Byproducts and Specialty Products from Low cost Fish and Fishery Waste

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Modern fish processing industry in India is five decades old. Over the years, the export of marine products increased and recorded 4.6 lakhs tones, worth rupees six thousand and eight hundred crores in 2003. This phenomenal increase of export of marine products and development of fish processing industry has been more or less based on a single item namely frozen prawn which constituted about 28.58% in volume and 66.97% in value of the total export of marine products from India.

A majority of marine fish landed comes as bycatch from shrimp trawlers. The low priced miscellaneous fish are generally discarded in the sea or converted to fishmeal. In the tropics, small fish contributes 80% of the catch. As this bycatch does not yield good price, these are not subjected to ideal pre process handling techniques like chilling and packaging. However, being a valuable protein source these can be further processed in to variety of value added products, which are stable at ambient temperatures and can easily be transported.

Fish meal

One of the important byproduct is fishmeal produced mainly from under utilized miscellaneous fish and bycatch. Fishmeal is a highly concentrated nutritious feed supplement consisting of high quality protein, minerals, vitamins (particularly B group) and other unknown growth factors. Fishmeal is rich in all essential amino acids. It is prepared from whole miscellaneous fish mainly caught along with prawns or from suitable waste from processing like filleting etc. Important species of fish which are mainly used for fishmeal include jew fish, small fishes from the group sole, silver bellies, ribbon fish etc. Other raw materials used for fishmeal production are fish waste from fish canneries. The composition of fishmeal differs considerably due to the variations in the raw material used and in the processing methods and conditions employed.

Traditional fishmeal production in India was from the sun-dried fish collected from various drying centers all along the coast and the products were mainly used as manure. Better quality fishmeal has been a prominent item of export from the very beginning. Indian standards Institution has brought out the Indian Standards Specification for fishmeal as livestock feed for facilitating proper quality control.

Table. The proximate composition of meal

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

Manufacturing process

Fish can be reduced to fish meal by two general processes namely dry rendering and wet rendering.

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, the fish 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 dryer. The cooker dryer may be operated at atmospheric pressure or under partial vacuum. Being batch operation the process has only limited capacity and labour cost will be 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 fishmeal 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 pressed cake, drying, grinding and packing the meal. The press liquor is centrifuged to remove suspended particles and to separate oil and concentrating the stick water. 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 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 and 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 fishmeal present in the press liquor is separated by centrifugal sedimentation and the oil is collected 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 fish oil industry reveals that the extraction is done on a cottage scale in isolated places near the landing centres and is not well organized. The method of extraction followed is cooking the fish in iron vessels followed by pressing and separating the oil. Apart from sardine oil, fish body oil is also obtained from the fishmeal plants operating in the country. In India oil sardine is a fishery, which exhibits 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 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 oil revealed that they contain high amounts of polyunsaturated fatty acids (PUFA).

Fish liver oil

The therapeutic values of fish liver oil were discovered in 18th century and fish

liver oil is a common medicinal product especially for Vitamin A and Vitamin D. Cod, shark and haddock livers are the important source of Vitamins 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 was 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 liver contains about 45% to 67% oil. The species of shark such as dog fish (*Squalus acanthias*), Greenland shark (*Somniosus microcephalus*) and basking shark (*Certrohinus maximus*) have large fatty liver 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 percentage. Depending on the oil content and vitamin A potency fish livers are generally classified in to three groups.

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

Processing and storage

The processing procedure 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.

Squalene, a highly unsaturated aliphatic hydrocarbon, is present in certain shark liver oils, mainly of the family squalidae and cod. Chemically known as 2,6,10,15,19,23 hexamethyl, 2, 6, 10, 14, 18, 22 tetracosahexaene, squalene has a wide commercial application.

Vitamin oils are stored in rust free, well washed and dried airtight drums. The headspace should be kept minimum to avoid oxidation. It is advisable to fill head space with an 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, α tocopherol, BHT, NDGA etc. can be used to preserve the oil for longer periods.

Fish silage

Fish silage can be defined as a product made from whole fish or parts of the fish to which no other material other than acid has been added and in which the 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 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, cuttle fish/ squid waste etc. can be used for the preparation of silage. The production of silage involves 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. Fish silage

is also prepared by fermentation. 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.

Fish protein concentrate

Fish protein concentrate (FPC) is a stable fish preparation, intended for human consumption. Fishmeal, as produced throughout the world is a low cost 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 rancid fat is unacceptable to consumers. There is a 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 type of FPC as stated below.

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 of flavour, but definitely having a fishy flavour and a maximum fat content of 3%.

Type C: Normal fishmeal 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 consumer non-acceptance.

Fish hydrolysates

Fish hydrolysate is also liquefied fish product but it differs from silage. It is produced by a process employing commercially available proteolytic enzymes for hydrolysis of protein from fish waste. By selection of suitable enzymes and controlling the conditions, the properties of the end product can be modified. Hydrolysates find application as milk replacement and food flavouring agents. Enzymes like papain, ficin, trypsin, bromelin and 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 or spray drying of the product. This is a deliquescent product and therefore care should be taken to keep it in airtight bottles. It can be incorporated in to beverages as a high-energy drink for children and convalescent persons.

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. 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 is 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 1/4" 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. 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 forms 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. Generally mechanical devices called debonning 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 debonned 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 frozen immediately at -40°C and stored at -20°C.

An important use of fish mince is in the preparation of surimi, which is an intermediate product in the formulation of a number of value -added products. Because of its characteristic ability to form gels, it finds application in developing a variety of products conforming to consumer fancies. Surimi is myofibrillar protein concentrate produced by repeated washing of fish mince in order 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. 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.

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 the surimi prevents loss of functional properties during frozen storage. Fish having white meat and low fat content is generally used for the production of surimi and the fish which are most sought after include Alaska Pollock, pacific whiting,

hoki, croaker, lizard fish, barracuda, ribbon fish, threadfin bream etc.

The basic steps of production of surimi are heading and gutting of fish, mincing, washing and screening, refining, dehydrating, mixing with cryoprotectants, freezing, packaging and storage.

Table 2. General characteristics of surimi

Colour	White – grayish
Moisture	72-83%
pH	6.8-7.2
Gelation temp	40/90°C
Protein content	16-19%
Fat content	0.5%
Ash content	0.5%
Sucrose	4.0%
Sorbitol	4.0%
Phosphates	0.3%

Surimi-based products

Surimi is an intermediate product, which has characteristics gelling and elastic properties. It is 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. Following are the traditional surimi products of Japan.

Chikuwa - tube shaped fish paste

Kamaboko - boiled fish paste

Satsumaage - fried fish paste product

Hampen - floating type boiled fish paste

Diversified traditional products like Kanikama (artificial crab leg) hampen, cheese sandwiched hampen, easy to eat kamaboka, Satsuma age with hampen taste, squid surumi 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 operations.

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, lengths 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 fishermen. 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 year. 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 are in greater demand due to its more attractive shape and size.

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.

Utilization of prawn shell waste

The head and shell 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 hearing compounds and converted into shrimp extract having potential use as a natural flavouring material. Chitin and Chitosan, manufactured from prawn shell have applications in many fields.

Chitin

The residual shell waste obtained after extraction of protein with hot 0.5% caustic soda may contain small amounts of protein. The protein is removed by boiling with 3% caustic soda for few minutes and filtering of the liquor. After neutalisation, demineralization is done by treatment with dilute hydrochloric acid at room temperature.

Chitosan

Chitin is dried or centrifuged or pressed to remove water. The deacetylation is done by heating at 90-95°C with 40% (w/w) caustic soda for 90-120 min. 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 after fortification if necessary. The residue is washed with water till free of alkali. It is then centrifuged and dried in the sun or an artificial drier at a temperature not exceeding 80°C and pulverized to coarse particles.

Chitosan is almost colourless, light in weight and soluble in dilute organic acids but insoluble 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 namely 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.

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 mother liquor by adding alcohol.

Products as a human health diet

There is a very good demand for seafood-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 powder available in the market. There are dry products rich in dietary constituents like protein and minerals. The soup powder prepared out of miscellaneous fish is also rich source of animal protein and other nutritional factors.

Fish flakes or wafers

Fish wafers are partially deodorized fish meat homogenized with starch and salt and made in to thin flakes. On frying, the wafers swell to two to three times of its initial size and become crisp and delicious, making it an ideal snack. Fish mince and starch are the base materials for the preparation of wafers. Beside cooked fish meat, refined tapioca starch, corn starch, salt and water are other ingredients in the preparation of fish wafers.

Fish noodles

This is similar to ordinary noodles available in the market, but contains high proportion of fish 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 pas through the extruder. Gelatinized noodle is dried under sun or in an electrical drier at 50°C to a moisture level of 30%. The dried noodle is packed in airtight containers or polythene bags. The product has good rehydration property.