

High Value Products from Fish Processing Wastes

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Processing of fish for human consumption results in enormous quantity of waste in the form of skin, head, viscera, scales, bones, trimmings and frames. The quantity of waste generated depend on the type and size of fish and the product manufactured out of it. Industrial fish processing for human consumption yields only 40% edible flesh and the remaining 60% is thrown away as waste. Annual discard from the world fisheries were estimated to be approximately 20 million tonnes (25%) per year which includes “waste” or by-products also. The immense scope for high end product from fishery waste has been realized and different technologies have been developed with a view to utilize processing waste, for converting them into products for human consumption, animal nutrients and products of pharmaceutical and nutraceutical significance. Among the most prominent current uses for fish waste are fishmeal production, extraction of collagen and antioxidants, isolation of cosmetics, biogas/biodiesel, production of chitin and chitosan, food packaging (gelatin, chitosan) and enzyme isolation. Fish waste is prone to faster spoilage since it contains easily digestible protein. The microbial population associated with the digestive process are the major reasons of spoilage. Since the processor does not bother to preserve the waste the problem of environmental pollution is enhanced. Accumulation of fishery waste results in nauseating and obnoxious smell due to the release of volatile nitrogenous compounds during decomposition.

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, miscellaneous fish, filleting waste, waste from canneries and 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 centers and the products were mainly used as manure. Better quality fish meal has been a prominent item of export from the very beginning of this industry. 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 devices 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 dryer 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 India 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 centers 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 oil content of 17%. By the wet rendering process the fish will yield, on 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). At present the medicinal values of fish oils are well known.

Fish liver oil

The therapeutic value of fish liver oil was discovered in 18th 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. The 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 in to 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 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.

Presentation and storage

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 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, α tocopherol, BHT, NDGA can be used to preserve the oil for longer periods.

Fish hydrolysates

This is also liquefied fish product but it differs from silage. They 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 replacer and food flavouring agents. Enzymes like papain, nisin, trypsin, bromelein, pancreatin are used for hydrolysis of fish protein. The process consists of chopping, mincing, cooking, cooling to the desired temperature, hydrolysis, sieving, 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 airtight bottles. It can be

incorporated in to 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 deepwater 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 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.

Fish Gelatin

Skin of fish constitute nearly 3% of the total weight and is suitable for the extraction of gelatin. Bones and scales can also be processed into gelatin. The process involves alternate washing of skin with alkali and acid and extracting gelatin with hot water. Gelatin finds applications in pharmaceutical products as encapsulation and in food industry as gelling agent. Fish gelatin has better release of a product's aroma and flavor with less inherent off-flavor and off-odor than a commercial pork gelatin.

Fish calcium

The recommended daily intake of calcium is 1000 mg for the adults, and 1300 mg for elderly women. Fish bones and scales are excellent source of calcium. Whole small fish or fish bone/scale can be used for calcium separation. The filleting frames of carps and other fishes can be used for extraction of calcium. The frames are washed and boiled to separate the adhering meat portions. It is washed again and treated with enzymes to remove the adhering connective tissue, washed, dried and powdered. Fish calcium is essentially dicalcium phosphate which has better nutritional qualities.

Hydroxyapatite

The hydroxyapatite extracted from the scale are having uses as bioceramic coatings and bone fillers. The coatings of hydroxyapatite are often applied to metallic implants to alter the surface properties so as to avoid rejection by the body. Similarly,

hydroxyapatite can be employed in forms such as powders, porous blocks or beads to fill bone defects or voids. For permanent filling of teeth hydroxyapatite is found to be a better option for import substitution.

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 bearing compounds and converted into shrimp extract having potential use as a natural flavoring 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 polyelectrolyte, 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 dilute 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 is done by heating at 90-95°C with 40% (w/w) caustic soda for 90-120 min. The water present in the chitin cake should also be taken in to 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°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 viz; 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 treatment, agriculture, photography, cosmetic applications and textiles, and in nano applications.

Conclusion.

Since the fresh water aquaculture is increasing every year the future utilization and development of high value items from this sector has high potential. Hence utilization of fishery waste for the development of high value products is gaining importance in recent years. A variety of by products can be developed which is found to have different applications in medical, food, and other fields. By simple cost effective techniques, valuable products can be developed which will enhance the revenue of the fishermen and allied industries. In fact, the materials which caused problems to the fish processing industry due to the environmental pollution has become raw materials for valuable products with versatile application
