# Recent Developments in Fishery Byproducts

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The modern fish processing industry in India is five decades old. Before the independence we used to export dried fish products to different countries. The export of marine products rose to 4.6 lakhs tonnes worth of six thousand and eight hundred crores in 2003. This phenomenal increase of export of marine products and development of fish processing industry have been more or less based on a single item namely frozen prawns which constitute about 28.58% in volume and 66.97% in value of the total export of marine products from India.

However this trend is not so apparent in various other fish products and by-products. A majority of marine fish landed has been caught as by-catch by shrimp trawlers. The low priced miscellaneous fish are either mainly discarded in the sea or converted to fish meal or dried. In tropics 80% of the catch is contributed by small fish. As it is not getting good price these fish are not subjected to ideal pre-process handling techniques like chilling and packaging. However, being a valuable protein source they can be further processed in to variety of value added products which can be produced on a cottage industry scale. These products are stable at ambient temperatures and its shelf life is very high and can easily be transported. The following is a brief description of various products that can be produced from fish by-catch or from fish processing waste.

**Fish meal**

Fish meal is highly concentrated nutritious feed supplement consisting of high quality protein, minerals, vitamins of B group and other vitamins and other unknown growth factors. Fishmeal is rich in essential amino acids. It is produced by cooking, pressing, drying and grinding the fish, by-catch fish, mscellaneous fish, filleting waste, waste from canneries and waste from various other processing operations. The composition of fishmeal differs considerably due to the variations in the raw material used and the processing methods and conditions employed.

Traditional fishmeal production in India was from the sun dried fish collected from various drying centres and these products were mainly used as manure. Better quality fish meal has been a prominent item of export from the very beginning of this industry. Bareau of Indian Standards (BIS) has brought out the specification for fish meal as live stock feed for facilitating proper quality control.

The proximate composition of fish meal in general is given below:

| | |
|---|---|
| Protein | - 50-57% |
| Fat | - 5-10% |
| Ash | - 12-33% |
| Moisture | - 6-10% |

**Manufacturing process**

Fish can be reduced by two general process (1) Dry rendering (2) Wet rendering process.

***Dry rendering process***

Dry rendering or dry reduction process is suitable for only lean or non oil fish such as silver bellies, jew fish, sciaenids, ribbon fish, sole, anchoviella, carcasses of shark, fish offal and filleting waste. In this process, it is dried to moisture content of 10% and pulverized. If the quantity to be handled is sufficiently large a steam jacketed cooker dryer equipped with power devises for stirring is used. Sometimes, if the size of the fish is comparatively large a coarse grinding is also done before being fed into the cooker drier. The cooker drier may be operated at atmospheric pressure or under partial vacuum. Being batch operation the process will have only limited capacity and labour cost is very high. Merit of this process is that the water-soluble materials are retained in the meal.

### *Wet rendering process*

Wet rendering or wet reduction process is normally applied to fatty fish or offal where simultaneous production of fish meal and fish body oil is envisaged. The process consists of grinding, cooking to soften the flesh and bones and to release the oil, pressing to expel the liquor and oil, fluffing the press cake drying, grinding and packing the meal. The press liquor is centrifuged to remove the suspended particles and to separate oil. The stick water is concentrated. The process requires elaborate equipment and is normally a continuous one and therefore adaptable to the reduction of large quantities of fish.

In a continuous wet reduction process the coarsely ground fish or fresh raw fish or offal is passed through a stationary horizontal cylindrical cooker by means of a screw conveyor at a predetermined rate. Steam is admitted through a series of jets. The cooked mass is passed through a continuous screw press. The press cake is fluffed and dried to a moisture level of 8%. The suspended fish meal present in the press liquor is separated by centrifugal sedimentation and the oil by centrifugation or other conventional methods.

### Fish body oil

The main source of fish body oil in our country is oil sardine. A survey of the oil industry reveals that the extraction is done on a cottage scale in isolated places near the leading centres and is not well organized. The method of extraction followed is cooking the fish in iron vessels and pressing and separating the oil. Apart from sardine oil, fish body oil is also obtained from the fish meal plants operating in the country. In India oil sardine is a fishery which exhibited wide fluctuations from as low as 1% to as high as 32% of the total landings. The seasonal variation in oil content is predominant in Kerala and Karnataka coast. During the peak season fish has an oil content of 17%. By the wet rendering process the fish will yield, on an average 12% oil having analytical characteristics similar to other fish oils. Fatty acid composition of the oil revealed that they contain high amounts of polyunsaturated fatty acids (PUFA). At present the medicinal values of fish oils are well known.

### Fish liver oil

The therapeutic values of fish liver oil were discovered in $18^{th}$ century and fish liver oil becomes a common medicinal product especially for Vitamin A and D. Cod, shark and haddock livers are the important sources of Vitamin A and D. The weight of liver, fat content and presence of vitamins are dependent on a number of factors like species, age, sex, nutritional status, stages of spawning, and area from where it is caught.

In cod (*Gadus collarius*), coal fish (*Pollahius vireus*) and haddock (*Melanggrammus aenglefinus*), the weight of liver normally amount to 4-9% of whole fish and livers contain about 45 to 67% oil. Some species of shark such as dog fish (*Squalus acanthias*), Greenland shark (*Somniosus microcephalus*) and barking shark (*Certrohinus maximus*) have large fatty livers weighing up to 10-25% of the whole fish containing 60-75% oil. But halibut, tuna, and whale have 1% liver having 4 to 25%

oil with high vitamin A & D content. Depending on the oil content and vitamin A potency fish livers are generally classified into three groups.

| | | |
|---|---|---|
| Low oil content | - | high vitamin A potency |
| High oil content | - | low vitamin A potency |
| High oil content | - | medium vitamin A potency |

***Processing***

The processing procedures of fish liver without affecting the quality of the oil extracted can be summarized as (1) steaming (2) solvent extraction and (3) alkali/enzyme/acid digestion. The process selected should depend on the vitamin and oil content of the livers.

Certain species of shark contain high oil content with high hydrocarbon content, viz. squalene. Squalene a highly unsaturated aliphatic hydrocarbon is present in certain shark liver oils, mainly of the family squalidae, cod and some vegetable oils like olive oil, wheat gum oil, and rice bran oil. Chemically it is known as 2,6,10,15,19,23 hexamethyl, 2,6,10,14,18,22 tetracosahexane having a molecular weight of 410.70. It is an isoprenoid compound containing six isoprene units.

*Preservation and storage*

Vitamin rich 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 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. Small amounts of antioxidants like BHA, $\alpha$ tocopherol, BHT, NDGA can be used to preserve the oil for longer periods.

**Fish silage**

Fish silage is defined as a product made from whole fish or parts of the fish to which no other material has been added other than acid and the liquefaction of the fish is brought about by enzymes 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 non oily fish are used. The use of oily fish requires oil separation. This involves expensive equipment and is suited to fairly large scale operation. Almost any species of fish can be used to make fish silage though cartilaginous species like shark and ray liquefy slowly. Fish waste and cuttle fish/ squid waste can be used for the preparation of silage. The production of silage involves addition of preferably organic acids like formic acid (35kg/tonne) to preserve the fish and then allow the enzymes already present in the fish to liquefy the protein. When 3.5% formic acid is added to the fish the pH will be nearly 4. Mineral acids like sulphuric acid also can be used for this purpose. But in this case pH would be about 2.5, which requires neutralization before formulating feeds to the poultry or cattle. . 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 *Lactobacillus plantarium.*

**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. Fishmeal as produced throughout the world is very cheap potential FPC, but it is not intended for human consumption. It is not normally made under sufficiently hygienic conditions. It usually contains rancid fat, which destroys certain vitamins and may lower the nutritive value of the protein. More over the flavour of the rancid fat is unacceptable to the consumers. There is slight risk that the rancid fat may have a cumulative toxic effect if consumed over a long period.

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

**Type A**: A virtually odourless and tasteless powder having a maximum total fat content of 0.75%

**Type B**: A powder having no specific limits as to odour or flavour, but definitely having a fishy flavour and a maximum fat content of 3%.

**Type C**. Normal fish meal produced under satisfactory hygienic conditions. These are made by hydrolyzing fish protein by enzymes or chemicals followed by concentrating the product into paste or extract. Canadian process, Viobin process and CIFT process are the important methods used for the preparation of fish protein concentrate. This product has not become very popular, because of the consumer dislike.

**Fish hydrolysates**

This is also liquefied fish product but it differs from silage. These are 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. Hydrolysates find application as milk replacers and food flavouring agents. Enzymes like papain, nicin, trypsin, bromelin, pancreatin are used for hydrolysis of fish protein. The process consists of chopping, mincing, cooking, cooling to the desired temperature, hydrolysis, siewing, pasteurizing the liquid, concentrating and vacuum drying or spray drying of the product. This is deliquescent, so care should be taken to keep it in fine air tight bottles. It can be incorporated into beverages as a high energy drink for children and convalescent persons.

**Fish maws and isinglass**

The world isinglass is derived from the Dutch and German words, which have the meaning sturgeon's air bladder or swimming bladders. Not all air bladders are used for this preparation. The air bladder of deep water hake is most suitable for production of isinglass. In India air bladders of eel and catfishes are used for the production of isinglass.

The air bladders are separated from fish and temporarily preserved in salt during transport. On reaching the shore they are split open, washed thoroughly, outer membrane removed by scraping and then air dried. 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 scraper for the removal of any adhering dried material. The rolling process converts the isinglass into thin strips or sheets of 1/8 to ¼" thickness. There are processes for the production of isinglass in powder form also.

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 other such products. Process has been developed to produce the finished products from fish maws.

**Surimi and surimi based products**

Mince processing technology has emerged as one of the most successful techniques for the utilization of fish, especially the unconventional low cost fishes. The first step in the mince technology is the hygienic collection of the meat. Usually mechanical devices called deboning machines are used in which the fish is forced against the perforated surface of a drum and the flesh passes through the openings as a finely ground paste. The mechanically deboned fish meat is more susceptible than intact muscle tissue to quality deterioration, since the mincing operation causes tissue disruption and exposure of flesh to air which accelerates lipid oxidation and autolysis. Generally mince has a shelf life of 6 months if *immediately after deboning it is frozen at* -40ºC and stored at -20ºC.

An important use of fish mince is in the preparation of surimi, which is an intermediate product which because of its characteristic ability to form gels, can be used to develop a variety of products conforming to consumer fancies. Surimi is the myofibrillar protein concentrate produced by repeated washing of fish mince in order to remove water soluble nitrogenous matter and flavour compounds. Washing enhances the gel forming capacity of the structural proteins. Surimi is used as a raw material for the preparation of seafood analogues, but in Japan, surimi is mainly used to prepare the traditional Kamaboko products.

Surimi process involves washing the fish mince in chilled water to remove blood, sarcoplasmic proteins, pigments and odour bearing compounds. The washed mince, which has high concentration of myofibrillar proteins, readily forms gel as a result of unfolding and cross linking of actomyosin, the major muscle protein complex. Gel formation occurs rapidly when surimi is heated at 80-90ºC but also takes place slowly at 40-50ºC and even at 0ºC when held at over night. Surimi paste that has initially been set at 40-50ºC gives a stronger gel if subsequently heated to 80-90ºC.

During gel formation, water is bound by the protein matrix, which is held together by hydrogen and hydrophobic bonds. Optimal gel formation is assisted by 2-3% sodium chloride, which enhances protein solubility. Gel formation is essential for the proper binding of ingredients and for obtaining an acceptable texture. Mixing of appropriate amounts of cryoprotectants to surimi prevents loss of functional properties during frozen storage. Fish having white meat and low fat content is generally used. Alaska Pollock, pacific whiting, hoki, *croaker, lizard fish, barracuda, ribbon fish,* threadfin bream etc. are used for the production of surimi.

***The basic steps of production of surimi***

1. Heading and gutting of fish.
2. Mincing
3. Washing and screening
4. Refining
5. Dehydrating
6. Mixing with cryoprotectants
7. Filling
8. Freezing
9. Packaging
10. Storage

***Technical data of a surimi sample***

| | | |
|---|---|---|
| Colour | - | White – grayish |
| Moisture | - | 72-83% |
| pH | - | 6.8-7.2 |
| Gelatinization temp. | - | 40/90ºC |
| Protein content | - | 16-19% |
| Fat content | - | 0.5% |
| Ash content | - | 0.5% |
| Sucrose | - | 4% |

| | |
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| Sorbitol | - 4% |
| Phosphates | - 0.3% |

*Surimi based products*

Surimi is an intermediate product, which has characteristics gelling and elastic properties. It can be used to develop products that can imitate the appearance, flavour and texture of expensive items like lobster tail, shrimp, scallop, crab leg etc. It can also be used as a substitute for ground beef in certain foods. Texturisation of surimi involves modification of elasticity with ingredients such as egg white, starch, polyphosphates etc. The flour is modified by the addition of salts and extracts of natural seafoods. Following are the traditional surimi products of Japan.

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| Chikuwa | - tube shaped fish paste |
| Kamaboko | - broiled fish paste |
| Satsumaage | - fried fish paste product |
| Hampen | - floating type boiled fish paste |

Diversified traditional products like Kanikam (artificial crab leg), hampen, cheese sandwiched hampen, easy to eat kamaboko, Satsuma age with hampen taste, squid surimi kamaboko are also being marketed in Japan

**Byproducts from shark**

***Shark fins***

Shark fins are in great demand particularly among the Chinese for making ceremonial dish called shark fin soup. Dried shark fin is an item of export from India mostly to Singapore, Hongkong and United Kingdom. The preparation of shark fin does not require any elaborate treatment, but care is needed in cutting, trimming and drying operation.

***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 cartilages present and physical presentation etc. The process of extracting good quality shark fin rays is simple and can be adopted even in small fishing villages by the fisherman. There is good scope for 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. The production process is essentially the same as that followed for making leather from animal hides. The principal constituent of leather is collagen.

***Shark teeth and bones***

Shark teeth and bones have become an export commodity in recent years. The tooth has become an export commodity to countries like USA, U.K., Canada and Australia. This is used as ornaments for ladies. Among the various species, tiger shark teeth has greater demand due to its more attractive shape and size.

***Shark bones***

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

**Utilization of prawn shell waste**

The head and shall of prawn and other crustaceans form the major fishery waste. The waste contains a good percentage of protein and chitin other than minerals. The protein can be extracted along with the flavour bearing compounds and converted into shrimp extract having potential use as a natural flavouring material. Chitosan, a deacetylated chitin, is one of such products, which has application in many fields. It is a *modified* natural carbohydrate polymer. It is a cationic polyelectrolite, insoluble in water, organic solvents and alkaline solutions and is soluble in most organic acids, and dilute mineral acids except sulphuric acid. It can form ionic bonds and films. Chitosan finds applications in many industries.

### *Chitin*

The residual shell waste obtained after extraction of protein with hot 0.5% caustic soda may contain small amounts of protein. This is then removed by boiling with 3% caustic soda for few minutes and filtering off the liquor. It should be washed free of alkali before demineralisation. The demineralization is done by treatment with dil. hydrochloric acid at room temperature. Demineralization reduces the volume of the shell considerably and therefore deproteiniser can hold more material if the demineralization 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 and diluting 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 can be separated by adding alcohol.

### *Chitosan*

Chitin is dried or centrifuged or pressed to remove water. The deacetylation of chilin is done by heating at 90-95$^{0}$C with 40% (w/w) caustic soda for 90-120 min. 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 the dissolution is completed 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 drier at a temperature not exceeding 80$^{0}$C and pulverized to coarse particles.

Chitosan is almost colourless, light in weight and soluble in dilute organic acids but soluble in water, alkali and organic solvents. It gives viscous solution when dissolved in dilute 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 haemostatic agent

Wound healing

Biodegradable films as a substitute for artificial skins for removing toxic heavy metals

Wine clarification, industrial effluent flocculation, agriculture, photography, cosmetic applications and textiles

### As a human health diet

There is very good demand for sea food based products in ready to eat/ready to cook convenience form. There are number of products prepared from low cost fishes which have very good demand.

### Fish soup powder

Fish soup powder can be formulated from any type of fish having very low fat content. There are different types of soup available in the market. These are dry products rich in dietary constituents like protein and minerals. The soup powder prepared out of miscellaneous fish is also a rich source of animal protein and other nutritional factors.

**Fish flakes or wafers**

Fish wafers are partially deodourized thin flakes of cooked fish meat homogenized with starch and salt. On frying the wafers well to two to three times of its initial size and become crisp and delicious. It is an ideal snack. Fish mince and starch are the base materials for the preparation of wafers.

*Ingredients*

| | |
|---|---|
| Cooked fish meat | - 2kg |
| Refined tapioca starch | - 2kg |
| Corn starch | - 1kg |
| Common salt | - 5% |
| Water | - 3.5 L |

*Process*

The cooked fish meat is homogenized in a wet food grinder. Starch, salt and water are added and continued grinding till they become a fine paste. Small portions of the homogenized mass is poured into a flat aluminium tray and spread a film of 1 to 2mm thickness. The material is cooked in a steam chamber for 2 to 3 minutes to gelatinize the starch. After this the film becomes firm and it can be cut in to desired shapes. The gelatinized flakes are dried in an electrical drier at 45-50°C or it can be sun dried. Fry in edible oil and serve hot.

**Fish noodles**

This is similar to ordinary noodles available in the market, but contains 21% protein. Surimi is used as the base for the production of fish noodles. Cooked surimi is kneaded with salt and maida. The mix is allowed to pass through the extruder.

Gelatinized noodle is dried under sun or in an electrical drier at 50°C to a moisture level of 8%. The dried noodle is packed in air tight containers or polythene bags. The product has good dehydration property.