free fatty acids if any fish oil is present. If silage is made from oily fish it is desirable to separate the oil after liquefaction.

Composition of Silage

Except for slight dilution involved by the addition of the acid silage has the same composition that of the raw material from which it is made. Nutritional studies have shown that there are no palatability problems with pigs and it is considered as equivalent to fishmeal.

There are some advantages and disadvantages for silage over fishmeal. In the case of silage the capital investment is significantly less and no skilled personnel is needed. But, in the case of silage the bulk is not reduced and so storage and transportation face problem. There is no considerable smell for silage in fact it is having a pleasant smell. Smell is a difficult problem in the manufacture of fishmeal. Marketing of fishmeal is well established, whereas silage is still not well known to the farmers. Recently silage production is considered to be the best method to address the problem of environmental production due to processing waste and underutilized by-catch.

There is an alternate method of production of silage by fermentation. The fish is mixed with a carbohydrate source like molasses and lactic acid is produced in the system to reduce the pH by introducing a lactic acid producing bacteria like *Lacto basillus plantorum*

Fish Protein Concentrate

Fish protein concentrate (FPC) is any stable fish preparation, intended for human consumption, in which the protein is more concentrated than in the original fish. The idea of producing a fish protein concentrate is by no means new. However, it is only in the last twenty-five years that extensive endeavors have been made to produce fish protein concentrate. Fishmeal as produced throughout the world is very cheap potential FPC, but it is not intended for human consumption; it is used for making pig and poultry feeds for farming. Ordinary fishmeal is unsuitable for human consumption for three main reasons:

It is not normally made under sufficiently hygienic conditions to rule out the risk of occasional contamination by disease-causing bacteria.

It usually contains rancid fat, which destroys certain vitamins and may lower the nutritive value of the protein; a fishmeal diet might precipitate vitamin deficiency in poorly nourished people. Moreover, the flavour of the rancid fat is unacceptable in many societies, though not in all.

There is a slight risk that the rancid fat may have a cumulative toxic effect if consumed over a long period.

The first of these reasons is the most important; thus, fishmeal made under hygienic conditions is called FPC type C.

The Food and Agriculture Organization of the United Nations defines three types:

- Type A: a virtually odourless and tasteless powder having a maximum total fat content of 0.75 per cent.
- Type B: a powder having no specific limits as to odour of flavour, but definitely having a fishy flavour and a maximum fat content of 3 per cent.
- Type C: normal fishmeal produced under satisfactorily hygienic conditions.

Fish Hydrolysate

This is also a liquefied fish product but it differs from silage. These are products produced by a process employing commercially available proteolytic enzymes for isolation of protein from fish waste. By selection of suitable enzymes and controlling the conditions the properties of the end product can be selected. Hydrolysate fluid application as milk replacer and food flavouring. Enzymes like papain, ficin, trypsin, bromelein, pancreatin are used for hydrolysis. The process consists of chopping,

mincing, cooking, cooling to the desired temperature, hydrolysis, sieving, pasteurizing the liquid, concentrating and drying (by vacuum or spray drying).

Fish maws and Isinglass

The word isinglass is derived from the Dutch and German words which have the meaning sturgeon's air bladder or swimming bladders. Not all fish air bladder are suitable for isinglass production. The air bladder of deep-water hake is the most suitable for production of isinglass. In India air bladders of eel and cat fishes are used for the production of isinglass.

The air bladders are separated from the fish, and temporarily preserved in salt during transport. On reaching the shore, they are split open, thoroughly washed and the outer membrane is removed by scraping and then air dried.

The cleaned, desalted, air dried and hardened swimming bladders (fish maws) are softened by immersing in chilled water for several hours. They are mechanically cut into small pieces and rolled or compressed between hollow iron rollers that are cooled by water and provided with a scraper for the removal of any adhering dried material. The rolling process converts the isinglass into thin strips or sheets of 1/8 to 1/4 " thickness. There are processes for the production of isinglass in powder form.

Isinglass dissolves readily in most dilute acids or alkalis, but is insoluble in alcohol. In hot water isinglass swells uniformly producing opalescent jelly with fibrous structure in contrast to gelatin. It is used as a clarifying agent for beverages like wine, beer, vinegar etc. by enmeshing the suspended impurities in the fibrous structure of the swollen isinglass.

India exports dried fish maws, which form the raw material for the production of isinglass and such other products. Process have been developed to produce the finished products from fish maws.

Shark fins

Shark fins are in great demand particularly among the Chinese, for making the ceremonial dish called shark fin soup. Dried shark fin is an item of export from India mostly to Singapore, Hongkong and the United Kingdom.

The commercial value of the fins depends on their colour, size, variety and quality. Depending on the quality and quantity of rays present in the fins they are broadly classified into two varieties, generally known as black and white. The black fins usually fetch a lower price than the white fins. Fins are generally marketed in dried form.

The preparation of shark fin does not require any elaborate treatment, but care is needed in cutting, trimming and drying operations.

Fins are cut from sharks of about 125 cm or more in length as soon as they are landed avoiding as much flesh as possible and are washed thoroughly in water after removing the adhering flesh. They are then dusted with salt in the ratio 1:10 (salt to fin), the cut portion being sprinkled liberally with salt. A little lime also is often sprinkled at the cut portion and the fins are set aside for 24 hours. They are then dried in sun after gently rinsing with clean water to remove solid salt and excess lime to a moisture content not more than 10%. The dry fins are graded according to the size and type of the fin.

ISI has laid down standard specification for dried shark fins.

Fin rays

The dried fins are further processed, for the "rays". The process followed differs considerably from place to place and also depending on the quality and type of final product. The price of fin rays depends mainly on colour, length and thickness of individual strands, quantity of connective tissues and cartilage present, physical presentation etc. The product can be classified as semi-prepared skin off but otherwise retaining the shape, small individual strands made in the form of cake, individual strands, skin off but made into flaps by splitting at the middle along the cartilage.

The process of extracting good quality shark fin rays is simple and can be adopted even in small fishing villages by the fishermen.

Though both white and black varieties of fins contain rays the yield from the black variety is only about half of that from white varieties. There exists wide variation in the content of rays in the fins from different body parts, the caudal fins containing the least.

There is good scope of developing the industry for producing more sophisticated product of high unit value for export.

Shark skin leather

Skins of fishes especially of shark, seal, porpoise, dolphin, skates and rays are suitable for conversion to leather particularly for manufacture of small novelties. Shark skin leather is a by product from shark fishery. The production process is essentially the same as that followed for making leather from animal hides, the principal constituent in fish skin also being collagen. The important variation is that the scale of shagreen is removed from fish skin while hair is removed from land animal skin. In the case of shark, the shagreen is removed by chemical process and not by scrapping which is a delicate operation. Vegetable tannages are generally used on shark and other fish skins. The tanning process has been worked out at CLRI at Madras. The skin from sharks can be peeled off or flayed carefully and preserved using salt before it is taken for tanning.

Shark Teeth and Bones

Shark teeth and bones have become an export commodity in recent years. The teeth so far neglected and thrown away by the fishermen have now become a valuable item for export to countries like USA, UK, Canada, Australia etc. In these countries, shark teeth are in very great demand for making fancy ornaments. Depending on the size and shape of the teeth the price also varies considerably. Teeth of at least 20 mm length are preferred. Among the various species, tiger shark teeth are in greater demand due to their more attractive shape and size.

The method of extracting the teeth is simple. From the shark head, the jaw portion with the teeth intact is cut off separately and washed well in good clean water. After that, the jaws are boiled in dilute 2% sodium hydroxide for 5 min. when the muscle starts disintegrating. The teeth then become loose and can be easily removed. The jaws are taken out from the boiling alkali and put in cold water. The teeth are removed manually. After carefully cleaning the teeth in good water to remove all adhering dirt, blood etc. the teeth are put in hydrogen peroxide for some time for bleaching and thus to give an appealing appearance. The cleaned teeth are wiped dry and packed in polythene bags in suitable lots (unpublished).

Shark bones

Shark bones are cleaned and processed for use as source of chondroitin sulphate which is used for treatment of arthritis and colon cancer.

Squalene

Liver of certain species of deep-sea sharks, centrophorus sp. are rich in squalene, C₃₀H₅₀ which is being now used in cosmetics and medicine.

Pearl essence

A lustrous substance is present in the epidermal layer and on the scales of most pelagic fishes, such as sardine and mackerel. The lustrous effect is due to the presence of an organic compound, guanine, (2-amino, 6-oxypurin) a constituent of cell membrane.

The crystalline guanine can be extracted from the fish scales. The suspension of guanine crystals in a suitable solvent is called "Pearl essence". When the particles are deposited on the inside of hollow beads or outside of solid one, they produce an optical effect very similar to genuine pearls.

There is good demand for the product in countries like Japan.

Shrimp extract

Prawn head and shell waste meant for the extraction of the protein and conversion to shrimp extract should be collected fresh and stored in ice to minimise spoilage. It should be collected fresh and stored in ice to minimise spoilage. It should be washed in potable water to remove all adhering dirt, sand and other extraneous matter. The protein is then extracted by boiling with 0.5% sodium hydroxide solution in water. The boiled mass is filtered through appropriate sieve to separate the residual shell. The filtrate is neutralised with hydrochloric acid initially, and with acetic acid towards the end to a pH 6.8 to 7.0. the neutralised filtrate is concentrated by boiling in an open stem jacketed kettle to a semi solid mass with a moisture content of about 35 to 45%.

The paste so prepared is generally known as shrimp extract. It contains on an average 40% moisture, 40% partialised hydrolysed protein and 10 minerals. The yield is about 20% of the fresh head and shell.

Chitin

The residual shell waste obtained after extraction of the protein with hot 0.5% caustic soda may contain small amounts of protein. This is then removed by boiling with 3% caustic soda for a few minutes and filtering off the liquor. The residue will contain the minerals present in the shell apart from chitin. It should be washed free of alkali before going for demineralisation. The demineralisation is done by treatment with dil. hydrochloric acid at room temperature. Dry shell waste from which the protein is not to be collected for making shrimp extract can be demineralised before deproteinisation with 3% caustic soda. Demineralisation reduces the volume of the shell considerably and therefore the deproteiniser can hold more material if the demineralisation is done initially.

Glucosamine Hydrochloride

Chitin can be hydrolysed to glucosamine hydrochloride by adding concentrated hydrochloric acid and warming until the solution no longer gives opalescence on dilution

with water. The excess acid can be distilled off under vacuum. The crude glucosamine hydrochloride is diluted with water and clarified with activated charcoal. The solution is filtered and evaporated under vacuum. The crude glucosamine hydrochloride coming as the residue can be separated from the mother liquor by adding alcohol.

Chitosan

Chitin meant for deacetylation to chitosan is to be either dried or centrifuged or pressed well to remove as much water as possible. The deacetylation is done by heating at 90-95°C with 40% (w/w) caustic soda for 90 -120 mts. The water present in the chitin cake should also be taken into account while preparing caustic soda solution. To achieve this 50% caustic soda is prepared and calculated quantity of it is added to the chitin cake. The reaction is followed by testing the solubility of the residue in 1% acetic acid. As soon as complete desolution is reached the caustic soda is removed from the reaction mixture. The drained caustic soda can be reused for the next batch of deacetylation by fortification if necessary. The residue is washed with water free of alkali.

It is then centrifuged and dried in the sun or an artificial dryer at a temperature not exceeding 80°C and pulverized to coarse particles.

Chitosan is almost colourless, light in weight and soluble in dil. Organic acids but insoluble in water, alkali and organic solvents. It gives viscous solution when dissolved in dil. Organic acids such as formic acid, acetic acid etc.

Chitosan finds extensive applications in following areas:

- Food industries
- Pharmaceutical applications
- Chemical industries
- Dental and surgical uses as a haemo-static agent
- Wound healing
- Biodegradable films as a substitute for artificial skins
- For removal of toxic heavy metals like lead, mercury, cadmium etc. from industrial effluents.
- Wine clarification
- Industrial effluent flocculations
- Agriculture
- Photography
- Cosmetic applications
- Textiles
- As a human health diet etc.

The above listed are only some broad areas of developed uses of chitin and chitosan. There are more than 300 products containing chitosan in the international markets and more applications are under investigation. It is likely that this waste from shrimp may fetch more money than the shrimp meat in future.

Packaging and storage

Most of the battered and breaded products like fish fingers or portions are individually packed into small boxes on a weight basis or by a specified number of pieces. When individually packed, layers of the product will be separated by a waxed paper to prevent further product damage. The boxes are labeled and over wrapped with a polythene film to prevent moisture loss and freezer burn during storage. The packed boxes are stored at around -20 0 C until shipped.