5. VALUE ADDED PRODUCTS FROM SECONDARY RAW MATERIALS

Binsi P.K.

Fish Processing Division, ICAR-Central Institute of Fisheries Technology, Cochin

* zynu@rediffmail.com

Introduction

With growing population, waste generation is also increasing and major proportion of by-products generated by contemporary food remains underutilized which may often contain high-value substances. Crucial problem faced by industries and society during food processing is disposal of food waste. Seafood items are rich in several valuable nutrients and other useful components. The rising global demand for the community is witnessing an increasing quantity of processed seafood entering world markets. Commercial processing of seafood items for diverse products results in significant amounts of wastes consisting of shells, heads, intestines, scales, bones, fins, etc. Moreover, fishing operations aimed at popular species also lead to the capture of substantial amounts of fish that are commercially nonviable and, therefore, regarded as by-catch. Currently, most of these materials are discarded as landfill or converted on a limited scale into products such as animal feed and leather, which leads to serious environmental hazards. With rapid developments in biotechnology there is vast scope to make use of the wastes as sources of valuable nutraceuticals and other ingredients, which encompass proteins including collagen and gelatin, protein hydrolyzates, bioactive peptides, lipids rich in polyunsaturated fatty acids, squalene, carotenoids, polysaccharides such as chitin, chitosan, glycosaminoglycans and their derivatives, mineral-based nutraceuticals, among others. These products, depending upon their characteristics, have potential for various applications such as natural food additives, bioactive compounds, nutraceuticals, medicinal drugs, biodegradable packaging, and as encapsulation materials for diverse nutraceuticals. This chapter highlights the potential benefits of secondary processing of seafood discards, for the isolation of various valuable compounds, such as unsaturated oils, carotenoids, minerals, fine biochemicals, enzymes, proteins, nucleic acids and pharmaceuticals, antimicrobials, antioxidants, enzyme inhibitors, and other bioactive compounds.

The food and nutritional value of fishery products have been well recognized in the last few decades. The diverse species of fish and shellfish from varied marine environments provide opportunities for the development of food products with different flavor, high nutritional value, and hence good consumer acceptance, which has resulted in a rising global demand for the commodity. Historically, fish has been considered as an important food source and even today it is one of the most traded commodities in international markets. Interestingly, about 15% of the world requirement for animal proteins is being met from fish alone which accounts to 4–5% of the calculated minimum requirements for protein (Guerard et al., 2005). The estimate in 2013, indicated a slightly higher value of 17% which account to 6.7% of all protein consumed (Seafish, 2014). However, there are growing concerns about the sustainability and management of seafood industry, in parallel with the increasing global demand for seafood. Recent reports project a figure of US$ 50 billion as the loss from seafood sector every year, due to poor management of available resources. Wastes are generated at different points in the value chain, viz. by-catch, onboard handling, landing centres, transportation, storage, retailers, and consumers. The waste generation begins with the practice of ‘discard at sea’ of unintentional catches. Subsequently, during processing operations, only the muscle parts are consumed and the rest is discarded. Global fish waste generation is estimated to be in excess of 100 mMT, and in the Indian scenario it is >4 mMT. It is estimated that fish processing waste after filleting accounts for approximately 75% of the total fish weight. This figure is too high before the challenging task of feeding the 9 billions of world population by the middle of this century.

Waste and By-products: Global Terminologies

In literature, quite often by-products, waste, discards etc are cited as alternate terms. However, a cleardistinction between by-products that can be used for human consumption and waste ⁄ discards ⁄ viscera is made in regulatory papers (Rustad, 2003). The term ‘waste’ includes the remnants that cannot be recycled or converted to another high value products, and have to be composted, burned or destroyed (Bekkevold & Olafsen, 2007). On the other hand, the term ‘by-products’ refers to the left outs that are not generally regarded as conventional marketable products, but can be converted to industrial or edible products. Whereas, the EC regulation on animal by-products (ECNr 1774 ⁄ 2002, 2002), adopted on 3 October 2002, definesanimal by-products as whole carcasses or parts of animalsor products not intended for human consumption; by-products intended for human consumptionis not included in this definition. There are several other terms in usage to alternatively represent the by-products,such as waste via co-products or co-streams etc. Lately, as more and more research evidences were mounted on the potential biomolecules derived from marine sources, especially from fish other than meat part, there is a raising tendency to treat these as raw material rather than 'discards/waste'. Consequently, the term 'rest raw material' and 'secondary raw material' is the newly evolved expression today to highlight the importance of treating these materials as equivalent to 'targeted product'. Moreover, the term 'by-product' is an overqualified term as these materials only for the raw material for a value-added by-product, and not exactly the product. For instance, fish skin is a rest raw material, whereas collagen is a by-product.

Global waste generation Profile

In seafood industry, the general understanding is that the edible meat part constitute forms the 'main product' and the remaining parts including head, trimmings, skin, viscera, scale, bone etc. are considered as 'left over', now as 'rest raw material/secondary raw material'. In a different angle, this perception is a bit ironical. This becomes more apparent, when a global estimate of waste generation profile is taken in to account. The amount of waste generated from seafood sector begins at the site of harvest itself. For the last few decades, the FAO estimate on postharvest losses in seafood sector remains to be 20-35% of the catch, at various stages of value chain. Approximately, 17.9 to 39.5 million tonnes of whole fish is discarded each year by commercial fishing operations. Apart from the quality losses in the supply chain, worldwide, around 130 million tonnes of fish waste is produced each year, which is approximated to more than 75% of total fish production. Normally in capture fisheries, a considerable portion of marine catch is dumped back to the sea, either as untargeted catch or as 'discards' in the case where on-board processing activities are carried out. Generally, bulk of demersal catch is processed on board. As the waste material is rarely landed onshore, a considerable proportion (11%) of the total capture biomass is disposed of at sea, mainly in the form of viscera and heads. This figure may be a bit less in the case of culture fisheries.

Table 1: Waste generation during industrial processing of fish in India

Products	Waste Generated (%; w/w)
Shrimp products	50
Fish fillets	65
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

Nature and composition of secondary raw materials from seafood industry

The nature and 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

Global utilisation pattern of secondary raw materials

Presently, a major portion of the discards and low value catch, mainly pelagic varieties, are going for the production of fish meal and oil, which accounts to as much 30% of the world’s total catch. A significant, but declining, proportion of world fisheries production is processed into fishmeal and fish oil thereby contributing indirectly to human consumption when they are used as feed in aquaculture and livestock raising. 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. Apart from fishmeal, a reasonable portion is going for fermented products such as fish sauce and silage. Norway is the main producer of fish silage that is used almost entirely for feed. A meagre portion is used for human consumption, to the tune of maximum 10%.

Value addition options and opportunities

Generally, two different methods, mass transformation and sorting, have been developed to improve the economic value of fish wastes. Mass transformation involves the conversion of fish waste into a single product. Sorting enables the production of specialised products such as liver oil, gelatin, omega-3, protein containing sports food and drinks, calcium, cosmetics, and pharmaceuticals. Wider acceptance and adoption of both methods could lead to significant reductions in wastes going to landfill and reduce the damaging impact of fish wastes on the environment.

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.

1) 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 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.

2) 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 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. 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, αtocopherol, 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 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.

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

****