

Course Name: Canning Technology and Value Addition in Seafood
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Lecture:26

Spoilage in seafood.

Welcome back to the new session on Canning Technology and Value Addition of Sea Foods. The course is offered by NPTEL. In the last two classes we have seen composition and nutritional quality of safe foods and muscle structure of the sea foods. In today's class, we will be dealing about spoilages that are very common to sea foods and the reason for these spoilages.

Now, to understand what is a spoilage, fish being a perishable commodity. Because of its high moisture content, it is prone to spoilage. In the last class, we had seen that it contains high amounts of protein and lipid. It's a cheap source of protein and these pose a reason for the perishability of the fish. Fish contains high amounts of moisture and because of this moisture content, the muscle tissue may undergo degradation. It could be of enzymatic or microbial degradation. Since it contains high amounts of protein, these protein denaturation and lipid denaturation is also very common and for these reasons, the fish need to be preserved immediately and spoilages usually starts immediately after the fish is captured or killed. It refers to the contamination that happens because of the undesirable changes that are caused in flavor of the fish, color, texture or odor or overall appearance of the fish.

Generally, spoilage of fish is also called putrefaction. But scientifically, putrefaction means denaturation or degradation of protein molecules to amines and smaller molecules, aldehydes and ketones which cause changes in odor and smell or flavor but sometimes these two words are used interchangeably. Generally, the spoilage characteristics include color change, fishy smell or sour smell, increased sliminess on the skins and scales, then loosening of scales and discoloration of backbone, loss of firmness of the fish tissue. All these are associated with the spoilage characteristics. These are actually sensory characteristics which one can observe on the surface of the fish and they can make out whether the fish has been spoiled or not. So, this figure shows whether a fish is good or bad. If you look at the figure here, the gills shown on the lower part they are bright red in color. So, it indicates that the fish is fresh and it is good for consumption.

However, on the upper figure, you can see that gills have turned grayish, so that shows spoilage. The spoilage has started, and similarly in the case of eyes, when the fish is good, it is bulged and dark in color, whereas when the fish has spoiled, it becomes faded and shrunk, and again the scales on the surface of the skin come out easily in the spoiled fish. So, these are some of the sensory indicators or organoleptic indicators by which one can make out whether the fish has spoiled or not.



Characteristics of fresh and spoiled fish		
	Fresh fish	Spoiled fish
Odor	Fresh, fishy odor	Sour/ putrid
Eyes	Shiny, bulging	Cloudy & shrunk
Color	Bright	Faded
Flesh	Firm, elastic and body is stiff	Soft and flabby
Scales	Bright & firmly attached	Loose and easily removed
Muscle tissue	White	Pinkish
Gills	Shiny, pink or red	Dull brown or gray
pH	6.0-7.0	<6.0

This is a tabulated slide where you can note down the sensory parameters: order, eyes, color, flesh, nature, and we can discriminate or identify if the fish is fresh or spoiled. For example, when we consider the order in the fresh fish, it will be a fishy order, but in the spoiled fish, it will turn to putrid or sour order because of the production of lactic acids and degradation of protein

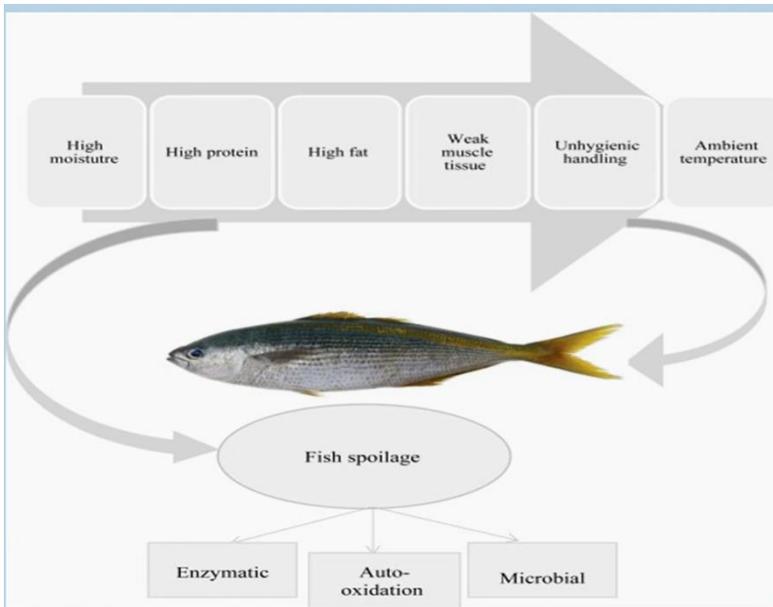
molecules. So again, the eyes will be shiny and bulging in fresh fish, but they will become cloudy and depress in the spoiled fish. The color will be bright in the case of fresh fish, but it will become faded. Similarly, on the flesh, when one puts pressure with the thumb, the thumb impression will be retained in the spoiled fish, whereas in the fresh fish its body will be firm and elastic. And scales, again, will be bright and firm in the case of fresh fish. In the case of spoiled fish, they will come out easily. The muscle tissue might be white or red, but it may become or turn pinkish. But then don't confuse it with the pinkish musculature because, again, the musculature we have seen in the last class that it is of three types: red, white, and pink. This pinkish color in the spoiled fish is because of deterioration. And gills, again, like I said in the beginning, become dull brown or grey in the spoiled fish. For all these reasons, the degradation of proteins and lipids cause reduction in the pH, which is shown by the reduction of pH. The pH comes down to 6, below 6 in the case of spoiled fish.

Usually, the flat fish undergo spoilage more rapidly. So again, we had seen what is a round fish and what is a flat fish. So, flat fishes undergo deterioration or spoilage more

rapidly than round fish because they undergo rigor mortis faster. This rapid deterioration is also due to the degradation of unsaturated fatty acids found in flat fishes.

The other common factors, the characteristics we have seen in the previous slides, are intrinsic to the fish or animal. But other reasons also contribute to spoilage, foremost among them being the quality of water. The quality of water, whether it's the water in which the animal was captured or the water used for processing or other preservation activities, can lead to contamination. Generally, microbial contaminations, such as those from *Pseudomonas*, *Acinetobacter*, *Moraxella* species, *Alcaligenes*, *Micrococcus*, and *Flavobacterium*, occur from water sources. In northern waters, being ice cold, cold-loving microorganisms thrive in these conditions. In our water conditions or tropical water conditions, we generally find mesophiles. In the gut system, numerous types of microorganisms are found, but main spoilage microorganisms like *Pseudomonas*, *Bacillus*, and *Flavobacterium* survive in the fish gut. Once the gut degrades, these microorganisms come out to the surface and cause spoilage. In freshwater fish, we generally find *Aeromonas*, *Lactobacillus*, *Alcaligenes*, *Streptococcus*, etc., and shellfish also harbor similar microbes. Apart from the usual ones, we also see *Proteus*, *Acinetobacter*, *Moraxella*, etc.

The surface slime, especially the slime on the gills and the intestinal fluid, harbors high microbial loads. It has been reported that slime can contribute to hundreds to millions of microbes per square centimeter. Similarly, in intestinal fluid, it can range between thousands to hundreds of millions, and in gills, it can also reach thousands to millions. So, it is just to show that these are the main sites from where microbial contamination starts immediately after the fish is captured. We have to wash it out so that the slime is removed and also degut it. That's why we said in the beginning that degutting is the only process that has to be done immediately so that microbial contamination or the escape of microorganisms from these places can be prevented. And also, we have to be careful about how the fish are handled with the equipment. If the handling is not proper, it is unhygienic, or the contact surfaces of animals are not properly cleaned or hygienic, they may also transfer microorganisms to the fish or the animal. Then, of course, we have seen moisture, fat, and protein are the main components that undergo deterioration, and microorganisms may survive on these macro components. But this only happens when the temperature is ambient, that is, the optimum temperature for microbial growth is provided. Only then the microbes will survive on these macro components and cause spoilage. Therefore, it is necessary to manipulate the temperature, either by reducing it immediately through chilling or freezing, or by increasing it through pasteurization or canning.

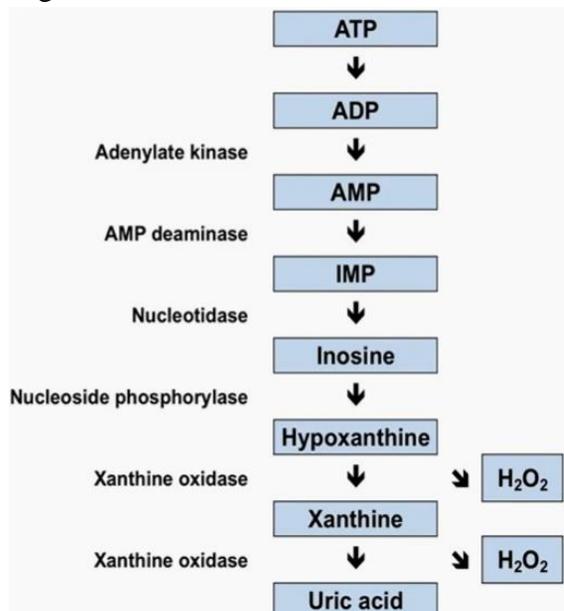


Then, generally, fish spoilage can be classified into three types: enzymatic, auto-oxidation, and microbial. So, the arrow mark moves from left to right just to indicate that ambient temperature is the most important factor, though moisture is also important for microbial growth. By maintaining or modulating the water content, we can

control moisture and consequently control microbial growth. But if the temperature is appropriate, it is very hard to control microbial growth. If you see in this line, temperature is the most important factor, and next is unhygienic handling. Therefore, while handling the fish, the person should be very careful, and the hands should be cleaned and washed properly to prevent contamination from the hands to the animal.

Now, let's see each type of spoilage. Autolysis or enzymatic degradation, as the name suggests, happens because of enzymes present in the body of the fish. They participate in or cause autolysis. During autolysis, the enzymes escape from the cell, causing cell lysis. These enzymes then escape to the external environment and degrade other macromolecules, thereby releasing micromolecules or forming other metabolites that affect the flavor and odor of the fish. One such example is the conversion of ATP to hypoxanthin. Whenever the animal dies, anaerobic degradation is seen, or glycogen is degraded to lactic acid. At the same time, ATP molecules are decomposed and

converted.



This is the flowchart of how it decomposes: one molecule of ATP has phosphate removed, converting it to ADP, then AMP, and finally to IMP. The conversion from ATP to IMP is a slow reaction, taking around 24 hours or less. But from IMP to hypoxanthin, it is a fast reaction. Once hypoxanthin is formed, it imparts bitterness or a bitter taste to the product. Therefore, hypoxanthin is taken as

an indicator or biomarker to determine the freshness of the fish.

Again, many enzymes are involved in this. It is not a simple conversion from ATP to IMP or hypoxanthin. It is a step-by-step process where enzymes like ATPase, AMP, D-aminase, nucleotidase, syn-nucleosidase, and xanthine oxidase play important roles in the degradation of ATP molecules. Generally, the freshness of fish is indicated by the K value, which is expressed in percentage. It's the ratio of inosine and hypoxanthin over the degradative products from ATP to hypoxanthin, and since it is expressed in percentage, we multiply it by 100.

$$K \text{ value (\%)} = \left[\frac{\text{Ino} + \text{Hypo}}{\text{ATP} + \text{ADP} + \text{AMP} + \text{IMP} + \text{Ino} + \text{Hypo}} \right] \times 100$$

Again, when the fish is killed or captured, it enters into rigor mortis. Enzymes, both exogenous and endogenous, are involved in rigor mortis and cause proteolytic enzymes and transglutaminases, which help in rigor formation or starting of rigor. Belly bursting is yet another activity seen, related to enzymatic degradation. Digestive enzymes degrade the belly part, usually seen in sardines where the belly bursts, and the gut contents spill out. Belly bursting is another activity happening due to enzymatic degradation and autolysis also causes black spot formation in shrimps, although it is not toxic or harmful for human beings if consumed. However, it interferes with the aesthetic appearance of the product. If a person sees black spots on shrimp, they may not prefer to buy it, affecting marketability and the product's cost. Protein-degrading enzymes release amines, carbon dioxide, ammonia, and fatty acids, causing a foul smell. Odor changes from fishy to sour or putrid.

The next spoilage is bacterial or microbial spoilage. The surface of the fish, like the gut lining and gills, harbors load of microorganisms. These microorganisms move to different parts of the body, causing spoilage when the fish dies. Bacteria attack the flesh, resulting in the formation of undesirable products. The microbial load of the organism and the different microorganisms seen on the fish's surface depend on the water from where the fish was captured, which is a crucial parameter.

Microbial spoilage includes the conversion of TMAO, as fish is rich in trimethylamine oxide, which is converted to trimethylamine, giving off an offensive odor. Secondly, the degradation of proteins to amino acids, and further degradation to primary amines, may result in poisoning. One such example is histidine. Histidine is converted to histamine by the organism *Morganella morganii* or *Klebsiella pneumonia*. This is commonly seen in

because histamine histidine is converted to histamines, and this is common in scombroid fish. Another one is ciguatera fish poisoning and puffer fish poisoning. Recently, there was news about an elderly couple being killed because of the consumption of puffer fish. Retailers catch the fish and deskin them. Usually, puffer fish skin has to be removed as it is rich in toxins. It is very difficult to identify the fish from where the meat has come. Because of this, the elderly people were not able to understand that it is from a puffer fish. Within 24 hours, both had passed away.

Again, sardine poisoning can occur due to algal bloom. Sardine poisoning can be halogenic fish poisoning, paralytic fish poisoning, etc. All this happens because of contamination of the fish by algae or contaminated water. The environment becomes contaminated, passing on to consumers. In shellfish poisoning, we have paralytic shellfish poisoning, neurotoxic shellfish poisoning, diuretic shellfish poisoning, amnesic shellfish poisoning. These are some common poisonings in shellfish. Apart from this, we also see contaminated water poisoning due to industrial discharges. They cause poisoning due to deposits of heavy metals in muscle tissue. Contaminated water contains high amounts of blue-green algae, cyanobacteria, and Pfiesteria-like organisms, which produce brevetoxin. This can cause spoilage or contamination of muscle tissue, making the product unsuitable for consumers.

How to detect the quality of the fish? We have seen different spoilages, how it happens, and how it can be understood that the spoilage has occurred. When we get a sample, we need to know whether it has been spoiled or not. There are different methods to identify this. There are physical, chemical, and biological methods. Then, of course, we have subjective and organoleptic methods. In the physical method, we commonly use a Torrymeter.



It's an equipment vertically placed on the surface of the fish, giving a digital reading. A value around 10 is considered fresh, below 3 indicates spoilage, and values between 3 and 6 are considered acceptable. The

Torrymeter is very commonly used in commercial industries.

Subjective method includes sensory or organoleptic. You can call it sensory method or organoleptic method. In this case, a person will use all five senses: sight, smell, taste, touch, and feel to assess the product. So, all the senses are being used in this method. We also use the same test we had seen earlier, where you check the gills, eye, and thumb impression to see if it is retained. These are the sensory methods that can be used under this category.

Then, we have biochemical methods. Proximate testing is a very common test done whenever a fish sample is collected. In this, one detects the moisture, protein, lipid content, and ash content. But generally, this is not accepted because sometimes it gives a false result. For example, protein is usually detected by Kjeldhal method. In Kjeldhal method, all the nitrogens will be converted, or we detect nitrogen, which is converted to protein. So, in Kjeldhal method, all the nitrogens will participate in the reaction. It need not be from the protein; it can be from other sources. So, any nitrogens that are formed by contamination or microbial spoilage will also be calculated along with the protein, which is why it gives a false result. Then, hypoxanthin value is very critical. We use hypoxanthin value to identify whether the fish is fresh or not. It is generally said that a value between 7 to 8 micromoles per gram indicates that the fish has spoiled. Similarly, trimethylamine oxide is converted to trimethylamine because of the enzymatic reaction. A slight amount of TMA formation is not there in the fish, but it is formed in the fish because of the enzymatic action. A value of even 1.5 milligrams is sufficient to say that the fish has undergone spoilage.

Another biochemical parameter is ammonia, which you can smell and can identify the presence of ammonia also indicates spoilage. Then, peroxidase and TBA value (thiobarbutyric acid) both indicate oxidative rancidity, whether the liquid has undergone any oxidation. A value less than 10 for peroxidase value indicates that the fish is of good quality, whereas a value above 20 indicates rancidity. In the case of TBA, less than 2 is accepted by the consumers.

Now, coming to the biological method, we can test the TPC, which is the first test usually done to identify the total count of bacteria. Total plate count can be done, and we can also go for the detection of individual bacteria. If a person suspects that a particular kind of microorganism might be there, they can go for selective methods and use selective media to detect the organisms. Usually, in such cases, we identify *E. coli*, *Shigella*, and other coliforms. This indicates bacterial spoilage or the biological method to detect the contamination.

To conclude, in today's session, we have seen the different types of spoilages that may be seen in fish and the methods to detect these spoilages. We have seen biochemical methods, physical methods like torrimeter, chemical methods, and subjective methods, which are the organic methods by which one can detect and determine if the fish is spoiled or not. By using all these methods, we can identify whether the sample has spoiled or not. So, with these words, let's wind up for today.