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Diversification in Fishery Byproducts

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Bycatch fish have received very little attention even though they contribute almost one third of the total fish catch. Fish sauce, silage and other fermented products are important areas of bycatch utilisation. Wastes from processing factories can be converted to useful food or non-food products. Crustacean processing waste has opened a new field of research and development and new products like chitin and chitosan with many novel applications have emerged. Shark cartilage, squalene etc. are other products, which find applications in medicine and cosmetics. This paper describes these diversified fishery byproducts.

Key words: Fermented fish products, hydrolysed fish products, squalene, fish bones, chitin, chitosan

Out of around 100 m t annual world fish catch nearly 30 m t are considered bycatch not directly used for human consumption. Conversion to fishmeal and oil is an important method of its utilisation. However, there are several other possibilities to be considered. All fish, in general, contain 15-20% protein and some contain high amount of oil. The 30 m t bycatch represents about six m t protein and about one m t oil as a renewable resource. Even the quality fishes yield only about 50% edible meat. The remainder like frame, head etc. is also high in protein. All processing operations turn out large quantities of waste, which contain protein and other nutrients in varying proportions. Several products for direct human consumption or for animal nutrition as well as industrially useful ones can be processed out of this waste. An equally important area is utilisation of shrimp and other crustacean waste. The important consideration is the most effective use of all materials with maximum value addition and minimum environmental hazard. In addition to the traditional byproducts, there are others such as chitin and its derivatives, fish bones, squalene, etc. having potential applications in various fields including drugs and pharmaceuticals. The present status of fish fermentation technology, hydrolysates, squalene, fish bones and, chitin and its derivatives is discussed in this paper.

Fermented Fish Products

Fermentation is an age-old technology of preservation of highly perishable fresh water and marine animals and are localised in production and seasonally fluctuating (Ruddle, 1989). The technology appears to have evolved with the availability of salt and non-pastoral way of life. There is strong correlation throughout the world between the uses of fermented fish products and cereals, especially rice and vegetables (Ishige, 1989). These are simple to process and have long shelf life. They are generally stored at room temperature. They provide meaty flavor and the dietary needs of amino acids, vitamins and other nutrients.

Classification of fermented fish products

The original fermented fish product was probably the liquid exuded from salted fish. Fermentation without salt employing other agents is also now practised. Depending on the amount of salt added the products are classified into high salt (>20%), low salt (6-18%) and no salt products (Fig. 1).

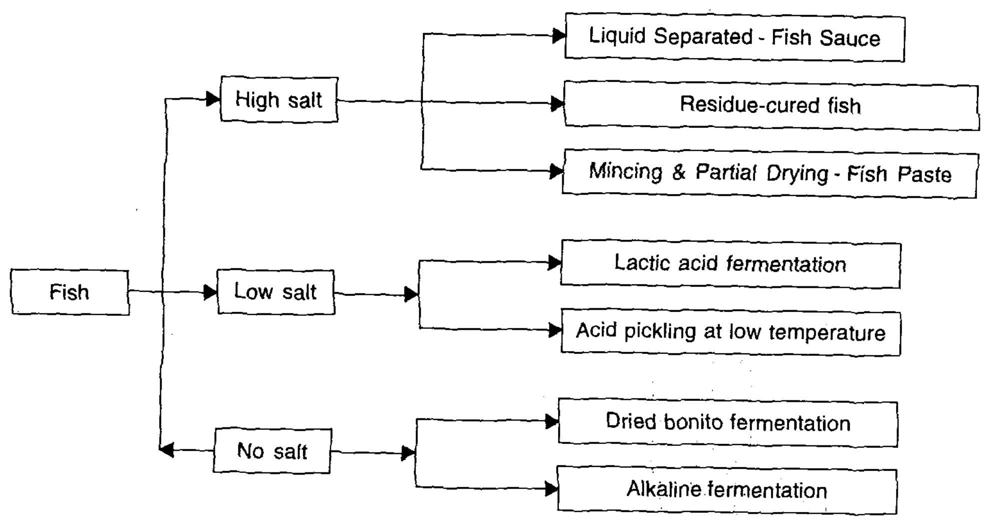

Fig. 1. Fish fermentation technology - various types

When salt concentration is higher than 20%, pathogenic and putrefactive micro-organisms cannot grow and the product does not need other preservatives. The first criterion for the subdivision of this group is the degree of hydrolysis, which is influenced by time and temperature of fermentation, added enzymes if any, and the water content. The fully hydrolysed liquid is fish sauce. Cured fish is the partially hydrolysed product which retain the original shape of the fish immersed in the exuded liquid (Lee *et. al.*, 1987; Boon-Lang, 1987). When the salt concentration is less than 20% the fish is prone to spoil and other means of preservation is needed. In low salt processes, lactic acid fermentation with added carbohydrate is also practised. Rice, milk, flour and syrup or sugar is used as the carbohydrate source. Carbohydrate and salt control the extent of fermentation and the keeping quality. An alternative method is keeping the low salt fermented fish with added vinegar at low temperature, practiced in the Scandinavian countries. Fermentation without salt is not a common practice. In some local specialties alkaline fermentation of half-spoiled fish using leafy plant ash is practised (Sovana *et. al.*, 1987). Bonito processing by propagation of mould in dried fish is another example of non-salt fermentation (Kanazava, 1986). Owens and Mendoza (1985) classified fermented fish products on the basis of fermentation technique namely enzyme hydrolysis/microbial fermentation. Enzyme hydrolysed products are subdivided into four groups. (1) hydrolysis in >20% salt (2) hydrolysis in salt + drying (3) hydrolysis at low temperature and (4) hydrolysis at low pH. The products preserved by microbial fermentation are subdivided into two groups (1) fermentation with added carbohydrates and (2) fermentation without added carbohydrates. The need for quality improvement and process innovation in the area of fermentation has been widely recognised in recent years. Acceleration of enzymatic hydrolysis in fish sauce production is a major concern in Philippines, Taiwan and other Southeast Asian countries (Mahesa and Babau, 1989; Chen, 1989; Putro, 1989). However, the utmost concern in the marketability of fish sauce is the branded aroma developed by blending sauces from different sources.

Hydrolysed Fish Products

As fishmeal and fish protein concentrate lack in the important functional properties such as dispersibility, solubility and emulsification, water soluble hydrolysate from fish is of considerable interest. Fish hydrolysate is produced by employing proteolytic enzymes. This differs from the processing of liquefied fish products or silage in that the latter uses the enzymes naturally present in the fish for hydrolysis, which is a slow and uncontrolled process. Hydrolysis can be accelerated and controlled using proteolytic enzymes. The extent of hydrolysis depends on the enzyme used and the conditions employed. A typical process for fish hydrolysate is shown in Fig. 2.

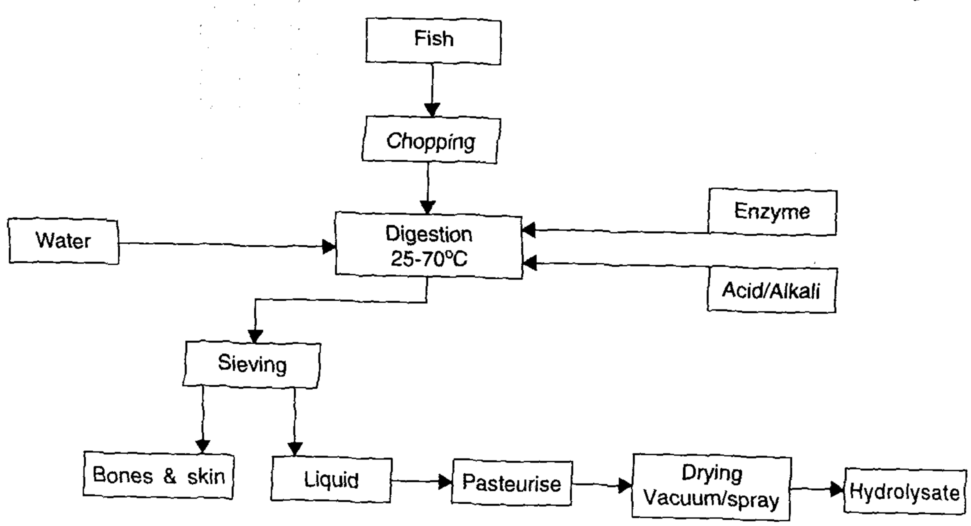

Fig. 2. Flow diagram for fish hydrolysate

Filleting waste and/or bycatch fish are the raw materials generally used for production of hydrolysates. The process can be applied to any species of fish but the fish with high content of body oil needs its removal before hydrolysis to prevent the formation of strong flavour in the product. In order to achieve commercial significance it must be developed from cheap fishes and filleting waste.

Squalene

Squalene is a branched long chain unsaturated hydrocarbon present in the liver oil of certain species of deepsea shark and is extensively used by the pharmaceutical and cosmetic industries. (Buranudeen and Rajadurai, 1986; Summers and Wong, 1992). The liver oil of these sharks were not considered important because of the absence of vitamins A and D and high content of unsaponifiables. Liver is heated to below boiling with 2% aqueous caustic soda for 30-45 min with stirring and the supernatant oil is skimmed off after settling. Squalene is isolated by fractional distillation under vacuum and is stored in inert atmosphere. Being highly unsaturated it undergoes oxidation on storage. Hydrogenated squalene, called squalane, is generally used in cosmetics and skin care products. Encapsulated squalene is now marketed as a hypocholesterolemic drug. The following species of deepsea shark have high amount unsaponifiables in the liver oil of which more than 80% is squalene.

Species	Unsaponifiables (%)
Shortspine spurdog (*Squalus mitsukuri*)	87-90
Leafscale gulpa shark (*Centrophorus samosus*)	70-85
Needle dog fish (*Centrophorus acus*)	60-65
Gulpa shark (*Centrophorus astromarginatus*)	58-60
Basking shark (*Centrophorus meximus*)	22-55

Fish Bones

Bones of cartilaginous fish like shark are being used as a source of chondroitin sulphate used as anticancer and antiarthritis drug. A process for refining bones from shark intended for manufacture of chondroitin has been developed at Central Institute of Fisheries Technology (Nair, 1996) and the process is being commercially exploited. Bones of several species of tuna are discarded throughout the world. This is a source of high quality calcium having application in food and pharmaceuticals. A new product, fish calcium, has been developed from the backbone of skipjack tuna which accounts for 2% of the total weight of the fish (Sada, 1984). Fish bones collected from the canning plants is crushed and the protein is removed enzymatically. It is then washed thoroughly, dried, ground to 300 - 400 meshes and sterilised. The product is marketed as fish calcium

Administration of fish calcium minimises bone failure and spine curvature in children arising from insufficient intake of dietary calcium. Fish calcium is also used in confectionery, cookies and in food for the aged.

Chitin, Chitosan and Derivatives

Processing waste from crustaceans is an abundantly available renewable source of chitin. Until its importance as raw material for chitin and its various derivatives having wide and varied applications in several fields was recognised it was causing serious environmental problems.

The total waste generated by shellfish processing is 65 to 85% of the landed weight depending upon the species and the method of processing (Mendenhall, 1971). However, a conservative estimate can be 50%, which could be available for chitin production. On this basis, the annual global availability is estimated as around 4,68,000 t. Squilla (*Oratosquilla nepa*) with an annual landing of more than

50,000 t and discarded by trawlers in India is a good source of chitin (Madhavan & Nair, 1975; Moorjani *et. al.*, 1978). Antarctic krill (*Eupheria superba*) and red crab (*Pleurocodes plenipes*) which, at certain times, congregate in huge fishable concentration are also good sources of chitin. The shell residue after separating protein from Atlantic krill amounts to 40% by weight. However, because of the extreme remoteness of the fishery, adverse weather and short fishing season Antarctic krill is not an important source of chitin at present though Poland has started producing and marketing krill chitin (Brzeski, 1982). In the immediate future, the principal source of chitin will remain shrimp and crab waste.

Production

As chitin is present as a chitin-protein complex along with minerals in shell waste, production of chitin involves deproteinisation using dilute caustic soda and demineralisation with dilute hydrochloric acid. Chitin on deacetylation with strong hot caustic soda yields chitosan (Madhavan and Nair, 1974; Nair and Madhavan, 1975). Water soluble derivatives of chitin and chitosan are made by carboxy methylation or dehydroxypropylation (Somorin *et. al.*, 1982; Rinudo *et. al.*, 1991). India has emerged as one of the leading producers of chitin and chitosan.

Application

The important applications of chitin and its derivatives have been a matter of considerable research input over the past three decades. These efforts have been well documented in the different world conferences held on the subject (Muzzarelli and Pariser, 1978; Hirano and Tokura, 1982; Muzzarelli *et. al.*, 1985; Skjak-Braek *et. al.*, 1989; Brine *et. al.*, 1992; Karnicki *et. al.*, 1994; Domard *et. al.*, 1996)

The important food related applications are in purifying drinking water, recovery of protein from poultry and fish processing wastes, clarification of fruit juices etc. The non-food related applications of chitosan includes removal of mercury from water, improving the functional properties of paper, in making non-woven fabrics, and sustained release of liquid fertilizers and pesticides. A thin coating of chitosan on seeds enhances the chitinase activity, which helps to germinate without infection. Chitin increases water retention in soil and controls nematodes. Efficiency of chitin as a feed additive in broiler chicken (Nair *et. al.*, 1987) and in prevention of mastitis in milch cow (Carolan *et. al.*, 1991) has been reported.

Chitin, and its derivatives can be used as bacteriostatic agent, haemostatic agent, drug delivery vehicle, in enzyme immobilisation, dialysis membrane, contact lens, as hypocholesterolemic agent, in nerve regeneration etc. Commercialisation of at least some of the above applications has been able to absorb a sizable quantity of chitin and chitosan. Water treatment, paper and textiles, drugs and pharmaceuticals and cosmetic industry have already started using chitin and chitosan.

Conclusion

Development of byproducts based on under-utilised and non-conventional species of fish, shellfish and processing waste could provide significant quantity of protein for human as well as animals. It also provides valuable chemicals having applications in several fields including pharmaceuticals and cosmetics. It will generate more employment opportunities and additional income to fishermen in addition to controlling environmental pollution.

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