High Value Secondary Products from Fish Processing Discards

A. Jeyakumari
Fish Processing Division
ICAR-Central Institute of Fisheries Technology, Cochin
Email: jeya131@gmail.com

Processing of seafood for human consumption results in enormous quantity of waste in theform of skin, head, viscera, scales, bones, trimmings and frames. The quantity of waste generateddepend on the type and size of fish and the product manufactured out of it. Industrial fishprocessing for human consumption yields only 40% edible flesh and the remaining 60% is thrownaway as waste. Fishery 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 fisherywaste results in nauseating and obnoxious smell due to the release of volatile nitrogenous compounds during decomposition.

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. The fish waste utilization technology evolved by ICAR-CIFT helps to eliminate harmful environmental effects and improve quality in fish processing. Research carried out at the Central Institute of Fisheries Technology, Cochin, paved the way for production of valuable food and industrial products namely protein extract, chitin, chitosan and its derivatives and glucosamine hydrochloride from the head and shell waste of prawns, crab and squilla.

1.0 Nature and composition of secondary raw materials from seafood processing

In seafood industry, the general understanding is that the edible meat part constitute about main raw material and the remaining parts include head, trimmings, skin, viscera, scale, bone etc. Quantum of secondary raw materials generated in seafood industry depends on several factors, which may be broadly categorised into resource related factors and process related factors. The former category includes species, size, age, biological nature (including presence of toxins and allergens) and morphological features. Generally, 40- 70% of original raw material is discarded in commercial processing operations depending on intended product, style of dressing, type of handling (manual/ mechanical), skill of handling person, intended use and to a greater extent on the quality of raw material. Largely, seafood processing operations generate both liquid and solid wastes; solid waste being the bulk ranging from 30% to 65% of the weight of the landed fish. Head, viscera, skin, fin, swim bladder, bone, frame meat, dark meat, scale, gills, shells (crustacean, mollusca), cephalopod pen, ink sac etc. are the major components of solid waste. The liquid effluents mainly consist of blood, slime, mucus, wash off and other soluble. In surimi processing, soluble proteins are washed off to a greater extent during repeated water washing steps.

Table 1. Percentage of waste generated (%) during seafood processing

Products	**Waste Generated (%; w/w)**
Shrimp products (peeled and deveined, peeled and undeveined, Headless etc.)	50
Fish fillets	70
Fish steaks	30
Whole and gutted fish	10
Surimi	70
Cuttle fish rings	50
Cuttle fish whole	30
Cuttle fish fillets	50
Squids whole cleaned	20
Squid tubes	50
Squid rings	55

Table 2. Seafood products and their respective waste

Major Sea food Products	Major Waste	Major Compounds
Fish based Product	Head, frames, skin, intestine, roe, tails, fins, scales, etc.	Protein, fat, Minerals, enzymes, Chondroitin, Fe
Shrimp based products	Carapace (head) Telson (tail) Rostrum Antennae Appendages Eggs Cook juice	Chitin, Protein, Pigments
Frozen Squid (Whole Cleaned, Fillet, Rings	head behind the tentacles Visceral mass Beak Ink sac and ink Squid pen Skin membrane	Protein, Enzymes, Melanin, Chitin
Cuttlefish (Whole cleaned, deskinned	head behind the tentacles Visceral mass hard Beak Ink sac and ink Cuttle bone Skin membrane	Protein, Enzymes, Melanin, Chitin
Lobster Meat	Lobster shell Appendages	Chitin
Pasteurized crab meat	Crab shell	Chitin Pigments
Fish products (fillet, surimi)	Head Frame/bone Skin Scales Gills Fins Visceral mass Wash water	Proteins Lipids Enzymes Minerals
Frozen clam/Mussels	Shells Shuck water	Calcium oxide Protein

2.0 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. As per FAO projection, by 2025, fish meal produced from fish waste will represent 38% of world fish meal production, compared with 29% for the 2013 to 2015 average level.

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

Protein - 50-57%

Fat - 5-10%

Ash - 12-33%

Moisture - 6-10

2.1 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.

2.2 Fish liver oil

The therapeutic value of fish liver oil was discovered in 18th century and fish liver oil become 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

2.3 Squalene from shark liver oil

Liver oils of some deep-sea sharks mainly Centrophorus sp. It contains 85% – 90% unsaponifiable matter which contains the hydrocarbon squalene. Squalene and its hydrogenated product are used for several decades as base for cosmetic products. It also used as skin rejuvenating agent. It is mild on human skin and imparts softness without oily appearance. The demand of squalene by cosmetic and pharmaceutical industry is on increase. Realizing the importance, ICAR- CIFT has developed a method of extraction, isolation and purification of squalene from shark liver oil

2.4 Fish silage

The product of the process of preserving and storing wet biological material in a silo (a pit or airtight container) is called silage. Fish silage is a liquid product and it can be prepared from whole fish or fish waste by adding acid, enzymes, lactic acid producing bacteria or by naturally occurring enzymes in fish. Fish silage is rich in protein and aminoacids and it can be used as protein source for animal feeding. Production cost for fish silage is very cheap, cost effective and eco-friendly. Fish silage preparation usually depends on locally available raw materials and conditions (Hasan, 2003). Depending on the process employed, fish silage can be categorized into two methods, viz. acid silage and bio-fermented silage. Acid silage is produced by mixing fish waste with organic acid (formic acid, acetic acid, propionic acid), inorganic (sulphuric acid, hydrochloric acid) and or a mixture of both organic and inorganic acid. In case of bio-fermented silage, fermentation process is carried out by lactic acid bacteria (LAB) which are already present in a fish mass or added externally.

2.5 Protein Compounds from secondary raw material

2.5.1 Fish hydrolysates

Fish protein hydrolysate is a product prepared from proteins sourced from fish meat/fish processing by products via enzymatic or chemical process. Enzymatically produced hydrolysates are widely accepted which contain mixture of peptides of varying sizes and free amino acids. 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. Enzymes like papain, nisin, trypsin, bromelein, pancreatin are used for hydrolysis of fish protein. Hydrolysates find application as milk replacer and food flavouring agents. The proximate composition of fish protein hydrolysate would vary with the raw material (head, bone, skin, viscera), type of process, type of drying, extent of hydrolysis and any other pre-treatment of raw material. Fish protein hydrolysate are proven to have specific health role other than the nutritional benefit. Protein hydrolysates or peptides present in the hydrolysate have demonstrated to have antioxidant, anti-obesity, immune modulation, anticoagulation, anti-microbial, anticancer and antihypertension etc.

2.5.2 Fish Gelatin

Fish skin and scales which constitutes about 30% and 5% of the total seafood processing discards,respectively are considered as the richest source for collagen and gelatin, which have wideapplications in nutraceutical product development due to its biocompatibility, biodegradability,and bioactive properties like antioxidant, antimicrobial, antihypertensive. Skin of fish constitutenearly 3% of the total weight and is suitable for the extraction of gelatin. Bones and scales can alsobe processed into gelatin. The process involves alternate washing of skin with alkali and acid andextracting gelatin with hot water. Gelatin finds applications in pharmaceutical products asencapsulation and in food industry as gelling agent. Fish gelatin has better aroma and flavor with less inherent off-flavor and off-odor than a commercial pork gelatin.

2.5.3 Fish collagen

Collagen is a structural protein having a characteristics triple helix structure. Collagen is insoluble in water and fibrous in nature. Approximate molecular weight of a collagen molecule is 300KDa. Collagen derived from fish is generally of Type I and Type III. Type I and Type III collagen are the building blocks for connective tissues, bones and skins. Collagen is not soluble in water. However, fish type I collagen is unique in its extremely high solubility in dilute acid compared to avian and mammalian collagen. The solubility of collagen is affected by the pH and NaCl concentration of the solution

2.5.4 Collagen and gelatin hydrolysates

Although collagen/gelatin has several functional properties, its bioactivity is lower due to its high molecular weight. Hydrolyzing will enhance the bioactivities of the collagen/gelatin. Collagen or gelatin hydrolysates are produced by controlled hydrolysis of collagen or gelatin. Acid, alkali, enzyme or heat may be used for hydrolysis. During hydrolysis the peptide bonds are broken down producing low molecular weight peptides. The molecular weight of hydrolysate is generally in the range of 5.0-25 kDa

2.5.5 Fish maws/ isinglass

The world isinglass is derived from the Dutch and German words, which have the meaning ' air bladder of deepwater hake is most suitable for production of isinglass. In India air bladders ofeel and catfishes are used for the production of isinglass. The air bladders are separated from fishand 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 ¼" for the production of isinglass in powder form also. Isinglassdissolves readily in most dilute acids or alkalis, but is insoluble in alcohol. It is used as a clarifyingagent for beverages like wine, beer, vinegar etc.

2.5.6 Fish enzymes

Fish visceral waste contains rich sources of enzymes, which have potential applications in different sector includes food, biomolecule extraction, descaling of fish, stain removal and pharmaceutical applications. It has been reported that fish visceral waste contains rich source of proteolytic enzymes namely, pepsin, trypsin, chymotrypsin and collagenases. Enzyme extracted from marine sources has found application in Fish curing and fermentation, hydrolysed products production, pigment extraction, wastewater treatment and meat tenderizing. These enzymes also used as a component of biosensor for rapid assessment of fish quality.

2.5.7 Hemoproteins and Carotenoproteins

Hemoproteins are complex proteins, composed of a protein molecule and a non-protein compound (prosthetic group). Hemoglobin and myoglobin belong to the category of hemoproteins involves in transport of oxygen in the blood and tissues of animals, respectively. The heme portion can be recovered from blood as well as muscles discards. The recovered material may be used iron supplement or as a chemical substrate for production of the cooked cured-meat pigment. During the production of hydrolyzates from meat, hemin could be recovered as by-product.

Carotenoproteins and carotenoids are other classes of compounds found in the flesh and skin of fishes and in the exoskeleton of shellfish. Astaxanthin, a ketocarotenoid pigment naturallyfound in crustaceans and represent 74 and 98% of the total pigments. It has found wide applicationin food, feed, pharmaceutical and cosmetic products. It is also used as dietary supplement with very potent antioxidant effect for human health.

2.6 Mineral compound from secondary raw material

2.6.1 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. The hydrolysis of collagen or gelatin yields bioactive peptides that have great potential in processing industries as natural preservatives. Collagen and gelatin peptides are known to have excellent antioxidant properties unlike its parent molecules. Recently gelatin hydrolysate has been explored as plastisizer in protein film, identified as antihypertensive, cryoprotectant in additions to its wide known antioxidant activity.

2.6.2 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.

2.7 Polymer compound from secondary raw material

2.7.1 Chitin

Chitin is the most abundant organic compound next to cellulose in the earth. Chitin represents 14-27% and 13-15% of the dry weight of shrimp and crab processing waste, respectively. Chitin is present as chitin-protein complex along with minerals mainly calcium carbonate. So the process of chitin production consists of deproteinisation with dilute alkali and demineralization with dilute acids. Chitin on deacetylation gives chitosan and on hydrolysis with concentrated HCl gives glucosamine hydrochloride.

2.7.2 Chitosan

Chitosan is prepared by deacetylation of chitin. 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 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

2.7.3 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.

2.7.4 Chitosan derivatives

Chitosan is not soluble in water but is soluble in dilute acid solutions like 1 % acetic acid. This has limited its applications in water soluble environments like human health and plant protection. Hence, the free amino and hydroxyl groups can be derivatized with new molecules to improve the functional properties of Chitosan. Advantages of Chitosan derivatives includes They are biodegradable and biocompatible; They are non-toxic and water soluble; They can be modified to impart special properties. Examples for chitosan derivatives are **N**-Trimethylene chloride Chitosan (TMC), Esters of chitosan with glutamate, succinate and phthalate Carboxymethyl chitosan (CM-Chitosan).

Major Applications of Chitosan derivatives includes 1) Controlled release and drugdelivery 2) Scaffolds for biomedical applications like stents, organs 3) Tissue engineering, woundhealing and regenerative medicine 4) Food supplements and natural preservatives 5) Anti-viral andanti-tumor applications 6) Bio-composite materials with functional properties

CIFT has developed technology for production of chitin, chitosan, glucosamine hydrochloride and carboxymethyl chitosan from prawn shell waste.

2.8 Other High value product from secondary raw material

2.8.1 Pearl essence

Pearl essence is the suspension of crystalline guanine in water or organic solvent. Guanine is an iridescent material found in the epidermal layers and scales of most pelagic species of fish likeoil sardine, mackerel, herring etc. When guanine particles are deposited on the inside surface ofsolid beads, an optical effect similar to that of real pearl is obtained. It is used in the manufactureof artificial pearls. It is also used on diverse articles such as shoe, pencil, fishing rod and spectacle frame

2.8.2 Shark cartilage

The skeleton of shark is made of cartilaginous bones, which is about 10-15% of the body weight. Until recently, only very small quantity of these bones was made use of, that too from the small shark, for making buttons and necklaces. This cartilage is rich in chondroitin sulphate which has got application in medicine for treatment of atherosclerosis, blood vessel thrombosis and also to prevent infections. Now there is very good demand from Europe, USA and Australia for processed shark bones. The collected head and vertebral column of the shark are to be processed to a presentable and stable form before export. A procedure has been developed for the processing of the cartilage into a clean, dry, white, attractive material without any characteristic smell. The products are well accepted by the overseas buyers. The ban on shark fisheries is going to affect all these products, as mentioned above.

2.8.3 Shark fin rays

Shark fin rays are valuable products of export from India. Formerly, only shark fins were being exported. But now, fin rays are extracted and exported. CIFT has developed a technique for extracting rays from shark fins. The dried fins are soaked in dilute acetic acid for sufficient time to get the muscle and skin softened. The skin is then scraped off and the fins further treated with the dilute acetic acid when separation of the rays in clusters becomes easy. The rays are then dried and packed in polyethylene bags. The rays are utilised in the preparation of soup in many foreign countries. There is good internal demand also for shark fin rays especially in major star hotels.

2.8.4 Shark leather

Skin from both demersal as well as pelagic fish varieties are suitable for the leather production. Skins of shark can be processed into fine leather suitable for manufacture of fancy items. Leather tanned from Indian shark skin is about one and half times superior to that from cow hides in strength and durability. Shark skin has a protective coating of a calcareous deposit known as “Shagreen”. It is used as a suitable raw material for manufacture of suitcases, shoes, belts etc.

3.0 Conclusion

Seafood waste is prone to faster spoilage since it contains easily digestible protein and enzymes. The microbial population associated with the digestive process are the major reasons of spoilage. Accumulation of fishery waste results in nauseating and obnoxious smell due to the release of volatile nitrogenous compounds during decomposition. Hence utilization of seafood waste and development of high value product has high potential 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.