Fish Products & Byproducts Technology

Dr. B.A. Shamasundar
Dr. Sukumar

AgriMoon.Com
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Author

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Index

Unit 1- Principles of Fish Preservation

Expected learning outcome

• Composition of fish
• Understanding the perishable nature of fish
• Methods available for fish preservation
• Principles of fish preservation methods

1.1. Composition of fish

I. What is the composition of Fish? Or fish is made up of what?

- Composition refers to elements involved in composing
- Fish and shellfish are made up of various chemical constituents.
- Chemical composition of fish and shell fish makes them distinct from other animal meat

1.2. Proximate composition

What is proximate composition?

- Relationship of the major chemical constituents in terms of proportion to the whole weight expressed in percentage

What are all the parameters affecting the proximate composition of fish?

- Body part
- Species
- Age
- Sex
- Size
- Sexual maturity
- Habitat
- Fishing season
- **Note:** Protein content shows less difference in different fishes, whereas lipid content shows wide variations.
- Fat content decreases from tail towards head and from ventral towards dorsal portion.
- Fin fishes differ from terrestrial animals by the presence of dark muscle. Dark muscle contains more fat than white meat in some fatty fishe

1.3. Seafood spoilage

What is seafood spoilage?

Physical or biochemical deterioration of breakdown of tissue makes the fish unfit for human consumption

Fish is highly perishable. Why?

All the food commodities are perishable. But fish is highly perishable. Because

- High moisture
- Low glycogen reservoir leads to postmortem pH near neutral favors the Microbial growth
- Low connective tissue makes the major protein more susceptible to proteolytic degradation
- Highly unsaturated fatty acids more prone to oxidation
- High content of non protein nitrogenous compounds

What are all the causes of seafood spoilage and intrinsic characteristics of fish that supports the causes?

Note: Other animals' meat have post mortem pH in acid range, compared to fish muscle and high connective tissue content delay the degradation of protein by endogenous proteases as well as secreted from bacterial origin.

1.4. Fish preservation

To prevent spoilage of fish, some form of preservation is necessary.

What is preservation?

Preservation means keeping the fish, after it has landed, in a condition whole some and fit for human consumption for a period ranging from days to months depending upon type of preservation.

What are all the fish preservation methods available?

Some of the preservation methods commonly employed in fish preservation are listed below

- Chilling
- Freezing
- MAP
- Curing (drying, salting and smoking)
- Canning and Retort pouch packaging
- Marinating
- Boiling
- Fermentation
- Irradiation
- Freeze-drying

1.5. Fish preservation methods and principles

At present different methods are used to preserve the fish and fishery products based on the desirable end product properties. Most commonly used fish preservation methods are; chilling, freezing, curing (drying, salting and smoking), canning, marinating, boiling and fermentation. The other methods such as preservation by irradiation, freeze-drying, modified atmospheric packaging, retort pouch packaging are also used for preserving fish.

1.5.1. Chilling

Preservation by chilling is mainly due to the lowering of the temperature of the fish as low as possible (near to 0°C) to delay both biochemical and microbiological processes. With the lowering temperature the lag period of microorganisms will be extended, resulting in delayed growth. The lower the fish temperature, the low will be the activity of enzymes and microorganisms.

1.5.2. Freezing

In freezing along with the effect of low temperature, mechanical rupture of bacterial cells during ice formation, freezing out of the major fraction of water in substrate also contributes to the death of microorganisms, thus by extending shelf life. The lower the fish temperature, the low will be the activity of enzymes and microorganisms. The oxidative rancidity problem is controlled by glazing the product before freezing.

1.5.3. MAP (Modified Atmospheric Packaging)

The preservation in MAP is by retarding the growth of microorganisms by changing the gaseous composition of the environment, thus by creating unfavorable conditions for microbial growth (mainly due to the effect of carbon dioxide on microorganisms) and by avoiding the lipid oxidation.

1.5.4. Curing (drying, salting and smoking)

Unlike canning (which engenders the destruction of micro-organisms and their spores) curing preserves by rendering the medium unsuitable environment for microbial propagation. Increasing the concentration of soluble substances in the medium either by abstracting water or by causing soluble substances to diffuse in (salting, brining or sugar curing) are the principal means of accomplishing this. In addition to concentrating the soluble substances by brining and dehydration, smoking preserves by depositing bacteriostatic chemicals like formaldehyde and phenols in the system.

The addition of salt is more effective for weight than the addition of sugar because salt ionizes to a sodium cation and a chloride anion each of which attracts a sheath of water molecules. These ionically associated water molecules are unavailable for use by micro-organisms and there is a tendency for the ionic forces to pull water molecules from the microbial cells dehydrating them to the point where they die or sporulate and lie dormant. Sucrose also withdraws water molecules from the system and holds them by hydrogen bonding. However, far fewer molecules become bound or unavailable in this way than is the case for an equal mass of sodium chloride. This availability of water in the system for use by micro organisms directly relates to the effectiveness of preservation and can be represented physically by the water activity (a_w).

1.5.5. Canning and Retort pouch packaging

The preservative effect in both the cases is mainly by subjecting the products in hermetically sealed containers / pouches, to high temperatures in order to bring the commercial sterility, where most of the microorganisms cannot survive, except highly heat stable spore formers. In this method the products are heated to high temperatures (121°C) for certain time with the intention of achieving commercial sterility to avoid the risk of pathogens and toxins, mainly *Clostridium botulinum*, which is a high heat resistant spore forming and toxin producing bacteria occurs in canned foods.

1.5.6. Marinating

The marinades are preserved by keeping them in acid medium (acetic acid and propionic acid) containing salt at a pH 4.5. At a pH 4.5 or below most of the spoilage causing and all food poisoning bacterial growth is arrested, resulting in a product with a characteristic flavor and an extended but limited shelf life. Acetic acid controls the pH and selectively allows the autolytic reactions to take place. The salt (sodium chloride) causes the removal of water and coagulates the protein. It also controls the hydrolytic action and allows it to proceed within desired limits. However some bacteria and enzymes will remain active and cause spoilage, which can be slow down by storing at low temperatures (below 10°C). The amounts of acid and salt required can be reduced when the product is kept chilled until eaten.

1.5.7. Boiling

The action of boiling fish in water at normal temperatures and pressures denatures (cooks) the proteins and enzymes and kills many of the bacteria present on the fish. The normal spoilage that occurs in a dead fish is thus stopped or drastically reduced. Often salt is added before, during or after processing; high levels of salt in the final product will help to extend the shelf life.

1.5.8. Fermentation

The fermentation processes are those in which organic catalysts (enzymes or ferments) break down complex organic molecules to simpler ones. Many of the processes used in fish preservation aim at keeping the fish flesh as near as possible to its original condition. With fermentation, however, we are considering methods by which the wet protein is broken down to simpler substances which are themselves stable at normal temperatures. In some of the processes we shall be considering, breakdown is only partial and is controlled by the addition of salt; thus the process is designed to produce a particular flavour as well as to preserve the product.

1.5.9.Irradiation

Food irradiation is the process for the treatment of food products to enhance their shelf life and to improve microbial safety. Electromagnetic radiations, namely gamma, and X-rays having short wavelength (< 300 μm) and higher energy than visible light can significantly penetrate the material including foods causing ionization of atoms and molecules by removing electrons from their outer shell. The inactivation of living cells (microbial cells) by irradiation is essentially due to scission of single or double strands of DNA, which is essentially caused by the OH radical formed by radiolysis of water. In addition to DNA damage, ionizing radiation has also been shown to cause damage to the membrane and other structures causing sub-lethal injury.

1.5.10. Freeze-drying

Freeze drying is a dehydration process typically used to preserve a perishable material or make the material more convenient for transport. Freeze-drying works by freezing the material and then reducing the surrounding pressure to allow the frozen water in the material to sublimate directly from the solid phase to the gas phase (i.e., it does not transit through the liquid state) under vacuum. Freeze-drying benefits heat-sensitive products by dehydrating in the frozen state without intermediate thaw. Freeze-drying of meat yields a product of excellent stability, which on rehydration closely resembles fresh meat. Adequate control of processing conditions contributes to satisfactory rehydration, with substantial retention of nutrient, colour, flavour, and texture characteristics.

1.5.11.Hurdle technology

Hurdle technology (also called combined methods, combined processes, combination preservation, combination techniques or barrier technology) advocates the deliberate combination of existing and novel preservation techniques in order to establish a series of preservative factors (hurdles) that any microorganisms should not be able to overcome.

Unit 2 - Traditional methods of fish preservation

Expected learning outcome

- Traditional methods of fish preservation
- Introduction to salting, drying, marinating and fermentation

2.1. Preservation

What is preservation?

Preservation means keeping the fish, after it has landed, in a condition wholesome and fit for human consumption for a period ranging from days to months depending upon type of preservation.

2.2. Traditional methods of preservation

What are the traditional methods followed for preservation of methods?

- Salting
- Drying
- Marinating
- Fermentation
- Combination of the above methods

Though the methods are traditional, these are widely adopted in developing and under developed countries.

What are all the advantages of traditional methods of preservation?

- Cheapest methods of preservation
- No expensive technology
- Can be employed in both small scale and large scale
- Used for the preservation of low value fishes
- Make the product available in the remote area as well as throughout the year
- Operational skill is not required
- No need of technically qualified people

Which is the traditional method of preservation practiced widely?

Simple sun drying is the widely practiced traditional method of fish preservation.

What is the principle of preservation by sun drying?

Preservation by sun drying was achieved by lowering of water content in the fish, thereby retarding the activity of bacteria and fungi. The heat was able to destroy the bacteria to a certain extent.

2.2.1. Salting

Salting refers to addition of salt or soaking the fish in brine solution. Salting practiced as such or in combination with drying or smoking and is considered a practice as old as drying.

What is basis of preservation by salting?

When salt introduced into the flesh in sufficient quantity, it delays the activity of bacteria or even inactivates them and reduce enzymatic action by reducing the water activity.

What are all the Advantages of salting?

- Low cost of production
- Easiness and compatible with other preservation methods such as drying and smoking
- Does not require any special equipment
- Finished product does not required any special storage facility
- Any type of fish, preferably, low and medium fat fishes
- Product has good shelf life
- Nutritionally comparable with other preservation methods

2.2.3. Marinating

Marinating refers to a process of dipping the fish in to marinate before cooking to get a desirable flavour and texture. Marinate is a liquid, mixture of salt and acetic acid.

How preservation is achieved by Marinating?

Salt added in the marinating process retard the bacterial activity. Due to the addition of acid the marinades are at the pH of 4.5, at a pH of 4.5 or below, that is moderately acid, all food poisoning bacteria, and most spoilage bacteria, are prevented from growing.

What are all the Advantages?

- Products having a characteristic flavour
- Flesh of the fish firmer in texture
- Extended but limited shelf life

2.2.4. Fermentation

Breakdown of larger molecules into their respective smaller components by enzymatic action is called fermentation.

What is fermentation?

Process of hydrolysis of food components polysaccharides, proteins and lipids by the enzymes particularly amylases, proteases, lipases produced by invaded or overgrown edible microorganisms. This process produces nontoxic products with flavors, aromas and textures pleasant and attractive to the human consumer.
If the products of enzyme activities have unpleasant odors or undesirable, unattractive flavors or the products are toxic or disease producing, the foods are described as spoiled.
Fermented foods were made several hundreds of years ago by the use of lactic acid

bacteria. Most of these fermentations were natural or accelerated by the addition of part of the product fermented previously. Fermentation of fish is brought about by autolytic enzymes from the fish and microorganisms in the presence of high salt concentrations.

Unit 3- Salting and Drying

Expected Learning Outcome

- Understanding the theory of salting
- Different methods of salting
- Understanding drying and dehydration
- Methods of drying
- Understanding different spoilage in salted and dried fish
- Awareness of quality standards

3.1. Salting

What is salting?

Salting refers to addition of salt or soaking the fish in brine solution. Salting practiced as such or in combination with drying or smoking and is considered a practice as old as drying. Salting is usually done as such or in combination with drying or as a pre-treatment to smoking.

What is basis of preservation by salting?

When salt introduced into the flesh in sufficient quantity, it delays the activity of bacteria or even inactivates them and reduce enzymatic action by reducing the water activity. Loss of water due to salting and reduced water activity limits bacterial growth and enzyme activity, thus preserving the fish. The high salt content prevents the growth of normal spoilage microflora in the fish; but halophiles, which can survive 12-15% of salt, will survive.\

3.1.2. Theory of salting

How salting takes place (Theory of salting)?

During salting osmotic transfer of water out of the fish and salt into the fish takes places, which effect fish preservation. It is based on different factors like diffusion and biochemical changes in various constituents of the fish. Movement of salt molecules from the brine into the fish takes place through a layer of salt solution covering the fish but having a salt concentration below that of the brine. This layer is formed because the water diffuses out at a faster rate during the initial stages from the fish than the salt solutes, which enters the fish. As the period proceeds the thickness of this covering layer diminishes as its salt content grows. At this point, diffusion of water from the fish ceases and the salt concentration in the layer equals to that of the salt concentration in the in the brine solution. Penetration ends when the salt concentration of the fish equals that of the surrounding medium.

3.1.4. Factors of salt to be considered before using for salting

What are the factors related to salt to be considered before using for salting?

- Physical properties
- Chemical impurities
- Microbiological contamination

Effect of physical properties on salting

A mixture of large and small grain sizes is recommended for any salting of fish. If fine grain is used directly on the fish, salt burn may occur due to the rapid removal of water from the surface and no penetration of salt to the interior of the fish.

Main chemical impurities of commercial salt and their effect on salting

- Calcium chlorides and sulphates
- Magnesium chlorides and sulphates
- Sodium sulphate and carbonate
- Traces of copper and iron

Calcium and magnesium chlorides slow down the penetration of salt into the fish, thus increasing the spoilage rate.

Magnesium chloride is hygroscopic in nature and tends to absorb water thus making the fish more difficult to dry.

Excessive quantities of calcium and magnesium compounds impart a bitter taste to the fish and make it brittle when dry.

Traces of copper gives a brown appearance to the fish making it look spoiled.

Microbial contamination of salt and their effect on salted products

Halophilic bacteria are present in most commercial salt. A particular group of halophiles called Red / Pink cause reddening of wet or partially dried salted fish. These do not grow in brine or in fully dried fish.

Halophilic moulds on the other hand tend to grow on fully dry fish, causing dark patches. These are called “dun”.

3.1.5. Types of salting

What are all the methods / types of salting process?

- Dry salting
- Wet salting
- Mono curing
- Pit curing
- Colombo
- Curing

Dry salting

This is the most widely used method of fish curing. All types of fishes except fatty fishes, big or small are cured by this method. Here, the fish is gutted, beheaded or ventrally split open and the viscera removed. The fish is then washed clean. Larger fishes are dorso ventrally split open and cleaned thoroughly. Scores are made also the thick flesh portion for better penetration of salt. Salt is then applied in the ratio 1:3 to 1:10 (salt to fish) depending upon the size of the fish. The fish is then stacked in clean cement tanks or other good containers. The bottom of the tank is covered with salt and a layer of fish is placed. Both fish and salt are alternately placed in the tank and wooden planks are put on the top and weighed down. The salt draws out the water in the fish and the weight placed keeps it under pressure. The fish is kept in this condition for 24-48 hours. After this the fish is taken out, washed in brine to remove adhering salt and trained. It is then hygienically dried in the sun preferably on clean racks. Yield of the product by this method is about 35-40%. This product has a shelf life of 6-10 weeks.

Wet salting

The initial stages of processing and salting are the same as for dry curing. Once the fish is put into the tank it is allowed to remain in the self-brine. The fish is not dried at all. The wet fish is then drained and packed in palmyrah leaf baskets or coconut leaf baskets and taken to the market. The fish is taken out only when there is demand. This method is particularly suitable for fatty fishes. This is mainly done for fishes like oil sardine, mackerel, ribbonfish etc. In such fishes the fat gets oxidized on exposure to air. These products have moisture content of 50-55% and the salt content around 25%. They are most susceptible to fungal attacks, bacterial degradation and general putrefaction. They have a very short shelf life.

Mona Curing

Mono curing is mainly done on medium to small size fishes. The curing is done without splitting the fish open. The intestine and entrails are removed by pulling out through the gill region. The fish is then salted and kept in tanks. The flesh is not exposed during salting thereby causing less contamination. The yield is about 70% and product has a shelf life of 50 days.

Pit Curing

The fish is mixed with salt in the ratio 4:1 and put in pits dug on the beaches. The pits may be lines with palmyrah / coconut leaves. After 2-3 days the fish is taken out and packed in bamboo baskets and transported to markets without drying. The quality is poor and the fish is highly contaminated with sand and has a shelf life of about 20 days. This is commonly called as ‘Kuzhi Karuvadu’.

Colombo Curing

Colombo curing is actually a pickling process for wet salt curing of pelagic fish. Colombo curing was practiced by the fishermen of South Canara and Malabar regions of the west coast of India. In the past, Colombo-cured mackerel and sardines were exported from India to Sri Lanka in large quantities. This method has now become obsolete after the advent of freezing and canning for fish processing and the widespread use of ice. Mackerel and sardines, available in huge quantities during the rainy season, were chiefly used for Colombo-cured fish is sour in taste and fibrous in texture. Several years ago, Sri Lanka stopped the import of Colombo-cured fish from India. All these factors have contributed to the disappearance of this once well known process.

Mackerel *(Rastrelliger kanagurta*). Sardine (*Sardinella longiceps*), and non-fatty pelagic fish are suitable for Colombo curing. The fish is headed and gutted and washed of all dirt and slime. It is mixed with salt in the ratio of 3:1 or 4:1 (w/w) in large cement tanks. Pieces of a sour fruit, locally called "gorukapuli" (*Garcinia cambogia*), are mixed with the fish salt mixture. This gives acidity to the pickle. Processing time is 3-4 months. After this it is filled in wooden barrels along with liquid pickle up to the top and exported.

Fruits of *G.cambogia* are yellow and contain tartaric acid. Smoke dried pulp, which is black, is used for pickling. The dried fruit is back, soft and acidic. It is extensively used for fish curry preparations in southern and western India. There are wide variations in the practice of the technique. In another well known processing practice, a dried pieces of gorukapuli is placed inside the belly flap of each fish. After this treatment, fish and salt are arranged in layers in large wooden vessels made of white cedar or mango wood. The vessels are filled up to the top, kept tightly closed upto 3 months, and thereafter sold in the open market. Colombo curing, although it became extinct in India, is still practiced in Sri Lanka where the process is known as '
"jadi".

3.2.1. Factors effecting drying

What are all the factors affecting the constant rate drying period?

- Air velocity
- Temperature
- Product surface area
- Relative humidity and
- Product thickness

Air velocity

The higher the air velocity, the greater is the drying rate. The moisture to be carried away should move through a stagnant surface layer of air by diffusion. Once through this layer, the moisture is transferred to the outer layer by convection. The higher the air velocity, the thinner is the surface layer, and greater will be the evaporation of moisture.

Relative Humidity

Humidity influences the drying rate by limiting the amount of water the air can absorb. If the air is saturated, then the fish cannot dry at all. If the RH is less than

100% the air can absorb moisture and drying will take place until the air gets saturated.

Temperature

The amount of heat transferred to the product is proportional to the difference in temperature between the air and the product. High temperature differences increase heat transfer and drying rate. Warm air holds more moisture than cold air. If the temperature of the air is increased without the addition of water, the relative humidity falls. Lower RH favours more rapid evaporation and higher drying rates.

Surface area

The more the surface area, the greater is the surface available for drying. More area is exposed; faster will be the drying rate. Hence larger fishes are split open to increase the surface area.

Product thickness

Increased product thickness result in longer drying period, than in the falling rate period. Thinner fishes tend to dry faster than thicker ones mainly because of the increased surface area to volume ratio for thinner fishes.

3.2.2. Falling rate period

What is falling rate period in Drying?

It is second phase of drying. As the water evaporates from the surface of the fish, the water present in the interior of the muscles is transferred to the surface. This is mainly by diffusion of the water. This process is generally slower than the surface evaporation, and hence diffusion limits the drying rate. This period is generally characterized by a slowly decreasing rate of drying, partially due to the fact that the drier the product is, the slower will be the diffusion of water to the surface. Thus this second phase is called the falling rate period.

3.2.2.a. Factors affecting the falling rate period

What are all the factors affecting the falling rate period?

Since the surface moisture of the fish has been removed, further drying of the fish depends on the movement of moisture from the interior portion of the fish to the surface.

Factors affecting falling rate period are

- Fat content of the fish
- Shape of the fish
- Temperature
- Water content

Fat content of the fish

Fish with a high fat content tend to take a longer time to dry than lean ones.

Shape of the fish

The shape and thickness of the fish influence the rate of drying of the fish. Since, diffusion is a function of thickness, thicker products require a longer time for drying.

Temperature

Diffusion will increase with rise in temperature. Drying will therefore proceed more rapidly with temperature increase.

Water content

As the water content is decreasing the rate of diffusion of water to the surface layers is also reduced.

What is case hardening in drying process?

If the drying process is above ambient temperature, the constant rate period can be very fast. Here there is every possibility that the surface of the fishes dry, whereas the interior remains moist. Here diffusion from the interior to the surface will take place very slowly. The product will be dry on the surface and transfer of moisture from the interior will not take place. This is known as case hardening and this is mainly due to the deposits of soluble proteins and other solutes on the surface.

3.2.3. Methods of drying

What are all the methods of drying?

Natural Drying

- Drying on the ground
- Rack drying

Solar Drying

- Solar Tent dryer
- Solar Collector Dryer
- Solar cabinet dryer

Artificial /Mechanical dryers

- Hot air dryers
- Cabinet dryer
- Kiln dryer
- Tunnel dryer
- Multi deck tunnel dryer
- Fluidized Bed dryer

Contact dryers

- Vacuum dryers
- Rotary dryers
- Spray dryer

• Drum Dryer
• Vacuum shelf dryer

3.2.3.a. Natural drying

Sun drying

Sun drying depends heavily on the natural weather conditions since the fish is dried by heat from the sun and the air current carries the water away. Here there is no control over the operations and many a time and losses cannot be substantiated. Hence it is necessary that the operations to be controlled to get a product, which has an extended shelf life, but at the time the texture, taste and flavour is maintained. It is here that artificial driers where processing parameters are controlled gain a lot of importance. Such products have advantages over sun-dried products since they have better keeping quality and longer shelf life.

Natural Drying

Sun drying can also be called as natural drying. In this type solar and wind energies are utilized as the energy source. Some of the essential requirements for production of high quality dried fish by natural drying in the tropics are:

- Sufficiently high air temperature in the range 35-40oC will be ideal. In many tropical countries temperature often becomes higher.
- Sufficiently low RH to permit drying fish to an a level not conducive for bacterial spoilage. RH above 70-75% will not help dry the fish to the desired level. Salted fish will tend absorb moisture from the surrounding air if the RH rises above 75%. In coastal regions the humidity will be often very high limiting the speed of drying.
- Use of raised platforms. Air movement at ground levels is comparatively slow. Better air movement can be ensured if the fish is kept raised by about one meter above the ground.
- Use of drying racks. Keeping the fish on racks kept above ground level will facilitate movement of air both under and over the fish, thus allowing drying from both upper and lower surfaces. Contamination of fish by dust or sand also will be minimized. Racks with sloping tops will allow for easy draining of any surplus water on fish surfaces in the beginning of drying.

Drying on the ground

In sun drying fish is conventionally dried on sand. This sort of drying gives a product, which is contaminated with sand, filth and other foreign matters. To reduce the contamination fish can be dried on coir mats, cement platforms, bamboo mats and jute sacks. Fish dried on cement platforms gets partially cooked due to the excessive heat. It also becomes necessary that the fish turned over often to ensure a uniform dried material.

Rack drying

The most hygienic method for sun drying fish is drying them on racks. Here the fish is dried on raised racks above the ground. This can be made by tying old webbings to poles made of locally available materials, which are fixed at specific distances from each other. This ensures circulation of air from both top and bottom and contamination of the product with sand or dust is almost completely avoided and a quality product is assured. Here the rack can be sloping type where there is a drain of the water, or it can be a multideck rack that consists of two layer, or more.

3.2.3.b.Solar Drying

Harnessing the solar radiation for solar powered driers has, of late, attracted considerable interest because of the absence of any energy cost and possibility of producing a dry fish in good hygienic condition even when the RH is high. Energy of the sun is collected and concentrated to produce elevated temperatures suitable for drying several commodities including fish. When the temperature of the air is raised, its RH will be reduced; in other terms its capacity to hold water will increase and hence, can absorb additional quantities of vapour.

Solar Tent Dryer

One of the simplest forms of driers to use solar energy for drying fish is the solar tent drier. This is working on the principle that a black surface absorbs sun's energy for more effectively than any light colored surface. The air thus heated is allowed to pass through the fish and escape our through a vent in the top simultaneously admitting fresh air inside through a vent provided at the bottom of the tent. Polythene tent drier is used to serve this purpose.

In a solar tent drier, the air temperature is known to rise to the levels of 60oC or more in tropical climate. This will adversely affect the nutritional as well as physical properties of fish and is considered a disadvantage. However, compared to normal sun drying solar drying has the following advantages:

- no energy cost
- very low equipment cost
- shorter drying periods
- no contamination from dust, insects
- Produces hygienic product with low moisture content.

Solar Collector Dryer

Here the solar energy is first collected in the solar collector chamber. The heated air is then passed through the drying chamber, where the fresh fishes are kept for drying on plastic mesh/trays. The hot humid air will escape through the chimney. Clear polythene sheet covers upper side of dryer, where as the floor of the dryer is spread with black PVC sheet. The rack for fish spreading and drying is made up of black plastic mesh.

Solar cabinet dryer

This is a rectangular shaped dryer made up of plywood. The front side of the dryer is double walled. Inlet and outlet are provided for air to enter and escape from the chamber. A clear polythene sheet covers the upper portion of the drier. Two doors are present for loading and unloading the fish into the drier.

3.2.3.c. Artificial /Mechanical dryers

In artificial driers, removal of water from the fish is achieved by an external input of thermal energy. This is an expensive method since there is need of fuel for heating and maintenance of the temperature. The drying chamber consists of a long tunnel in which the washed and cleaned fish is placed on trays or racks. A blast of hot air is passed over the material to be dried. After the required degree of drying the product is removed from the drier and packed.
These can be broadly classified into two types.

- The heat is transferred into the product through a hot gas, usually eg. Kiln dryers, cabinet dryers, tunnel dryers and fluidized bed dryers.
- The heat is transferred in to the product through a solid surface, which may also be used as the cabinet for the product to be dried. eg. Drum dryer, vacuum dryer.

Hot air dryers

In these dryers the air is heated by steam / electrically. The hot air is blown over the product by the help of a fan or blower. The different parameters like temperature, air velocity, and humidity are controlled. Different types of dryers in this type are

- Cabinet dryer
- Tunnel dryer
- Multideck dryer
- Fluidized bed dryer

Cabinet dryer

This is a simple batch operated model used for relatively small scale operations. A typical cabinet dryer consists of an insulated or non-insulated framed structure. Materials to be dried are spread uniformly on trays placed on permanent supports provided in the drier. A fan located inside the drier will blow air through a heat source, which pass across or through the material loaded in trays.

Kiln dryer

Kiln drier is a batch drier. A typical drying kiln will consist of a two story buildings. The floor of the upper story is slotted or may be composed of narrow slats on which the material can be spread. This story serves as drying room. The burners or furnace product hot gas is located in the lower floor. The hot gas passes through the product by natural conduction; often forced circulation with the help of a fan also may become necessary. The material being dried has to be tuned and stirred frequently to ensure uniform drying.

Tunnel dryer

This type of dryer is most commonly used for drying fish. These are made in the form of long tunnels, 10-15m long. Trolleys loaded with fish are moved at a predetermined schedule through the tunnel. Temperature and air velocity controls are provided. Hot air blown over the material is circulated with the help of fans. The movement is of air is maintained in either direction in relation to the flow of the material. If the air movement is in the same direction as that of product movement, dryer is called a parallel flow drying tunnel. In such dryers the hottest air comes in contact with the wettest fish. Therefore, higher temperatures can be used for drying. One serious disadvantage of the system is that the air towards the outlet side will become cool and highly humid; therefore the finished product may not be sufficiently dried.

If the movement of air is in the direction opposite to the movement of the product it is known as counter flow drying tunnel. Here, the hot dry air comes first in contact with the driest material, so that the finished product obtained will be sufficiently dry. However, the disadvantage is that in prolonged drying schedules the fish from one end of the tunnel may remain in humid air for long periods without getting sufficiently dry and result in spoilage.
Tunnel dryers should be designed based on the concept of hot air recirculation or by allowing part of the hot air passing over the fish to escape to the atmosphere. The recirculating air will become humid quickly and slow down the drying process, hence provision for de humidification and humidity control should be provided.

Multi deck tunnel dryer

In this type of dryer several tunnels are placed one above the other and air is blown in a zigzag manner thrice after which it is exhausted. Here all the controls, heater, air blower and exhaust fans are placed on one side.

Fluidized Bed dryer

The product is passed on a perforated conveyor bed and air is passed below, so that the product is partially lifted and dried. This is mainly used for fishmeal and fish powder.

3.2.3.d. Contact dryers

Vacuum dryers

Hollow shelves, through which the heating medium is circulated, are fitted in the chamber. The material to be dried is placed inside the chamber in metal trays, which rests on the shelf. Vacuum will be drawn and drying will proceed under vacuum. This is an expensive method, but suitable for drying fatty fishes where oxidation and rancidity fat can be minimized.

Rotary dryers

These dryers are used mainly for fishmeal. The source of heat is hot air, which is circulated through the shell or it can be supplied from a steam heat jacket. Rotary drum dryer, direct rotary dryer, indirect rotary dryer and steam dryer are some of the type of dryers used for drying purposes.

Spray dryer

Spray driers are generally used for drying foods which are in the form of liquids or suspensions. In principle a food in a liquid are paste form is atomized and dispersed as minute droplets which are suspended in a stream of hot air in a chamber where it gets rapidly dried. The dry particle suspended in the air stream flow into separation equipment where they are separated from the air, collected and packaged In the application of spray drying to fish products it is limited to products like fish protein hydrolysates and fish powders. The features of a simple spray drier are given below.

Better retention of colour, flavour and nutritive value are the advantages associated with spray dried foods.

Drum Dryer

Drum drier is an example where heat transfer to the product takes place through a solid surface. Drum drier is used for drying fluid materials. The food product in the form of slurry is deposited as a thin film on the drum. The drum is heated, generally by steam; while it is being rotated. Drying can be done keeping the drum open to the atmosphere. If the material is desired to be dried under vacuum, the drier can be enclosed in a vacuum chamber. The product when dry is removed from the surface of the drum used a scraper blade.

Drum driers are classified as single drum, double drum and twin drum types. Single drum drier comprises only one roll. Double drum comprises two drums rotating towards each other. Twin drum is similar to double drum, but rotate away from each other.

Vacuum shelf dryer

Vacuum shelf drier consists of a vacuum tight chamber of heavy construction with access door and outlet for gases and vapours. Hollow shelves, through which the heating medium is circulated, are fitted inside the chamber. The material to be dried is spread in fairly thin layers in metal trays which rest on these shelves. Alternately the material can be spread directly on the shelves. Heating is done by circulating hot oil, steam or any other suitable heating medium. Vacuum will be drawn in the chamber through the vapour outlet, and drying will proceed under vacuum. The initial drying rate will be high; however, as the drying proceeds the material will shrink and tend to curve away from the trays. This will reduce the effective are of contact of the material with the heating surface which will cause a decline of heat transfer to the material thus slowing down the drying rate.

Vacuum drying is considered an expensive process. However, it is quite suitable for drying fatty fishes where the probability of fat oxidation and rancidity in the product can be minimized.

3.3. Water activity

Relationship of water activity and preservation of fishery products by salting and drying

What is water activity?

Water activity is the measure of water available to support microbial growth and chemical reactions.

How the water activity is measured?

Water activity is frequently represented as the quotient of the vapour pressure exerted by a solution (P) and the vapour pressure exerted by the pure solvent, normally water, (P_o) at the same temperature.

$a_w = P/P_o$

More correctly, this is the relative equilibrium vapor pressure which, expressed as a percentage, is the quantity measured by 'water activity' meters. In such equipment, at a standard temperature, the percentage vapor pressure of the closed atmosphere surrounding the sample, after allowing the sample and atmosphere to come into equilibrium, is measured by hygrometry. The reading is termed the percentage relative humidity (% RVP) of the sample.

3.3.2. Water activity and water relationships in fish

Duckworth and Kelly (1973) concluded that in water/solute/polymer systems the minimum a_w at which solvent action (and, by implication Scott's 'water competition' between microbes and solutes) becomes apparent depends upon the solute not the polymer. The amount of water *unavailable* as a solvent in such a system depends upon the nature of the polymers present. The greater the solute concentration of the surface cells of fish, the more water is held by interaction with ions and polar groups such as (-CO-,-NH_2-,-OH) on other food components and, therefore, the lower is the vapour pressure compared with that of a free water surface at the same temperature. In addition to these, water may be bound into crystals or held by surface tension effects in capillaries both of which would tend to further reduce a_w.

3.3.3. Water activity and shelf life

- Objective of dehydration is to remove water from the deepest part of the flesh quickly enough to reduce water activity below the minimum for microbial growth, before significant spoilage takes place.
- Objective of salting is to ensure that the salt penetration is rapid enough to similarly lower the water activity in the deepest parts of the flesh.

On completion of the process, a saline equilibrium between the muscle and the surrounding salt solutions is achieved. The maximum concentration attainable is that which corresponds to a saturated brine solution (i.e. around 26%) under normal temperature conditions. Practically, concentrations would be lower than this due to the presence of other solutes in the fish cells. Salt fish, then, at least theoretically, would have the water activity of a saturated common salt solution, 0.75, notwithstanding the extent to which it has been dried during and after the salting process. However, salted fish reduced to 'biscuit cure' dryness in drying kilns, or in the open air at low humidity, can absorb a considerable amount of moisture before the 0.75 water activity is exceeded, thereby initiating microbial growth leading to spoilage.

3.4. Microbial spoilage in salted fish

What are all the Microbial Spoilage can happen in salted and dried fish?

Most of the micro-organisms normally associated with fish spoilage, for example, *Pseudomonas* spp., are halophobic and will not grow in salt concentrations exceeding 5%. There are, however, certain organisms that may be both common and pathogenic, and which are halotolerant, growing in a 10, or even 20% salt environment. *Staphlyococcus aureoous* is a highly significant example.

The most important spoilage micro-organisms are the halophiles which actually require salt for growth and will not grow unless 10% salt is present. These bacteria, which are responsible for **pink spoilage**, so called because of the colour of their colonies and consequent appearance of the cured fish, include *Halobacterium salinaria, H. cutirubum, Sarcina morrhuae* and *S. litoralis*. They are aerobic and usually not found in pickled fish where only limited oxygen access is possible through the brine. They are also thermophilic with an optimum growth temperature of about 42°C and minimum growth temperature of 5°C. The first sign of pink spoilage is a delicate pink sheen on the surface of the fish in wet stack or during pining. This can be easily rubbed off without damaging the fish. Treatment with formaldehyde or sulphur dioxide vapours, or dipping the fish in a solution of sodium metabisulphite prevents recurrence, although maintenance of the ambient temperature below 10oC is likely to prevent initial germination and growth. Cases of food poisoning said to have been caused by the consumption of pink spoiled fish have probably, in fact, been due to the growth of exotoxin producing *Staphylococcus aureus*. The latter will commence growth at water activities slightly higher than those required for growth of pink bacteria. Pink bacteria themselves have been proved to be non-toxic and non-pathogenic. The water activity of slat fish after drying is too low to support bacterial growth but, should temperature and humidity conditions become suitable, certain osmophilic moulds can grow. **Dun spoilage** derives its name from the brown surface discoloration caused by the growth of moulds of the *Wallemia* genus. They are able to grow in salt concentrations between 5 and 26% although they are not specific to sodium chloride and can grow on osmotic equivalent concentrations of potassium chloride, ammonium chloride, glycerol of glucose. Hence they are obligate osmophiles rather than halophiles. Other conditions for growth are: (I) temperature 10-37°C (optimum 25°C); (ii) pH 4.0-8.0 (optimum 6.0 to 7.0); and (iii) optimum relative humidity 75%.

Unlike the pink bacteria, dun moulds do not decompose the flesh but make the surface unsightly and, consequently, the product less saleable. They can be brushed off the surfaces but growth will rapidly recur if dry, cool conditions are not maintained. Old and rotting wood harbour such moulds, therefore wood should be avoided in dried fish stores or kept well covered. The causative agents of both pink and dun spoilage abound in solar curing salts, so the maintenance of low temperatures and humidity are the essential means of combating such spoilage during production and storage. Unfortunately, much of the market for dry salted fish is in areas where as hot, humid climate predominates, therefore the prevention of moisture ingress is an essential feature of any packaging used. The use of plastic bags is unsuitable because any temperature fall in the surrounding ambient would cause condensation. Dipping cured fish in vegetable oil approximately halves the rate of moisture uptake from a humid environment. This might be sufficient to delay microbiological spoilage beyond the required storage life.

3.5. Quality standards

During the last fifty years or so, extensive and periodical investigations on the quality of cured products involving large number of samples collected from different centres both of East and West coasts have been carried out. These investigations were mainly confined to the determinations of moisture, sodium chloride, acid insoluble ash, total volatile base and occasionally trimethylamine nitrogen. Microbiological study carried out in some cases was confined mainly to determination of total plate count and to pink discolouration. Table 1 gives the quality standards of some salted and dried fish as recommended by Bureau on Indian Standards.

Table1: Quality Standards for Salted and Dried fish as recommended by Bureau of Indian Standards

Unit 4 - Fish preservation by smoking

Expected learning outcome

- Understanding the principle of preservation by smoking
- The Chemical components of wood
- The Components of smoke
- Carcinogenic compounds in wood smoke and their removal

4.1. Smoking of fish

What is smoking of fish?

Smoking of fish refers to subjecting the fish to the smoke generated using various materials such as wood, coconut husk etc.

4.2. Preservation by smoking

How smoking exerts preservative action?

Spoilage of fish can be reduced by reducing some of the important substances like water content, enzyme content and fat content.

The smoking process is effective in reducing the water by evaporation.

This occurs due to:

- The movement of the gases in the smoke over the surface of the fish
- Raising the temperature of the fish

The chemical components such as phenols and formaldehyde exist in the form of vapor in the smoke exert antioxidant and antibacterial activity.

In addition the smoking process results in the penetration of the chemicals into the fish and loss of water from the flesh. A layer is formed which reduces the effect of oxygen that enters the fish from the surrounding air. Therefore the rancidity of the fat is reduced. This layer is called “barrier layer”.

4.3. Types of smoking

Based on the temperature at which the process is carried out, smoking can be characterized into two types.

- Cold smoking
- Hot smoking

What is cold smoking?

Carrying out the smoking process at a temperature upto 30°C is called cold smoking, in which cooking of the flesh does not occur.

Smoking effect is mainly due to the chemicals killing off the surface bacteria as reduction in water is not significant.

Cold smoked products should be cooked before consumption

Cold smoking takes 2-4 hrs when using a mechanical smoking kiln

What is hot smoking?

Carrying out the smoking process in which the fish is exposed to increasing temperatures up to at least 70°C is called hot smoking. It is having following effects

- The fish will be cooked
- Enzymes will be destroyed and chemical spoilage will be reduced
- Surface bacteria will be killed

How hot smoking is carried out?
In a mechanical kiln, hot smoking is carried out in three stages.
- A preliminary drying period at about 30°C. During this time the skin is toughened to prevent breakage occurring in the remainder of the process.
- A smoking and partial cooking period at 50°C
- A final cooking period at 80°C

The total time could be up to 3 hours. The actual times of each stage will depend upon:
- The species
- The size and thickness
- The fat content of the product
- The loading of the kiln
- The colour and taste requirements

Is it cooling necessary for hot smoked products before we pack?
Yes. If the product is packed in a warm condition mould is encouraged to grow.It is necessary to avoid the product turning mouldy. Products should be cooled down to room temperature then stored in chill room.

4.4. Materials used to produce the smoke

Smoke is prepared by "smouldering fibre" i.e. burning without flame. The source of producing smoke is the wood. All types of wood are not suitable
for smoking purpose. Depending on types of wood odour and taste differs.
For smoking, hard wood is suitable and we should not use soft wood. Types of wood used for smoking are mentioned below.
- Coconut shell and husk
- Sag wood dust
- Sag wood ships (leaves)
- Mango wood
- Paddy husk etc.

The species source of the sawdust affects end product flavour. Hard woods, such as oak, hickory, cherry, apple and beech, burn to give a smoke with more phenols, which both preserve and give a characteristic, 'medicated' flavour to the product.

What are all the chemical constituents of wood?
Freshly cut wood contains 40-60% moisture which is not suitable for smoking. A good wood containing <25% moisture is preferred for smoking. If the moisture is more than 25% then it is considered as damp wood. When wood is burnt it gives compound mixture of chemicals in addition to main gas like CO_2 and traces of H_2O and CO.

Wood consists of two parts
Combustible
Non combustible
Combustible substances
The main combustible substances are divided into three parts.
• Polyoses
• Lignins
• Resins (to some extent),
Polyoses
• Polyoses contain cellulose and hemicelluloses.
• The main component of hard wood
• In hard wood, polyoses comprise 2/3 rd of the wood.
• When wood is burnt polyose part gives out aliphatic chemicals and when temperature reaches 280°C, the released chemicals are alcohol, aldehyde, ketone and acids.
Lignins
• The main components of hard wood
• In hard wood, lignin comprise 1/3 rd of the wood.
• Lignin part is resistant to heat and when temperature reaches 350°C, they will burn and give out phenolic compounds.
Resins
• More common in soft wood eg. turpentine.

4.5. Components of smoke

Smoke is an emulsion of droplets in a continuous phase of air and vapours stabilized by electrostatic charges on the droplets. For flavouring, colouring and microbistatic purposes, the vapours are of greatest importance in smoking. When wood smoke is diluted by air, the concentration of the more volatile phenols falls to a greater extent than that of the non-volatile phenols. Within the temperature range 30-80°C, which covers all of the cold smoking process and most of the hot smoking process, adsorption of smoke vapours was independent of temperature, while deposition or absorption of the non-volatile phenols increased with temperature.

4.6. Carcinogenic compounds in wood smoke and their removal

Smoke has carcinogenic property due to the presence of 3,4-benzopyrene. It is a polynuclear aromatic hydrocarbon and its formula is $C_{20}H_{10}$. Depending on the method of smoking the amount of carcinogenic compound in smoke varies. To prevent the carcinogenic compound, electrostatic precipitation is used through which smoke is allowed to pass. The electrostatic precipitation can absorb the carcinogenic compound and we can get pure smoke. This can also be prevented to a large extent if liquid smoke is used for smoking. Liquid smoke is prepared from wood smoke condensate by functional distillation and water extraction. The undesirable polynuclear hydrocarbons are insoluble in water and thus absent in liquid smoke. Liquid smoking process, therefore, can be considered safe from usual health hazards.

Unit 5- Hurdle technology in fish preservation

Expected learning outcome

- Understanding the concept of hurdle technology
- Marinades and fermented fish products
- Fish and prawn pickle

5.1. Concept of Hurdle Technology

What is hurdle technology?

Hurdle technology (also called combined methods, combined processes, combination preservation, combination techniques or barrier technology) advocates the deliberate combination of existing and novel preservation techniques in order to establish a series of preservative factors (hurdles) that any microorganisms should not be able to overcome.

Why hurdle technology should be used in fish preservation?

Spoilage and poisoning of fish and fishery products by micro-organisms is a problem that is not yet under adequate control, despite the range of preservation techniques available (e.g. freezing, blanching, pasteurizing and canning). In fact, the current Consumer demand for more natural and fresh-like foods, which urges food manufacturers to use Only mild preservation techniques (e.g. refrigeration, modified-atmosphere packaging and biopreservation), make the preservation even greater difficult task.

5.1.1. Hurdles employed in fish preservation

Upto now about 50 hurdles have been identified for use in food preservation.

Commonly used hurdles

- Hig Temperature
- Low temperature
- Low water activity
- Acidicity
- Low redox potential
- Competative micro organisms
- Preservatives

Emerging Hurdles

- Ultra high pressure
- MAP
- Bacteriocins
- Edible coating

What are all the hurdles identified to be potential in food preservation?

1. Physical hurdles

• High Temperature: Sterilization, Pasteurization and Blanching
• Low temperature : Chilling and Freezing
• Ultraviolet radiation
• Ionizing radiation
• Electromagnetic energy (Microwave energy, Radio frequency energy, Oscillating magnetic field pulses and High electric field pulses)
• Photodynamic inactivation
• Ultra high pressure
• Ultrasonication
• Packaging film (Plastic, multi layer, active coating and edible coating)
• Modified atmospheric packaging (Gas packaging, Vacuum packaging, Moderate vacuum and active packaging)
• Aseptic packaging
• food microstructure

2. Physico chemical hurdle

• Low water activity (aw)
• Low pH
• Low redox potential (Eh)
• Salt
• Nitrite
• Nitrate
• Carbon dioxide
• Oxygen
• Ozone
• Organic acids
• Lactic acid
• Lactate
• Acetic acid
• Acetate
• Ascorbic acid
• Sulphate
• Smoking
• Phosphates
• Glucono lctones
• Phenols
• Chelators
• Surface treatment agents
• Ethanol
• Propyle glycol

- Maillard reaction products
- Spices
- Herbs
- Lactoperoxidase
- Lysozyme

3. Microbially derived hurdles
- Competitive flora
- Protective cultures
- Bacteriocins
- Antibiotics

4. Miscellaneous hurdles
- Monolaurin
- Free fatty acids
- Chitosan
- Chlorine

5.1.3. Basic aspects of Hurdle technology

Homeostasis and hurdle technology

Homeostasis is the tendency to uniformity and stability in the internal status of organisms. For instance, the maintenance of a defined pH is a prerequisite and feature of living cells, and this applies to higher organism as well as to micro organisms. In food preservation the homeostasis of microorganism is the key phenomena which deserves much attention, because if the homeostasis is disturbed by preservative factors (hurdles) in foods, they will not multiply, i.e they remain in the lag phase or even die, before homeostasis is repaired (re-established). Therefore food preservation is achieved by disturbing the homeostasis of micro organisms in a food permanently.

Metabolic exhaustion and Hurdle technology

Hurdles or preservative factors disturb the Homeostasis of microorganisms, and they try to repair them by every possible means, by doing so that they spend all the energy and die finally. This metabolic exhaustion leads to auto sterilization of foods. Due to auto sterilization hurdle technology foods, which are micro biologically stable, become safer during storage, especially at ambient temperature.

Stress reaction and Hurdle technology

Some bacteria become more virulent and resistant under stress, since they generate stress shock proteins. Synthesis of protective stress shock proteins induced by heat, pH, water activity, ethanol, oxidative compounds, etc. The various response of micro organisms under stress might hamper the food preservation and could turn to be problematic for the application of hurdle technology. Simultaneous exposure to different stresses will require energyconsuming synthesis of several or at least much more protective stress shock proteins which inturn may cause the micro organisms to become metabolically exhausted. Therefore, multi target preservation of fish could be the key to avoiding synthesis of of stress shock proteins which otherwise could jeopardize the microbial stability and safety of hurdle technology fish and fishery products.

Multi-target preservation

A synergistic effect could be achieved if the hurdles in a food hit, at the same time, different targets (e.g., cell membrane, DNA, enzyme systems, pH, aw, Eh) within the microbial cells and thus disturb the homeostasis of the micro organisms present in several respects. If so the repair of homeostasis and activation of stress shock proteins become more difficult. Therefore employing simultaneously different hurdles in the preservation of a particular food should lead to microbial stability. It is more effective to employ different preservative factors (hurdles) of small intensity than one preservative factor of large intensity.

5.2. Marinating

Marinating is a process of dipping the fish in to marinate before cooking to get a desirable flavor and texture. Marinate is a liquid, mixture of salt and acetic acid.

Basic of marinating process

The fish, subjected to one or more pre-processing techniques is rendered eatable by treating with acetic acid and salt. The products obtained this way are among the food items that can be consumed without any subjection to thermal treatment. Marinades are semi preserved foods; acid, usually acetic acid, and salt are added to the fish to retard the action of bacteria and enzymes, resulting in a product with a characteristic flavour and an extended but limited shelf life. Marinating also makes the flesh of the fish firmer in texture; the more salt that is added, the firmer the flesh becomes. The aim is to make a product that has a pleasant taste without being too tough, and one that is safe to eat after a reasonable shelf life. The amounts of acid and salt required can be reduced when the product is kept chilled until eaten.

The measure of acidity or alkalinity of a product is known as the pH, where a pH of 7 is neutral and a pH of 1 is very acid; at a pH of 4•5 or below, that is moderately acid, all food poisoning bacteria, and most spoilage bacteria, are prevented from growing, and marinated products at a pH of 4•5 will keep for several months at a temperature of 4°C.

Some bacteria and enzymes will remain active in marinades throughout storage, even in the presence of acid and salt, and eventually the flesh will break down completely. This residual action is desirable in some semi-preserves, for example those in which salt alone, or a mixture of salt and sugar, is used to preserve the fish; the products of bacterial and enzymic action produce the typical flavour of the product.

The ratio of fish to covering liquid should be between 1:1 and 2:1, and the liquid should contain 1-2 per cent acetic acid and 2-4 per cent salt. The acid taste of a marinade can be reduced by substituting citric or tartaric acid for some or all of the acetic acid, but care must be taken to ensure that the pH of the product does not exceed 4•5. Since not all acids are equally strong, expert advice should be taken where necessary when substituting for acetic acid. Vinegars produced by fermentation are also used instead of acetic acid to give a milder product; the acid

Maturing process
The first phase of marinating is comprised of complex physical and chemical reactions. Marinating process takes place with the effect of neither acetic acid alone nor salt. Salt and acetic acid which although have the same effect on fish meat are in fact, substances with opposite charges cancelling the effect of one another. While salt hardens the material, acetic acid softens it.

In the maturing process, salt and acetic acid transfer into fish tissue continues until the salt and acetic acid levels in the fish tissue liquid are equal with the salt and acetic acid levels in the solution. Although, it has been reported that this transfer is completed fast, generally in two day's time, it may still vary depending on temperature and meat thickness.
In marinated products, it is aimed to provide the product with a longer shelf life by stopping the activities of present bacterial enzymes in the product with the effect of acetic acid and salt.

Acetic acid and salt along with the enzymes from fish have an effect on the protein and lipid contents of fish although they cause destruction to a certain extent in the protein and lipid contents of fish and as a result, aromatic and delicious products are created

5.2.1. Fish Marinades

Fish marinades are fish or shellfish preserved in a mixture of acetic acid and salt so as to get a product with extended shelf life and flavour. Acetic acid is responsible of producing the tenderness of marinades. This is affected by the action of certain proteolytic enzymes, which cause a partial breakdown of the proteins with the release of some free amino acid. The salt removes the water and coagulates the protein. It also controls the hydrolytic action within the desired levels.

5.2.2. Types of fish marinades

• Cold marinades
• Cooked marinades
• Fried marinades

Cold marinades: Raw fish is preserved in a mixture of acetic acid and 10% salt at an optimum pH of 4.5. At no stage during the process the fish is heated. Bacterial and autolytic activities occur, and hence and shelf life is very limited at ambient temperatures.

Cooked marinades: The fish is placed in a hot solution of 1-2% acetic acid and salt at about 85oC. Here most of the bacteria are killed and the enzymes are inactivated or denatured. Shelf life is also of a longer duration.

Fried marinades: Here the fish are fried for 15-20 minutes in fat before packing in brine containing 2-3.5% acetic acid and 3-5% salt. Frying kills most of the bacteria and denatures the enzymes.

Marinades in general are stable only for a limited period. Shelf stability depends on storage temperature and on type of bacteria present. Spoilage in cold marinades is indicated by gas formation, in cooked marinades it is by gas formation and liquefaction and in fried marinades it is by gas formation and appearance of slime. The causative organisms for spoilage are hetero fermentative lactic bacteria in cold marinades, proteolytic bacteria in cooked marinades and slime formers in fried marinades.

5.3. Fermented fishery products

Breakdown of larger molecules into their respective smaller components by enzymatic action is called fermentation.

What is fermentation?

Process of hydrolysis of food components polysaccharides, proteins and lipids by the enzymes particularly amylases, proteases, lipases produced by invaded or overgrown edible microorganisms. This process produces nontoxic products with flavors, aromas and textures pleasant and attractive to the human consumer. If the products of enzyme activities have unpleasant odors or undesirable, unattractive flavors or the products are toxic or disease producing, the foods are described as spoiled.

Fermentation plays at least five roles in food processing.

- Enrichment of the human dietary through development of a wide diversity of flavors, aromas and textures in food
- Preservation of substantial amounts of food through lactic acid, alcoholic, acetic acid, alkaline fermentations and high salt fermentations;
- Enrichment of food substrates biologically with vitamins, protein, essential amino acids and essential fatty acids
- Detoxification during food fermentation processing
- A decrease in cooking times and fuel requirements

5.3.1. Types fermentation

- Fermentations producing textured vegetable protein meat substitutes in legume/cereal mixtures.
- High salt/savory meat-flavored/amino acid/peptide sauce and paste fermentations.
- Fish sauces and Fish paste coming under this category

• Fish sauces: Vietnamese nuocmam, Philippine patis, Malaysian budu,
• Fish pastes: Philippine bagoong, Malaysian belachan, Vietnamese mam, Cambodian prahoc, Indonesian trassi and Korean jeotkal.

- Lactic acid fermentations.
- Alcoholic fermentations
- Acetic acid/vinegar fermentations
- Alkaline fermentations.
- Leavened breads
- Flat unleavened breads.

5.3.2. Preparation of fermented products

Fermentation involves the breakdown of proteins in the raw fish to simpler substances which are themselves stable at normal temperatures of storage. In some processes where it is controlled by adding salt, only a partial breakdown of the protein takes place so that a desired type of flavour is produced simultaneously ensuring preservation of the product. Breakdown of proteins is brought about by the action of enzymes and sometimes microorganisms are also involved.

Fermentation technology for the preservation of fish has been very popular from time immemorial. Fermented fish pastes and sauces are relished as a condiment (flavoured salt) along with cooked rice in many of the South East Asian countries. On daily basis, nobody consumes large quantity of these products but almost every one consumes a little bit every day.

5.3.3. Types of fermented fish products

- Products in which the fish retain substantially their original form or preserved as large chunks. Examples: pedah siam (Thailand), makassar (Indonesia), buro (Philippines), Colombo cured mackerel (India)
- Products in which fish are reduced to a paste. Examples: ngapi (Burma), prahoc (Kampuchea), belachan(Malaysia), trassi (Indonesia), bagoong(Philippines)
- Products in which fish are reduced to a liquid. Examples: budu (Malaysia), patis (Philippines), nuoc-mam (Vietnam), nampla (Thailand)

Traditional fermented fish products are basically salt fermented products. Depending on the proportion of salt added, the products can also be classified into high salt (more than 20% of total weight), low salt (6 to 8%) and no salt products The dominant flavor giving components of fermented fish products are proteins and their hydrolytic cleavage products such as peptides, peptones, amino-acids; higher fatty acids and their esters; glycerides and their derivatives, monosodium glutamate, nucleotides and inosine monophosphate

Nutritive value of fermented fish products:

Fermented fish sauces and pastes generally contain amino acids and polypeptides equivalent to about 10% protein. Amino acids occur in such products without much change in composition and quality with respect to fish and hence contribute towards nutrition just like fish protein. They are good sources of calcium, iron and some B group vitamins. However, nutritional importance of these products is limited by its high salt content which restricts its bulk consumption. Moreover, these traditional products are used as a condiment rather than to derive nutrition

5.4. Fish and Prawn Pickle

Pickling of seafood is a recent concept and different styles of shrimp/fish pickle have been prepared to satisfy a wide range of consumers spread all over the country. Fish is rich in essential amino acids such as lysine, methionine, throenine and isoleusine. Fish fat is highly unsaturated which contains eichoso pentaenoic acid and docosa hexaenoic acid . This is essential to control blood cholesterol level so as to prevent heart attack. Fish is also rich in minerals like calcium, potassium, sodium, magnesium and iodine. To increase the utilization of underutilized low value fishes, which are rich in above nutrients, for human consumption value added fishery products can be prepared. Fish pickle / prawn pickle is of one such kind. Fishes belongs to family leiognathides, sciaenides, nemipterus, mullets and lutjanus of marine origin, catla, rohu, cat fish, common carp and thilapia of fresh water origin can be effectively utilized. Apart from fin fishes, shell fishes such as shrimps, crabs, cuttle fish, squid, chank, oysters and lobster meat can also be used. The product has a shelf life of 10-12 months at room temperature and can be used as condiments.

5.4.1. Preparation of fish pickle

- Raw material
- Washing
- Fillets are prepared from whole fish
- Fillets cut into small cubes (3 cm size)
- Fry fish meat cubes in oil and keep them aside
- Grate the peeled garlic, ginger and green chillies using mixer/grating
- Fry fenugreek, cumin seed, mustard, asafetida and make powder
- Add curry leaves to the remaining hot oil in the frying pan
- Add garlic, ginger and green chilly paste and fry for a while at medium flame
- Add the fenugreek, cumin seed, asafetida and mustard powder and continue to stir
- Add vinegar and salt allow to boil till characteristic smell emerges
- Add turmeric powder and chilly powder under low flame
- Add garam masal for good flavor and odour
- Add citric acid and sodium benzoate when the temperature of the content is little higher than the room temperature and mix thoroughly
- Add fried meat and mix with the gravy
- After cooling completely keep it over night for maturation
- Pickles are packed in sterilized glass bottles are laminated LD pouches (400 microns)
- Bottles are sealed air tight: ensure that the layer of oil floats on the surface of the pickle
- Label the bottles having statutory requirement and printed on it
- Storing at room temperature

Unit 6 - Extrusion

6.1. Extrusion

A continuous process by which moistened, expansible, starchy, and/or proteinaceous materials are plasticized and cooked by a combination of moisture, pressure, temperature, and mechanical shear.

6.2. Extruder

A tool used to introduce thermal and mechanical energy to food and feed ingredients, forcing the basic components of the ingredients, such as starch and protein, to undergo chemical and physical changes and form a predetermined shape. Cross sectional view of a extruder is given in figure

6.3. Extrusion cooking

Extrusion cooking is a modern high temperature short time processing

Purpose of extrusion cooking are as follows

- Sterilization
- Expansion
- Dehydration
- Stabilization

6.4. Extruded products

- First generation extrusion products
- Second generation extrusion products
- Third generation extrusion products- Protein enriched extruded snacks

6.5. Extrusion processing steps

Ingredients are propelled along the barrel of the extruder by one or two screws. The mechanical screw action and the friction it creates blends, shears and cooks the material (Held at 120-175°C for about 30 seconds). At the end of the barrel, the mixture is forced through a die at high pressure. Because of the difference between pressure inside and outside of the barrel, the material expands, and according the die shape and the cutter blade action, it creates a pellet of varying size, shape and density. Schematic representation of extrusion cooking is given in figure 2.

There are three zones in single screw or twin screw extruders.

- Input zone
- Kneading zone
- Cooking zone

Input zone - where th raw materials are introduced

Kneading zone - Where the ingredients are subjected to extreme mixing, pressure and stream heat

Cooking zone - uniformly blending the dry preconditioned ingredients, injected into the extruder on a cooking-extrusion system.

6.6.1. Single screw extruder

Based on the no of screw in the barrel

- Single screw extruder
- Twine screw extruder

Single screw extruder

The single screw extruder is an entry-level machine for small-scale operations. A large proportion of the expanded animal feed and modified raw materials such as soya bean and corn for feed purposes use single screw extrusion. The heat required to successfully cook the material relies upon the mechanical energy applied to the ingredients. This extruder is normally incorporated in a complete system with a hammer mill, mixer and cooler.

Types of single screw extruder

- The pasta extruder
- The high pressure forming extruder
- The low shear cooker extruder
- The collets extruder
- The high shear extruder

6.6.2. Twin screw extruder

A twin-screw extruder has two screws running in parallel with intermeshing flights for increased performance. Expansion of the ingredients is still limited without the introduction of additional heat and moisture. These extruders are therefore normally supplied with either a water mixer or steam conditioner for superior gelatinisation and expansion, by raising the moisture content of the mix to 20-25% prior to entering the extruder, or in the case of steam extrusion, the temperature of the material is also increased to approximately 55-65°C prior to entering the extruder barrel. This is controlled using metering systems and injected either into the preconditioner or sometimes directly into the barrel of the extruder. A higher amount of thermal energy can be supplied in this way in addition to the mechanical energy needed to cook the product.

Types of twin screw extruder

- Non intermeshing twine screw extruders
- Counter rotating twine screw extruder
- Co-rotating twin screw extruders

6.8. Advantages of extrusion cooking

- The heat and pressure created in the barrel can destroy harmful organisms such as salmonella.
- The raw material is expanded; Starch is gelatinized and oil cells are ruptured (improved digestibility).

- The heat and pressure deactivate destructive enzymes such as those that cause rancidity.
- Increase availability of carbohydrates
- Neutralizes growth inhibitors
- Increase availability of sulphur amino acids.
- Improves palatability.

Unit 7 - Fish protein concentrate

Expected learning outcome

- Understanding what is Fish protein concentrate
- Methods of preparation of Fish Protein Concentrate
- Types of FPC

7.1. Fish protein concentrate

Fish protein concentrate is any stable fish preparation, intended for human consumption, in which the protein is more concentrated than in the original fish.

What are all the advantages of preparation of fish protein concentrate?

- High nutritive value
- Low caloric content and
- Can be prepared from whole, edible-grade fish
- If used as dietary supplements, would alleviate the malnutrition condition in an economically viable way on a worldwide scale.

7.2. Methods used for preparation of Fish Protein Concentrate

Numbers of processes including enzymatic hydrolysis have been developed for preparation of FPC. The most popular ones employ some organic solvent to remove lipids and water from the raw or cooked fish meat. Commonly employed methods are

- Viobin Process
- Canadian process
- Azeotropic extraction method

Viobin Process

In this process, simultaneous dehydration and removal of lipids from ground whole fish is carried out using ethylene chloride. Ground fish is subjected to ethylene chloride treatment and the mass is then heated to boiling with indirect steam. Ethylene chloride forms a constant boiling mixture with boiling at 71° C. On condensation, the azeotropic mixture separates into two layers. The solvent layer is pumped back into the vessel to carry off more water. As the water content approaches zero the temperature of boiling will approach that of solvent indicating the completion of the process. Lipids will remain in the vessel in residual solvent. It is filtered off and the residue is washed once or twice with fresh solvent and then heated in a steam jacketed vessel under vacuum to remove as much as solvent as possible. Finally, vessel is flushed with dry steam to remove the last traces of solvent. The dry product is then pulverised and bagged.

Canadian process

It employs iso-propanol as a solvent for lipid extraction. It involves two stages. First stage involves grinding the fish, its suspension in water acidified with phosphoric acid (pH 5.5) and coking for 30 minutes at 70-80 °C with constant stirring followed by filtration of cooked mass and repeated washing with hot water until it becomes odourless. The residue from first stage is then suspended in iso-propanol and refluxed for 15 minutes. The solvent is removed by filtration and the residue is further treated with solvent to reduce lipids and water. The residue after final treatment is pressed and the press cake is dried and pulverised. The residual solvent is removed under vacuum.

Azeotropic extraction method

It is used in India where azeotropic mixture of hexane and ethyl alcohol is used as solvent. Minced whole fish is cooked in boiling water containing 0.5% acetic acid for 30 minutes. The solid matter is pressed well after draining off the liquid and is refluxed under constant stirring for 30 minutes with azeotropic mixture of hexane and ethyl alcohol containing 32.3 moles percent alcohol boiling at 58.68°C. The solid matter is refluxed again with fresh solvent mixture. The solvent is drained off and after distilling of the remaining solvent the extracted mass is steam-stripped under reduced pressure to drive off the remaining traces of the solvent. The mass is then pulverised to a fine mesh size.

Other methods of preparation of FPC

British process employs ethyl alcohol. Chilean process employs hexane followed by ethyl alcohol. The Moroccan process employs a mixture of solvents which include hexane, ethyl acetate and isopropyl alcohol.

7.3. Types of FPC

The Food and Agriculture Organization of the United Nations defines three types:

FPC resembles fish meal but there are other fish protein concentrates which are totally unlike fish meal. These are typically made by hydrolysing fish protein by means of enzymes or other chemicals and then concentrating the product into a paste or extract. Hydrolysed products have received much less technological attention than the variants of fish meal.

7.4. Proximate composition of FPC

FPC is a gritty, colourless, odourless powder, stable upto 3-4 years. Moisture content of the representative sample of FPC:

7.5. Use of FPC

It is intended for human consumption by incorporating as a protein supplement in the diet like bread.

Unit 8 - Fish Protein Hydrolysate

Expected Learning outcome

- Understanding what is Fish protein Hydrolysate
- Various methods of Preparation
- Advantages of preparation of fish protein hydrolysate
- Application of Fish protein hydrolysate

8.1. Fish protein hydrolysates

Hydrolysis

Hydrolysis means breaking the chemical bond with the help of water molecules.

Protein hydrolysis

Protein hydrolysis refers to breaking the peptide bond and adding a water molecule with the help of acid/alkali under the supplied heat or breaking the peptides bond using the biological catalysts called enzymes. In this reaction one hydrogen ion added to the amino group involved in the broken peptide bond and hydroxyl ions added to the carboxylic group.

Protein hydrolysates

A mixture of amino acids and peptides obtained after hydrolysis of a protein

Fish protein hydrolysates

Protein hydrolysates prepared using fish protein

8.2. Methods of protein hydrolysis

Chemical method

- Acid hydrolysis
- Alkali hydrolysis

Biochemical method

- Enzymatic hydrolysis with added enzymes
- Autolysis assisted hydrolysis

8.2.1. Acid hydrolysis

How it is being carried out?

Fish proteins are completely hydrolyzed with hydrochloric or in some cases Sulphuric acid at high temperature and often high pressure. The hydrolysates is then neutralized to pH 6.0 or 7.0 and concentrated to either a paste or further dried

Advantage

- More preferred than alkali hydrolysis
- Underutilized fish and secondary raw materials from fish is converted into fertilizer due to Low production cost and Extensive hydrolysis
- Total hydrolysis of fish protein is achieved in 18hrs at 118°C in 6N HCl
- Highly water soluble product

Disadvantage

- Process is harsh and hard to control
- Neutralization results in high salt (NaCl) interferes the functionality and palatability.
- Destruct the tryptophan which is an essential amino acid
- Usually product exhibit poor functional properties such as emulsion and foaming properties

8.2.2. Alkali Hydrolysis

This process involves hydrolyzing the protein at alkaline pH (12.5) and high temperature (95°C).

Rapid cleavage of large water soluble protein and further degradation at slow rate Alkali hydrolysis primarily use the fish protein concentrate as the substrate. Sodium hydroxide is commonly used as an alkaline reactant.

Advantage

- Used to recover and solubilize a broad range of protein
- Aid in modifying properties of insoluble FPC
- Solubilize collagen

Disadavantages

- Resultant product is Poor in functionality and process affect the nutritive value adversely.
- Recovery is low
- Racemization of L-amino acids produces D-amino acids which are not absorbed by human.
- Disulphide bonds are split with loss of Cysteine, serine and threonine via β-elimination reactions and formation of lysinoalanine, ornithinoalanine, lanthionone, and β-amino alanine can also occur
- May produce toxic substances like lysine alanine
- Alkaline hydrolysis reaction products have an inhibiting effect on proteolytic enzymes

8.2.3. Biochemical methods

Hydrolysing with added proteolytic enzymes

Proteolytic enzymes can be used to prepare the fish protein hydrolysate having the mixture amino acids and peptides.

Enzymes cleave the peptide bonds called proteases.

Based on the cleavage site proteases classified as

- Exopeptidase- Cleave the protein from the terminals
- Amino peptidase- Cleaves at amino terminal
- Carboxy peptidase-Cleaves at carboxyl terminal
- Endopeptidase- Cleaves the peptide bond within the protein molecule

It has been well documented that fish protein hydrolysates produced from fish processing waste and many of the under utilized fishes are possessing desirable functional and biological activities such as antibacterial activity, antioxidant activity

Advantages of using enzymes

- having the status of a natural substance
- high substrate and reaction specificity of biocatalysis
- mild reaction conditions and
- reduction in waste product formation

Source of enzymes

The enzymes can be from plant (papain, bromelain), animal (chymotrypsin, pepsin) bacteria (Alcalase, Protamex) and fungi (flavorzyme) sources. The digestive enzymes from animal origin can also be used.

8.3. Critical parameters while preparing Fish protein hydrolysate

- Enzyme concentration,
- Source of enzyme,
- Substrate and conditions of hydrolysis

By varying the above parameters a wide range of hydrolysates with different physical, chemical and biological characters can be obtained Uncontrolled or prolonged hydrolysis results in the formation of smaller and highly soluble peptides completely lacking the functional properties of native protein. Functional properties of protein can be defined as any set of physicochemical characteristics contribute to the structural, mechanical and other physicochemical properties and determine the behavior of food systems during processing, storage, preparation and consumption.

By careful control of hydrolysis, it is possible to suitably modify the functional properties such as water holding capacity (WHC), emulsifying capacity (EC), and foaming ability, which are useful in food formulation.

Degree of Hydrolysis

Ratio of broken peptide bonds to the total no of peptides present in the parent protein expressed in percentage.

Degree of Hydrolysis is the key; determine the functional properties as well as biological activities of fish protein hydrolysate.

8.4. Proximate composition and Nutritional value

- Moisture- 1-8%
- Protein-81-93%
- Fat- 0-5%
- Ash-3-8%

Evaluation of hydrolysates using nitrogen balance studies and growth experiments on rats established high nutritional values for the product.
The protein efficiency ratio (PER) of fish protein hydrolysates depends on the extent of enzymatic digestion and its amino acid profile. Usually the PER value is from 2-3.
The fish protein hydrolysates are found to have the essential and non essential amino acid in a defined proportion based on the hydrolysis condition.

Advantages
- No racemization of amino acids
- Control over the hydrolysis condition
- Utilization of secondary products from fish and underutilized fishes
- Resultant hydrolysate possess improved physico-chemical, functional and bioactive properties

Disadvantage
- High cost of enzymes
- Difficulty in controlling the extent the of hydrolysis that can result in heterogeneous products of varying molecular weight sizes
- Low yield
- Need to inactivate the enzymes add to processing cost
- Enzymes cannot be reused

8.5. Autolysis assisted hydrolysis of fish protein hydrolysate

Autolysis assisted fish protein hydrolysate preparation involves the digestive enzymes of fish itselfirly rich. The end product of autolysis process is generally a fairly viscous liquid rich in free amino acids and small peptides.
Autolysis also used in fish sauce and fish silage production.

Digestive enzymes
- Serine proteases trypsoin, chymotrypsin
- Thiol proteases pepsin
- All major enzymes of digestive tract
- Lysosomal proteases or catheptic proteases present in fish muscle

Advantage
- No enzyme cost

Disadvantage
- The endogenous enzymes in autolysis are a very complex mixture of enzymes, all with different activity which result in end products of different molecular profile

- Certain digestives enzymes and their concentration are highly seasonal, gender, species, age specific
- Hard to control the hydrolysis process

Fish sauce and fish silage are also autolysis assisted process.

Fish sauce

- Fish sauce contains 10% free amino acids and peptides 25% salt.
- Fish sauce preparation does not improve the nutritional quality but improves the keeping quality and sensory properties

Fish silage

- Animal feed ingredient
- Produced oil and protein fractions readily separated
- Substrates used are secondary raw material from processing plant
- Acid endogenous enzymes actively hydrolyse the fish protein

8.6. Application of fish Protein Hydrolysate

- Can be used as a source of essential amino acids
- Source of highly absorbable amino acids
- Can be used as a ingredient in formulation of functional foods
- Can be used as a source of health promoting peptides
- Used in Fertilizer preparation (Organic manure)

8.7. Advantages of preparation of protein hydrolysates

- Conversion of secondary fish processing products into valuble source of bioactive peptides
- Conversion of secondary fish processing products into high quality manure
- Value addition to low value fishes
- Concentrated protein supplement

Unit 09 - Fish meal and fish oil

Expected learning outcome

- Methods of preparation of fish meal and fish oil
- Significance of fish meal and fish oil
- Use of fish meal and fish oil
- Health beneficial aspects of unsaturated fatty acids

9.1. Introduction

The fishmeal and oil industry, which started in northern Europe and North America at the beginning of the 19th century, was based mainly on surplus catches of herring from seasonal coastal fisheries. This was essentially an oil production activity; the oil finding industrial uses in leather tanning and in the production of soap and glycerol and other non-food products. The residue was originally used as fertilizer, but since the turn of this century it has been dried and ground into fish meal for animal feeding. Depends on the target product and price fluctuation either the fish meal or fish oil becomes by product in the industry for each other. Small oily fish are the mainstay of the fishmeal and oil industry. Even in frozen storage these fish turn rancid rapidly unless special and expensive precautions are taken. With present knowledge they can be used best by reducing them to fish meal for animal feeding and using the oil for direct human consumption in products such as margarine. There is a good demand for high quality fish meal and oil and production can be highly remunerative if suitable raw material is available. The industry can also utilize the offal - from filleting, gutting and other fish processing operations - which often poses disposal problems. The production of fish body oil and fish meal is achieved in the same processing line at different stage.

9.2. Fish meal

The term fish meal means a product obtained by drying and grinding or otherwise treating fish or fish waste to which no other matter has been added. The term white fish meal is reserved for product containing not more than 6 per cent oil and not more than 4 per cent salt, obtained from white fish or white fish waste such as filleting offal.

These are semi legal definitions, and for convenience fish meal can be defined as a solid product obtained by removing most of the water and some or all of the oil from fish or fish waste.

What is the importance of fish meal?

Fish meal is traditionally used as live stock feed supplement, since it contains high quality of animal protein with essential amino acids like lysine and methionine and cysteine which the animal can not synthesized. It is also a good source of B group vitamins like cyanocobalamine (B12), choline, niacin, pantathonic acid and riboflavine. Fish meal is rich in minerals like calcium, phosphorous, copper and iron and is also the source of some trace elements refered as unknown growth factors (UGFs). Some unidentified constituents in fish meal contributing to animal growth is a unique feature of which highlights the importance of fish meal in animal nutrition. Fish meal protein is also having high biological value.

9.3. Use of fish meal as feed ingredient

Fishmeal as an ingredient is particularly suited to meet the demands of the contemporary food chain. It is a natural and safe product from responsibly managed fisheries with health, welfare and environmental benefits. The aquaculture sector consumed around 56% of world fishmeal production and 87% of total fish oil production in 2006. Other uses are poultry and pigs and other markets (mainly pet food).

- Fishmeal is fed to farm animals, not only to improve productivity, but also to protect health and welfare and reduce dependence on antibiotics and other drugs.
- Fishmeal has low antigenicity, making it easy for young animals to digest. Fishmeal has anti-inflammatory properties which improve animal's disease resistance
- Fishmeal and fish oil can claim to be the first "functional feeds" – offering, through their high omega-3 content, specific health and welfare benefits to both farmed livestock and to the human population eating the animal products.

9.4. Raw materials used in fish meal

Virtually any fish or shellfish in the sea can be used to make fish meal, although there may be a few rare unexploited species which would produce a poisonous meal. The nutritional value of proteins from vertebrate fish differs little from one species to another; whole shellfish would however give a nutritionally poorer meal because of the low protein content of the shell. Most of the world's fish meal is made from whole fish; the pelagic species are used most for this purpose. Where a fishery catches solely for the fish meal industry, it is known as an industrial fishery.

Countries with major industrial fisheries are Peru, Norway and South Africa. Some countries like the UK make fish meal from unsold fish and from offal that is the heads, skeletons and trimmings left over when the edible portions are cut off. Other countries like Denmark and Iceland use both industrial fish and processing waste. Fish meal made mainly from filleting offal usually has slightly lower protein content and a higher mineral content than meal made from whole fish, but a high proportion of small whole fish in the raw material can have the same effect.

Fish used for reduction to meal may be divided into three categories:

- fish caught for the sole purpose of fishmeal production
- by-catches from another fishery (by most fish-producing countries);

- fish off cuts and offal from the consumption industry.

A fishmeal industry requires a regular supply of raw material. When planning fishmeal factories, it is necessary to know the type of fish species available, the length of fishing season, the location of the fish, the catchability of the fish by different fishing gear and, if possible, the attainable catches per year for a continuous period.

9.5. Processing Method

To understand the principle of fish meal and oil manufacture, it is necessary to consider the raw material as composed of three major fractions:

- Solid (fat free dry matter)
- Oil
- Water

The purpose of process is to separate these fractions from each other as completely as possible with the least possible expense and under conditions rendering the best possible product. There are several ways of making fish meal from raw fish; the simplest is to let the fish dry in the sun. This method is still used, in some parts of the world where processing plants are not available, but the product is poor in comparison with ones made by modern methods. Almost all fish meal is made by cooking, pressing, drying and grinding the fish in machinery designed for the purpose. Although the process is simple in principle, considerable skill and experience are necessary to obtain a high yield of high quality product, and to make the plant efficient. There are two methods (wet reduction and dry reduction) and many minor variations of commercial fish meal production. A typical process is shown diagrammatically in figure 1. Common steps to all methods of practical importance are as follows:

- Heating, which coagulates the protein, ruptures the fat depots and liberates oil and physico-chemically bound water;
- Pressing (or occasional centrifugation), which removes a large fraction of the liquids from the mass;
- Separation of the liquid into oil and water (stickwater). This step may be omitted if the oil content of the fish is less than 3%;
- Evaporation of the stickwater into a concentrate (fish solubles);
- Drying of the solid material (presscake) plus added solubles, which removes sufficient water from the wet material to form a stable meal,
- Grinding the dried material to the desired particle size.

9.5.1. Wet reduction/rendering process

Wet rendering is a system which leaves a high amount of moisture in the product, until, or if, it is to be dried. This process used primarily for fatty fish (menhaden, herring, pilchards, anchovy, sardine etc., which are caught specifically for fish meal production) or offal contains high fat content, where simultaneous production of fish mea and fish oil is envisaged. This process is continuous rather than batch process and is particularly suitable for large scale operation.

The essential steps are as follows:

- Grinding or hashing of large fish
- Cooking and heating usually with steam
- Pressing to squeeze out water and oil

• The liquid portion is known as press liquor and is passed through ascreen to remove solid particle of fish which are then return to the solid portion called press cake which contains about 50-55% moisture and 3-4% oil

- Fluffing out of press cake
- Drying the press cake to a moisture level of 10%
- Grinding and packing the dried meal

Press liquor cam be treated, after screening to remove solids in a number of different ways; generally the liquid is heated and centrifuged to remove the suspended solid particles and the oil. The oil may then be further refined and polished while the solids are returned to the meal plant for drying. The liquor or stick water can be concentrated by evaporation of the water to about 50% solids. The concentrated liquor can be sold separately as fish soluble. If the fish soluble is added to the press cake and dried then the end product is called as whole meal.

9.5.2. Dry reduction/rendering process

The dry reduction process is principally applied to the conversion of fish or fish offal of low fat content. It is a batch process and is easier to manipulate than the wet rendering which is a continuous process. The essential steps in dry reduction process are as follows:

- Fish are coarsely ground in a hacker or grinder
- The hacked fish are cooked in a steam jacketed cooker with a stirrer.
- The cooker also acts as a drier and is usually referred as cooker/ drier. Presser and separate drier or optional extras with this type of plant the cooker/drier may be operated at atmospheric pressure or under slight vacuum to facilitate drying.

9.6. Equipments used in fish meal plant

- Hasher/Chopper
- Feeding machine
- Indirect steam cooker
- Strainer conveyer/vibrating screener
- Twin screw process
- Tearing machine/wet mill
- Indirect steam drier/direct flame drier
- Vibrating screen with a magnet
- Hammer mill
- Scale/weighing machine
- Decanter
- Stick water centrifuge
- Oil separator
- Evaporator

Based on the capacity, mode of operation and development in the technology there are wide variation in the use of equipments in commercial fish meal plants.

9.7. Fish meal quality

Quality of fish meal related to raw material and conditions of manufacture and storage

The quality of protein in fish that is the make up of amino acids in relation to animal's requirement and the availability to the animal are high, particularly in the whole fish. the quality of protein in skin, connective tissues and bone is lower; consequently the quality of protein in offal is some what lower than that in whole fish. For example the proportion of the essential amino acids methionine and lysine in the protein in white fish offal is approximately 10% lower than that in the whole oily fish such as anchovy and pilchards.

Raw material should have less than 80mgN/100g

Fish protein is sensitive to heat. So, the available lysine content is considered to evaluate the quality. There should not be more than 80% loss of available lysine content with reference to the raw material

Oxidation: Oxidative rancidity mainly affects the quality of fish meal. Addition of an antioxidant such ethoxyquin at 700ppm is desirable for oily species. Natural antioxidants such as α-tocopherol also used in order to retard the oxidation process.

Salmonella: The end product should be free from salmonella contamination. Salmonella should never be detected in fish meal. The contaminated lots must be disinfected for example in special apparatus in which the meal is heated at about 90oC with live steam for 10-15 min. Alternatively biocides such as formic acid and propionic acid can be used to treat infected fish meal.

Colour: Fish meal is brown powder. A very dark brown colour especially if accompanied by an aerid "scorched" smell may be the result of over heating. Particle size: The general practice for meals to have less than 10% that will pass through a1mm sieve and more than 90% passing through a 10 mm sieve.

9.8. Fish oil

Introduction

Fish oils may generally be described as flesh oil, liver oil, or oil of the whole fish. It can be the by product in fish meal plant or may be the target product in fish oil production plant. The product, however, is versatile and finds many applications in the food and technical industries and is still of considerable economic importance to producers.

Chemical structure of fish oil

It mainly consists of triglycerides of fatty acids (glycerol combined with three similar or different acid molecules) with variable amounts of phospholipids, glycerol ethers and wax esters. It is characteristic of the oils that they contain a wide range of long-chain fatty acids with the number of carbon atoms ranging mainly from 14 to 22, and high degree of reactivity (unsaturation) ranging up to six double bonds per molecule.

Raw material

According to the Food and Agriculture Organization (FAO) raw material used for the production of fish oil falls into three categories:

- Fish caught specifically for reduction to fishmeal and fish oil such as menhaden, anchovy, capelin and sardines.
- Incidental or by catch from another fishery (for example the global discards amounted to 27.0 million metric tons (mmt) with a range of from 17.9 to 39.5 mmt with shrimp by catch accounting for 11.3 mmt)
- Fish by-products from the edible fisheries such as cuttings from filleting operations, fish cannery waste, roe fishery waste and more recently surimi processing waste.

9.8.1. Production of fish oil

There are a number of processes that can be used to convert raw fish and cuttings into fishmeal and oil. These fall into several categories defined as wet rendering, hydrolysis, silage production (autolysis), dry rendering and solvent extraction.

9.8.1.a. Wet Reduction Process

The processing techniques involved in commercial production of edible fats and oils vary according to the type of raw material. Fish reduction to produce oil and fishmeal, generally employs the same principles, techniques and equipment common to the production of the other edible fats and oils. In general, fish are processed by the wet reduction method in which the principal operations are cooking, pressing, separation of the oil and water with recovery of oil, and drying of the residual protein material. Continuous processing from the time the fish are landed optimizes efficiency and maximizes product quality.

The wet rendering process is used in the majority of the factories that produce fish oil worldwide. This process is universal, i.e. factories all over the world both on land and on ships employ it with slight differences in equipment type, but the major steps of cooking, pressing, separating, and drying are always present. These steps are as follows:

Cooking

Steam cooking ruptures the fat cells, coagulates the protein and releases the oil

Dewatering / Pre-pressing

The cooked fish mass is screened to separate free liquid from the solids

Pressing

Pressing mechanically expresses the free liquid from the solids producing a press liquor (oil and water) and a press cake (semi-moist meat and bones). Some factories have used tri-canters instead of presses to separate solids, oil and water.

Press liquor Separation

This is 3 step process; decanters separate fine solids from the liquid fraction, separators split the liquid fraction into fish oil and water (stick water), and polishing water washes the crude fish oil before it is pumped to storage.

Evaporation

Stick water contains about 8% solids which are concentrated in multiple effect or waste heat evaporators to about 40-50% solids. If the factory uses steam dryers then the waste heat from the dryer can be used to heat and evaporate the stick water.

Drying

The drying process is generally done in 2 stages. The solids from the decanter separation and the press cake are mixed and partially dried. The partially dried fishmeal is then mixed with the concentrated stick water and the drying is completed to about 10% moisture. Factories use steam and indirect hot air dryers but older factories still use the old direct fired hot air dryers.

Grinding

Grinding reduces the particle size of the fishmeal

Cooling and Stabilization

The fishmeal is cooled and antioxidant is added. Generally ethoxyquin is the antioxidant of choice but for certain markets natural antioxidants based on tocopherols are used.

Packaging

The fishmeal is packaged in 50 kg bags or 1000 kg totes. The fishmeal can also be stored in bulk piles or in silos.

Carbon Treatment (Optional for Fish Oil)

If the crude fish oil is destined for the Omega-3, animal feed, aquaculture or pet food market and if analyses indicate the presence of dioxins, furans and or poly-aromatic hydrocarbons (PAH), it can be treated with activated carbon to reduce the levels of these compounds.

9.8.1.b. Dry reduction Process

In this process the raw material is "dried" (in cooker/drier) to remove the water (essentially the steam cooking process in the fishmeal wet rendering process. The resultant dry cake is then pressed to remove any oil. Because the water has been removed, the lipid fraction can contain high levels of phospholipids. The phospholipids normally hydrate in the wet rendering process and are recovered with the water fraction. In the dry rendering process, they are not hydrated and therefore remain dissolved in the lipid or oil fraction. Since there is interest in the fish phospholipids, it is possible to produce a PL fraction by hydrating the oil (also called degumming).

9.8.1.c. Processing of fish oil

In general terms, all crude oils and fats contain minor amounts of non triglyceride substances. While some of these are considered beneficial to the stability of the oil, such as tocopherols and astaxanthin (in salmon and krill oils) which protect the oil from oxidation, other impurities are objectionable because they render the oil dark colored, cause it to foam or smoke or are precipitated when the oil is heated in subsequent processing operations. Other impurities reduce acceptability because of the flavors and odors they produce in the fat or because they reduce stability and shelf life of the foods to which the fats are added.

Some impurities are common to all fats regardless of the source or end use:

- Suspended matter (insoluble impurities).
- Naturally occurring color bodies.
- Free fatty acids.
- Volatile, malodorous compounds dissolved in the fat or oil.

These non-triglyceride substances have also been classified according to their effect:

- Hydrolytic - moisture, insoluble impurities, free fatty acids, mono and diglycerides, enzymes, and soap.
- Oxidative - trace metals, oxidation products, pigments, tocopherols, and phospholipids.
- Catalyst poisons - substances which inhibit the hydrogenation reaction e.g. phosphatides, oxidation products, and compounds containing nitrogen, sulfur, and halogens.
- Miscellaneous - hydrocarbons, terpenes, resins, sterols, waxes, trace metals and sugars whose effect is less well known but can be classified as contaminants and also may have an effect on the final flavor of the oil

Processing steps and the compounds removed by them in purification of fish oil

Carbon Treatment

Removal of dioxins, furans, and polyaromatic hydrocarbons (PAH). This can be performed on the starting crude oil if the oil is to be sold into the non-industrial market.

Oil Storage

Insoluble impurities, trace moisture and some phospholipids will precipitate out in the tanks. The combination is known as "foots".

Degumming

Phospholipids, sugars, resins, proteinaceous compounds, trace metals and other materials.

Alkali Refining
Free fatty acids, pigments, phospholipids, oil insoluble material, water soluble material, trace metals

Water Washing / Silica Treatment: Soaps, oxidation products and trace metals

Drying: Moisture

Adsorptive Bleaching& Carbon Treatment
Pigments, oxidation products, trace metals, sulfur compounds, dioxins, furans, PAH and possibly some PCB's

Winterization
Higher melting triglycerides, waxes. Used to enhance the unsaturated triglycerides

Deodorization
Free fatty acids, mono-diglycerides, aldehydes, ketones, chlorinated hydrocarbons and pigment decomposition products. This is usually the finishing step and results in a bland tasting oil.

Vacuum Stripping or Thin Film, Molecular or Short Path Distillation
Removal of chlorinated hydrocarbons, fatty acids, oxidation products, PCB and free cholesterol. Sometimes this step is used as a replacement for the deodorization step

9.9. Unsaturated Fatty acids

Importance of Unsaturated Fatty acids

- Fish oil is rich in poly unsaturated fatty acids (PUFA). Unsaturated fatty acids are more to oxidation and cause rancidity which affect the quality as well as nutritive value of fish oil.
- Refined fish oils are rich in polyunsaturated fatty acids of the linolenic acid family. Current medical research suggests that these fatty acids might have a unique role to play in prevention of coronary artery disease and the growth of different types of cancers.
- The highly unsaturated properties make the oils (and particularly their highly unsaturated fractions) suitable for a number of technical applications, particularly as drying oils and varnishes. The saturated fatty acid fraction is a disadvantage for these purposes and must be reduced. Several specialized processes for this reduction are available.
- Fish oils are a significant source for the production of fatty acids with a wide spectrum of chain lengths. From these acids are produced several types of metallic soaps, some of which are used in lubricating greases while others are used as waterproofing agents. Small quantities of fatty; acids are used pharmaceutically and medicinally, and for scientific research purposes.

Health beneficial effects

- Fish oil helps with cholesterol by lowering levels of LDL while also increasing levels of HDL
- Heart problems, cholesterol, arthritis, and diabetes are some of the major conditions in which fish oil provides some form of benefit or improved health.
- Fish oil supplements seem to have an anti-arrhythmic effect on the heart as well as prevent cardiac arrest. In doing this, fish oil can help lower the mortality rate of those individuals having heart complications
- Fish oil can benefit the heart because the EPA and DHA that make up the supplement helps to prevent plaque deposits and blood clots inside arteries.
- Fish oil improves the ability of muscle cells to take up glucose in the presence of insulin. This proves to be beneficial to those with type II diabetes
- Fish oil has been shown to have anti-inflammatory effects, especially the Eicosapentaenoic acids (EPA). They can improve overall function in joints as well as limit the amount of other anti-inflammatory drugs that a patient must consume with conditions such as arthritis or other inflammatory disorders such as Inflammatory Bowel Disease.
- Fish oil has been shown to have effects in dealing with certain psychological disorders. It has been found that omega- 3 fatty acids are known to have membrane enhancing capabilities in brain cells. They cause more production of two neurotransmitters, serotonin and dopamine. This allows patients to focus better on tasks that are at hand without as many distractions. The effects of Serotonin have been shown to help individuals better deal with stress and other activities.
- Fish oil has also been shown to have a number of beneficial effect on the brain. It has been shown that 60% of the brain is made up of a structural fat, which has a high number of DHA in it, and the brain requires a regular intake of good fats such as the ones from omega-3 fatty acids. Low intake of omega-3 fatty acids can lead to conditions such as ADHD, dyslexia, depression, aggression, Alzheimer's Disease, or other dementia.

Unit 10 - Fish By- products

Expected learning outcome

Understanding the preparation and significance of various fishery products

- Isinglass
- Shark leather
- Fish glue
- Pearl essence
- Beach de- mer

10.1. Isinglass

Air bladder, also called sound or swim bladder consists of several membranous layers rich in collagen. Located in the abdominal cavity below the vertebral column, air bladder helps the fish in regulating its specific gravity. Cleaned and dried air bladder is called as Fish Maw, which is an excellent raw material for production of Gelatin.

Hake, Sturgeons and carps are good sources for air bladder.

Processing

The air bladder after washing with water and scraping of the outer layer is split open longitudinally and washed well further, sundried to 15 % moisture level by hanging or placing in trays. Dried product is Fish Maw.
Dried air bladder is immersed and soaked in water until it becomes soft. It is then rolled after cutting into small pieces between water cooled iron rollers to convert them into thin strips. They can be further compressed by ribbon rollers into ribbons about 0.4mm thick which are air dried and rolled into coils. This is Isinglass.

Uses

- Clarifying agent for beer, cider, wine, vinegar etc.
- Can be used as adhesive waste
- Isinglass dissolved in acetic acid forms a strong cement base
- Can be used as a sizing agent in textiles
- It is an ingredient in Indian ink.

10.2. Shark leather

Skin from fish and other aquatic animals offer a potential source of leather in the countries where climatic conditions and topography do not allow raising of goats and sheep's. Few such countries are Japan, Vietnam Thailand, Korea, Norway, Sweden etc. Skins of shark can be processed into fine leather suitable for manufacture of fancy items. The main component of skin is collagen. Collagen constitutes about 90% of all nitrogenous matter of the skin. 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 can be used as a suitable raw material for manufacture of suitcases, shoes, belts, vanity bags etc.
Both demersal as well as pelagic varieties are suitable for the leather production

Process
There are following operations for making of leather from shark skin

- Curing of skin: The skin is removed from shark body and cured with salt by spreading it with flesh side or skin may also be preserved by sun drying in tropical countries like India. More care is necessary for removal of skin from body of fish.
- Washing and soaking: skins are washed and soaked which plumps up skin and hides restoring them into their original texture and consistency.
- Liming: liming is done to remove epidermis layer using calcium hydroxide which attacks epidermal proteins exclusively but dermal layer containing collagen is not affected by liming
- Bating: bating is carried out with trypsin which hydrolyses elastin protein of the skin.
- Tanning: basically there are two principal types of tanning which includes vegetable tannage and mineral tannage. Vegetable tannage gives heavy leather while mineral tannage gives soft and pliable leather. Mineral tannage is preferred for shark skin where active ingredients are tannin which areglucosides of polyphenol.
- Drying: using tunnel drier preferably at slow rate.
- Finishing operations: lubrication of fibre with fat - liquor colouring and shading by combination of dyes

Removal of shagreen is necessary as it makes the leather rough.

10.3. Fish glue

Fish gelatin and fish glue are more or less same and can be prepared from fish skin and fish head. If required, fish skin can be preserved by salting and drying before processing into glue however, fish head should be processed fresh.

Process
Glue from fish skin : Skin whether fresh or salted is washed and soaked in fresh water for the periods in the range of 1- 18 hrs depending on the condition of the material (fresh or salted). Washed skins are immersed in 0.2% caustic soda solution to open the fibre bundles and remove cementing materials. It is then neutralised with HCl and washed again in cold running water. Swollen skin is then transferred to steam jacketed double bottomed kettle covered with an equal weight of water and is heated with steam. Small quantities of acetic acid also may be added to the mixture to hasten the hydrolysis of the stock into glue and to act as a catalyst. Cooking is continued for about 8 hrs and the glue liquid is drawn off from the bottom of the cooker. The second run is made in a similar manner which is then concentrated in open heated pans at atmospheric pressure until the solid content reaches to 50- 55 % and cooled. Sometimes small quantities of volatile essential oils may be added to preserve the glue and to mask the fishy odour.
Glue from fish head: It should be processed fresh with addition of some bleaching agents like sulphurous acid during cooking of the skin some glacial acetic acid is

added which softens the head bones.

Uses

- Can be used in furniture
- Box making
- Sizing agent
- Can be used in special cements
- Photo engraving plate manufacture
- Book binding and small repair work etc

10.4. 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 like oil sardine, mackerel, herring etc. When guanine particles are deposited on the inside surface of solid beads, an optical effect similar to that of real pearl is obtained.

Process

Freshly removed scales are collected and washed to obtain adhering foreign matter. Scale can be preserved in 10- 15% brine which is later drained off and scales are squeezed in muslin cloth bag and compressed. It can be stored at 0° C for several weeks without getting them dry. Pearl essence can be prepared as aqueous and no – aqueous suspension

Aqueous suspension can be prepared by agitating washed scales with water containing little ammonia. The mixture is then passed through a strainer. The pearly substance present as a suspension in the liquor is purified by settling in a cool atmosphere. Guanine settles and supernatant is decanted and replaced with fresh ammoniacal water. The process is repeated several times and 0.3% salicylic acid is used as preservative.

Non- aqueous suspension can be made by suspending it in organic solvents like acetone, amyl acetate, chloroform or acetic acid. It is presented in a form of thick paste of crystals suspended in viscous liquor of cellulose of amyl acetate.

Uses

- In the manufacture of artificial pearls
- It is used on diverse articles such as shoe, pencil, fishing rod and spectacle frame

10.5. Beche- de -mer

This is a product processed out of marine animal called sea cucumber belonging to class Holothuria which inhabits in tropical and temperate waters especially in Indo pacific regions. In India, sea cucumbers are found in south-east coast, Gulf of Mannar, Gulf of Kutch and Andaman and Nicobar and Lakshadweep. Holothuriascabra is the most abundantly used in India. Product prepared from sea cucumber is known as beche- de- mer or trepang. The animals are collected from shallow sea bed washed in clean sea water to remove dirt, sand and extraneous matter and then heated gently over a fire without any addition of water in galvanised iron or aluminium tubs. Then they are washed and cleaned and heated more strongly till sufficient water is expelled from their bodies to cover them completely. Boiling is continued for 50 min till a animal shrinks to half of their original size. The material is buried in sand and the sea water is sprinkled over to avoid drying up. After 18 hrs pit is opened out and skins are peeled off manually and taken in basket. De-skinning is carried out then washed and boiled with sea water. Water is drained and dried in the sun spread on mats. Smoking is carried out if it is desired by buyers.

Unit 11 - Chitin and Chitosan

Expected learning outcome

- Preparation of Chitin and Chitosan
- Uses of Chitin and Chitosan

11.1. Chitin and Chitosan

What is Chitin?

Chitin is the second most abundant naturally occurring biopolymer (after cellulose) and is found in the exoskeleton of crustaceans, in fungal cell walls and other biological materials. It is mainly poly (ß-(1-4)-2-acetamide- D-glucose), which is structurally identical to cellulose except that secondary hydroxyl on the second carbon atom of the hexose repeat unit is replaced by an acetamide group.

What is chitosan?

Chitosan is a natural polysaccharide comprising copolymers of glucosamine and N-acetylglucosamine, and can be obtained by the partial deacetylation of chitin, from crustacean shells, the second most abundant natural polymer after cellulose. Chitosan is derived from chitin by deacetylation in the presence of alkali. Therefore, chitosan is a co-polymer consisting of (ß-(1-4)-2-acetamido-Dglucose and (ß-(1-4)-2-acetamide-D-glucose units with the latter usually exceeding 80%.

11.2. Characteristics of chitin and chitosan

- Chitin is a white, hard, inelastic, nitrogenous polysaccharide and the major source of surface pollution in coastal areas
- Chitosan is a fiber-like substance derived from chitin
- Chitin is the fiber in shellfish shell such as crab, lobster and shrimp
- The chitin is deproteinized, demineralized and de-acetylated. It is a dietary fiber, meaning that it cannot be digested by the digestive enzymes of a person

11.3. Preparation of Chitin and Chitosan

What are all the sources of Chitin?

It is also found in common foods we eat such as grain, yeast, bananas, and mushrooms. Like cellulose, it functions as structural polysaccharides. Its natural production is inexhaustible; arthropods, by themselves, count more than 106 species from the 1.2 X 106 of total species compiled for animal kingdom, constitute permanent and large biomass source.

How are chitin and chitosan prepared?

Chitin can be converted into chitosan by enzymatic means or alkali deacetylation, this being the most utilized method. During the course of deacetylation, part of polymer N-acetyl links are broken with the formation of D-glucosamine units, which contain a free amine group, increasing the polymer's solubility in aqueous means.

Preparation of Chitin

The production of chitin from shrimp and crab waste involves two steps:

- Deproteinization
- Demineralization

Demineralization is achieved using mineral acid and deproteinization of demineralized mass is achieved using dilute solution of caustic soda. Shell waste is stirred with dilute HCl (1.2 N) for 1-2 hours until it becomes soft. The liquid is decanted and washed with water until free of acid. Demineralized mass is boiled in 5% caustic soda for few minute. The liquid portion containing protein is filtered and the residue is washed with water until free of alkali. The wet mass is dried under sun and the product obtained is chitin which is pulverized to required mesh size before bagging.

Preparation of chitosan

Chitin is mixed with 40 % solution of caustic soda and heated by indirect steam at 90-100 °C in steam jacketed kettle for 90-120 minutes. During heating, samples are drawn at intervals from reaction mixture washed free of alkali and tested for solubility in 1% acetic acid. Completion of deacetylation is indicated by complete solubility in acetic acid. At the end, caustic soda solution is drained off and residue is washed until free from alkali, dried in sun. Chitosan is pulverized to required mesh size before bagging.

11.4. Uses of Chitin and Chitosan

Chitin and chitosan have been successfully used as food wraps due to their film forming properties. Chitosan has been widely used in vastly diverse fields, ranging from waste management to food processing, medicine and biotechnology. It becomes an interesting material in pharmaceutical applications due to its biodegradability and biocompatibility, and low toxicity.

- As clarifying agent of food juices and in purification of drinking water
- Thickening and stabilizing agent in food
- Treatment of waste and sewage water
- In cosmetics as a moisturizer and for protection against UV rays
- As a base for chromatography
- As a haemostatic agent in surgery and dentistry
- In fiber, films and membranes
- Important characteristic of chitosan films is these films are tough, long-lasting, flexible and very difficult to tear.
- Chitosan coating offers a great advantage in preventing microbial surface growth on foods. It would allow the inhibition of development of Listeria monocytogenes while being a biopackaging.
- Chitosan has found wide applicability in conventional pharmaceutical devices as a potential formulation excipient.

- The use of chitosan in novel drug delivery as mucoadhesive, peptide and gene delivery, as well as oral enhancer have been reported in the literature.
- Chitosan exhibits myriad biological actions such as hypocholesterolemic, antimicrobial, and wound healing properties.
- Since chitosan is a new substance, it is important to carry out precise standardization for its pharmaceutical and biomedical applications like other auxiliary substances.

Unit 12 - Seaweeds

Expected learning outcome

- Resources in India
- Different types
- Utilization of seaweeds
- Agar agar
- Carrageenan and other hydrocolloids

12.1. Seaweeds

Seaweeds are one of the economically important marine resources of the oceans. They are primitive group of macro-phytes which do not have flowers, leaves and stems. The size varied from 30-60 cm (smaller green seaweed species) to 20 m in length (giant kelp).

How many species of seaweeds are there in the world?

About 720 species of seaweeds are available in the world, of which 221 species are commercially important. Among these 145 species are used for food purpose and 110 species for phycocolloid production.

What are the chemical constituents of seaweeds?

Seaweeds are very rich source of protein, amino acids, carbohydrate, iodine, minerals, vitamins, trace metals and bioactive compounds. Red seaweed contains 18 types of free amino acids including taurine, which control blood cholesterol. Besides, the red seaweeds is a preferred source of red pigments gamma-phycoerythrin that is used as a fluorescent tag in the medical diagnostic industry. The seaweeds are used as sources of agar, agarose, carragenan, alginates, iodines, etc. Seaweed polysaccharides are used in production of tooth paste, shaving cream, ice-cream, tomato ketch-up, dairy products, meat processing, chocolates, textile printing, paper manufacturing. It is also used in biotechnological and biomedical industries.

12.2. Types of seaweeds

They are broadly categorized in to 3 types:

- Red seaweeds
- Green seaweeds
- Brown seaweeds

Green seaweeds: About 900 species of green seaweeds belonging to several genera are available in the world of which the four genera namely *Enteromorpha, Ulva, Caulerpa* and *Codium* are economically important.

Brown seaweeds: Although 1500 species of brown seaweeds under different genera are available globally in seawater, the brown seaweeds belonging to the genus *Laminaria, Undaria, Sargassum* and *Turbinaria* are having commercial importance.

Red seaweeds: Out of 4000 species of red seaweeds that are available in different oceans of the world, the commercially important red seaweeds are coming under the genera *Porphyra, Gracilaria, Gelidiela, Eucheuma* and *Chondrus.*

12.3. Species of seaweeds cultured

The important seaweeds cultured in different parts of the world are-:
China: *Laminaria,* Japan: *Porphyra,* Philippines: *Eucheuma,* Korea: *Undaria,* Indonesia: *Eucheuma, Gracilaria, Gelidium* and *Hypnea,* India: *Gracilaria, Gelidiella, Eucheuma, Hypnea, Sargassum, Turbinaria.*

12.4. Seaweed resources of India

Seaweeds are abundantly available in the rocky or coral substratum of Tamil Nadu, Gujrat and the vicinity of Bombay, Ratnagiri, Goa, Karwar, Vizhinjam, Varkala, Lakshadweep and Andaman and Nicober Island. About 690 species are found in Indian water of which 60 species are having commercial importance. Agar producing red seaweed *Gracilaria* and *Gelidiella* is available throughout the year, whereas the algin yielding brown algae *Sargassum* and *Turbinaria* is available plenty during August to September in Southern Coast.

12.5. Utilization of seaweeds

Seaweeds are important component of the marine living resources. Seaweeds are mostly found in shallow coastal water area and rocky shores. Seaweeds are broadly grouped into green, brown, red and blue-green algae based on their pigmentation. Seaweeds are mostly harvested in Japan and China and are used as medicine, food, fodder and manure. Maritime countries used seaweeds as vermifuge, anesthetic and ointment as well as for the treatment of cough, wounds, gout, goiter, etc. Sailors have been treating wounds for last several years with seaweeds. Sterols and related compounds present in seaweeds have ability to lower blood plasma cholesterol level. Seaweeds dietary fiber perform varied range of function such as anti-oxidant, anti-mutagenic, anticoagulant, anti-tumor etc. High intake of calcium, potassium and sodium are associated with lower mean systolic pressure and lower risk of hypertension. Seaweeds contain high amount of potassium, which is identical with our natural plasma level. The research work in this type shown that seaweed extract is similar to human blood plasma.

In India, seaweed is used as manure especially for coconut plantations in Tamil-Nadu. Plants readily absorb the high amount of water-soluble potash and other minerals present in seaweeds. The carbohydrate and other chemicals present in the seaweeds improve the moisture retaining capacity of the soil and control certain plant diseases. So all kind of seaweed and sea-grasses can be used as manure either directly or in the form of compost.

Varieties of food items are prepared in Japan from seaweeds. The seaweed are being used as salad, boiled (Kelp), jelly (red seaweed), vinegar dish (brown and red seaweed) and spices (red green and brown seaweed). The most common use of *Porphyra* (Nori) is as ingredient in dishes like "Sushi" wherein the seaweed sheets are wrapped around flavored rice. Dried *Laminaria* serve as soup or eaten as a vegetable and large quantity consumed in Japan and China where it is called "Kombu". In India, people belonging to coastal belt of Tamil Nadu consume *Gracilaria lichenoides* as food in the preparation of porridge or "Kanji". Presence of all the amino acids in the protein needed in the human diets have been observed in the Indian seaweeds. Green seaweed and red seaweed contain 2-2.5 % of protein. The vitamins namely A, B and B12 are found higher in many algae as compared to much other food material.

In India, seaweeds are used to certain extent as food in coastal areas of Tamil Nadu where *Gracilaria edulis* is being used since decades for making gruel. Some common products prepared from seaweeds are, agar-agar, algin, seaweed meal, Ulva jam, seaweed salad, seaweed vegetable, seaweed curry, seaweed porridge, seaweed manure, seaweed compost, seaweed meal for poultry and cattle and some medicinal products.

12.6. Agar agar

Agar is used in food, confectionary and dairy industries as gelling, stabilizing and thickening agents mainly in the manufacture of sweets, jellies, and ice creams. Agar is also used in medicines. Fresh dried and processed seaweeds are utilized for human consumption. Food value of seaweeds depends on the mineral, trace elements, proteins and vitamin present in them.

Preparation

Gracillaria is used as a raw material for preparation of agar agar. Seaweed is blanched, and Cleaned by abrasion In a stone mortar to remove sand and other traces of foreign matter. Seaweeds are soaked in Soaked in 6-8 liters of soft water for 24 h and wet ground in stone mortar into pulp using soft water. The pulp is then leached in soft water of about 6-7 liters for a period of 24 h and separated by filtering with organdy cloth and extracted at 900 C in 3 liters of soft water for 1-2 h. Hot seaweeds are then filtered with 2-3 layer of cloth and sedimentation is carried out for suspended impurities in the solution. The agar solution is cooled at room temperature and shredding is carried out for agar gel. Sun dried gel strips on plastic netting can be known as agar agar.

12.7. Carrageenan

Carrageenan is one of the commercially important water-soluble polysaccharides extracted from certain red algae and is widely used in foods, dairy products and pharmaceuticals. There are several varieties of carrageen like kappa and lambda which are used in cooking and baking. Gelatinous extracts of the Chondrus crispus (Irish Moss) seaweed have been used as food additives for hundreds of years. Carrageenan is a vegetarian and vegan alternative to gelatin.

12.8. Other hydrocolloids

The cell wall of brown macro algae contains a range of different polysaccharides including alginic acids (alginates), laminarins (laminarans) and fucoidans (sulphated fucans). Alginic acid are used as thickeners, emulsifier, stabilisers, binding and gel forming agents in the food, cosmetic, textile, construction and pharmaceutical / biomedical industries.

Unit 13 - Diversified fish products/ value addition

Expected learning outcome

- Breaded and Battered Products
- Fish finger
- Fish cutlet
- Imitation products
- HACCP in product preparation

13.1. Breaded and Battered Products

Coating seafood, poultry or vegetable products with a batter and/ or breading before cooking is an established domestic as well as commercial practice. Of late, the emphasis of coated products has shifted from the home front to the restaurant and fast- food outlets. Prominent among the coated products are the seafood products. Battered and breaded fish finger or fish stick has been one of the forerunner in this field and still command a sizeable share of the battered and breaded seafood trade. Such products, when frozen in ready- to- cook form, offer a convenience of high consumer value and are called 'convenience foods'. Fish finger, fish portion and fish cake are the staple battered and breaded fish products. Breaded shrimp, scallop and oyster cater to luxury market.

The coating process:

The unit operations in development of coated products are portioning/ forming, predusting, battering, breading, fish frying, freezing, packaging and storage.

Predusting:

Predust usually a very fine, dry, raw flour material that is sprinkled on the moist surface of the frozen or fresh food substrate before any other coating is applied. It improves adhesion of the batter, because it absorbs part of the water on the surface of the food. If the batter is applied to a surface that is too moist, it can slip, leaving some areas uncovered. Also, the use of predust tends to increase pickup. The most commonly used predusts are wheat flour, gums and proteins, alone or in combination.

Batters:

Batters are of two types, adhesive and tempura. The traditional adhesive batter is a fluid, basically consisting of flour and water, into which the product is dipped before it is cooked or fried. A bond between the product and the coating is formed. The proportion of batter and water is usually in the ratio of 1:2. Higher amount of water might affect the functional need of fixing the crumbs onto the batter and also will necessitate longer time to freeze the batter. The desired viscosity and pick up decide the ratio of components in the batter mix.

The ingredients that constitute that constitute the batter include starch, salt, seasonings, gums, egg and many other items. The batter also usually incorporates a leavening agent to favour expansion of the product during frying.

Breading:
Breading is a serial- based coating, often of breadcrumbs. The main ingredients are almost same as for batters, and consist of flours, starch and seasonings. Breading is coarse in nature and applied to a moist or battered food product prior to cooking. Texture, mesh size, porosity and absorption re the major factors contributing to the texture of the breading. Mesh size may be coarse, medium or fine and is important in the formation of an attractive and economical coating system. Coarse particles are desirable to achieve textural targets; however, its excess use on a small surface area may cause its falling off during handling and transportation. Hence a balance among different mesh sizes is desirable. Cracker meal/traditional breading is widely used in fish products. Cracker-meal breaders, which are used to develop a cracker type, relatively hard texture, consist of unleavened flour. Home- style breadcrumbs are more porous than cracker meal and tend to absorb more oil and moisture. Japanese style crumbs, also called 'Oriental style or Panko crumb', has a characteristic flake- like elongated structure and excellent visual appeal, and provides a unique surface- texture when fried. Crumb coating are usually coloured with natural vegetable extracts to give a golden- brown appearance. These colours include paprika, annatto, turmeric or caramel.

Frying:
Fat is the frying medium. Besides being the heat transfer medium, it is also a food ingredient that will influence the eating quality. Some may have specific flavour which may be carried over the product. Usually bleached and refined vegetable oils are used for frying. At the high temperature of frying, some fat may undergo changes such as polymerization. It is therefore important to use an oil of good quality for frying. According to normal manufacturing process, prefrying in oil is carried out at 180°C to 200°C for about 30 sec followed by freezing the product.

Packing:
Conventional packaging materials like flexible plastic films alone are not suitable for packaging, since they provide little mechanical protection to the products. As a result, the product get damaged or broken during handling and transportation. The packaging may be a paperboard carton or a poly- lined paper bag or poly-bag, which is heat sealed. The bags are designated to give support to a larger quantity of items such as fish fingers. In recent times, thermo- formed containers are commonly used for packaging coated products. These trays produced from food-grade materials are suitable for packaging breaded items both for domestic as well as export markets. Trays are made of polyvinylidene chloride, high impact polystyrene (HIP) and high-density polyethylene (HDPE) are unaffected by subzero

temperatures and provide protection to the contents against desiccation and oxidation during prolonged storage.

13.2. Fish finger and FIsh cutlet

Fish finger:

Fish finger is a very popular product made out of fish mince. The mince is mixed with 1 percent salt, made into rectangular slabs and frozen. The frozen mince is cut into suitable uniform sizes. These pieces are given a coating of batter followed by breading. The battered and breaded fishfingers are flash-fried in oil maintained at 180-200°C for about 20 seconds. After cooling the fingers are frozen and stored.

Fish Cutlet:

Fish cutlet is another delicacy product among fish consumers. The basic raw material required for preparation of this product is cooked fish or mince (fish kheema). Kheema is the fish meal picked from whole fish by means of a meat picking machine.

Method of preparation:

Minced fish (65% of the total weight or mix) is cooked in boiling water for 20 min and excess water is removed. Salt and turmeric are added to the cooked meat and mixed well. Boiled and peeled potatoes are made into a paste and mixed with cooked fish. Onion, garlic and chillies are chopped into small sizes and fried in refined oil until golden brown in color and are added to the mixture. The whole mass is heated again for 3 min. Powered spices are added and mixed well. The mix is moulded into 40g size cutlets in oval or round form. They are then dipped in a batter of egg white and rolled over bread crumbs. The cutlets are then flash dried at 160-170°C for 5sec and then held in frozen storage at -20°C. Shelf life of frozen cutlet is 22weeks. They are thawed and fried in oil before use.

13.3. Imitation products

Several value added imitation products are made from surimi (water washed mince). These include imitation of shrimp lobster tails breaded scallops, imitation breaded crab claws, sushi products, sushi sticks, imitation crab shreds, minced sticks, filament sticks and others. These seafood analogs possess the accepted texture, flavour and appearance of the authentic products. For production of seafood analogs, the surimi blocks are chopped to create a paste. The paste is combined usually with additional amounts of cryoprotectants and other additives such as salt, soy protein, starch, egg white, alginate etc to promote cohesion among the protein molecules and thereby to improve the texture and flavour of the finished product. For chopping the frozen blocks, it is ideal to use a vacuum mixer, which helps to disintegrate the mince and make the proteins available for binding the ingredients. A vacuum mixer also removes any air that could be introduced in the chopped product, which can result in uneven heating during cooking. The chopped paste is extruded as a flat sheet (approximately 1-2 mm thick) molded into desired shapes and set by placing on a cooking belt where it is heated. Heating is done at 90-93°C for 30- 100 sec on a stainless steel belt, drum. Final texture is developed during thermal pasteurization, which is performed after bundling, cutting and packaging. The pasteurization step eliminates bacterial pathogens that might grow during the storage of the product. Generally surimi seafood should be cooled from 60 to 21.1°C or below within 2 h and to 4.4°C or below within 4h and should be held at 4.4°C or below at all times during storage and distribution.

13.4. HACCP in product preparation

HACCP is a total quality management system with emphasis on safety based on a systematic approach to identification, assessment and control of hazards. It is a preventive control system in which hazard is controlled or eliminated before it occurs. It concentrates on prevention strategies on known hazards and the risks arising out of them occurring at specific points in the processing schedule.

HACCP Concept

Food must be safe to consume and conform to certain standards. If some properties are monitored by plant, but without supplementary information, the tests will provide only a poor means for controlling and operation. If the product does not conform to specifications, it may have to be reprocessed or discarded. This contingency can be avoided if certain key variables in the process are monitored and controlled. Such a system is provided by HACCP. HACCP is based on a set of seven principles. The system envisages identification of potential hazards in seafood processing at all stages upto the point of consumption. The seven principles are

- Hazard analysis- Assess the hazards associated with capture, storage, raw materials and ingredients, pre-process and process operations, and all other activities upto consumption. Prepare a flow diagram of the steps in the process. Identify and list hazards and specify control measures.
- Determination of critical control points (CCP)
- Specification of criteria – Establish target levels and critical limits that must be met to ensure that each CCP is under control.
- Establishment of procedure and monitoring system to ensure control of the CCP and their implementation.
- Corrective action when the monitor indicates any deviation from the critical limits or that the process is out of control.
- Establishment of procedures to verify that the HACCP is working correctly and effectively.
- Establishment of documents concerning all procedures and records appropriate to these principles and their application.

Hazard:

A hazard is a biological, chemical or physical factor that has the potential to cause an adverse effect on human health. Biological hazards include pathogenic microorganisms, parasites, toxigenic plants, animals and products of decomposition like histamine. Pesticides, detergents, antibiotics, heavy metals, non-permitted food colours and food additives etc constitute the important chemical hazards. Extraneous matter like filth, metal or glass fragments, stones etc are important among physical hazards.

Hazard analysis:
This is a system using which the significance of a hazard to consumer safety can be analysed. By using this system it can be decided which hazards are of such nature that their elimination or reduction to acceptable levels is essential to produce a safe food product. Identification of hazards, their assessment and identification of control measures constitute the important functions of hazard analysis.

Critical control points:
A critical control point (CCP) is a point or a stage in the processing operation where failure to control effectively would most likely result in the production of defective/ unsafe food. In other words, it is a step which, if properly controlled, will eliminate or reduce a hazard to an acceptable level. A step/ point is any stage in the production. This includes raw materials, transport to processing plants, processing and storage. CCPs require constant checking to ensure compliance with all the requirements of the product.

Control points:
These are other points in the processing operation where failure to effectively control may not necessarily result in the production of defective/ unsafe food. These points require occasional checking throughout the production shift.

13.4.1. Determination of CCPs

The relevance of each identified hazard in each stage of the process is considered. If the hazard can be reduced, prevented or eliminated through some form of control at a particular stage, it is a CCP.
There are two types of CCPs, CCP1 and CCP2. The CCP1 will ensure the control of a hazard, whereas CCP2 will minimise the hazard, but will not assure its control. Both are important and should be controlled. A judgement of risk also must be made so that a level of concern can be ascribed to it. The four levels of concern are

- High concern, where without control there is a life threatening risk.
- Medium concern, where there is a threat to the consumer that must be controlled.
- Low concern, where there is little threat to the consumer; still is advantageous to control it.
- No concern, where there is no threat to the consumer.

The points which are not critical because of low risks need less control and monitoring. If a hazard can be controlled at more than one point, the most effective place for control should be decided.

13.4.2. Specification of criteria for control

The team should next identify the means by which the hazard can be controlled at each CCP. These may include level of chlorination in wash water, temperature during storage, moisture content, level of toxic materials, sensory parameters , time and temperature requirements for thermally processed foods etc. All these must be documented as clear unambiguous statements or included as specifications in operating manuals. The team will also have to set target levels and specified tolerances of the control measures at each CCP. Critical limits may also be derived from government regulations and guidelines, international codes of practices, experimental studies or any other recognised source.

13.4.3. Monitoring and checking system

There must be a mechanism to monitor, check and measure to ensure that processing procedures at each CCP are under control. The monitoring must be able to detect any deviation from these specifications. It should be rapid enough so that corrective action can be taken in time and loss of the product is avoided or minimised. The main methods to monitor a CCP are

- Visual observation
- Sensory evaluation
- Physical measurement
- Chemical testing
- Microbiological analysis

Visual observation is basic, but gives rapid results. Sensory evaluation can be used to check the quality of incoming raw materials. Rapid chemical tests e.g. chlorine in water, are useful to monitor CCPs. Other measurements possible are time, temperature, pH and salt concentration. Microbiological test is of limited use in monitoring CCP. It can, however, be employed for testing before starting processing, and for testing finished products before release.

13.4.4. Corrective action, verification and documentation

Corrective Action:

If monitoring indicates that there are deviations from the critical limits or that the process is out of control, corrective actions must be taken immediately. The corrective actions must be based on the assessment of hazards, risk and severity, and on the final use of the product. A plan should have been prepared in advance so that there will be no delay in taking corrective action. The team should prepare this plan specifying the corrective action, identify the persons to implement them and disposition actions needed to be taken with the food that has been produced during the 'out of control' period.

Verification:

Once the HACCP system has been drawn up for a product/ process it must be reviewed before it is installed and regularly reviewed while it is in operation. The appropriateness of the CCPs and control criteria can be determined and the extent and effectiveness of monitoring can be verified. The team should describe in detail the methods and procedures to be used to verify the system. Some of the methods that can be used in verification are

- Reviewing the HACCP study and its records
- Random sampling and analysis (microbiological)
- Detailed tests at selected CCPs
- Survey of conditions during storage, distribution, sale and use of products

- Interviewing staff

Documentation:

Proper records should be maintained on all actions in the HACCP system in order that origin, cause and point of occurrence of the hazard can be traced. Records should be maintained on the following aspects

- HACCP plan and supporting documentation
- Monitoring CCPs
- Records of corrective actions
- Records of verification activities and modifications
- Nature, coding and disposition of the product

13.4.5. Training of Personnel

Successful implementation of any programme will depend largely on the persons responsible for different activities in the programme. Individuals to whom quality assurance task is assigned should possess an in-depth knowledge of the various aspects of the discipline. This can be achieved only by education and training of the staff.