BIOCHEMICAL ASPECTS OF THE SPOILAGE OF PRAWNS

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[Certain features characterise spoilage of sea foods, as distinct from spoilage of protein foods in general. Among sea foods spoilage differs in the crustaceans, teleosts, or elasmobranchs respectively. High levels of free amino acids concentrations are characteristic of prawns and other crustacean muscle. Changes occurring in these influence pattern of spoilage. Differences also exist in the sea prawns and prawns taken from the backwaters. Melanosis is a characteristic feature of spoilage in prawns. Observations have shown that prawns are very suceptible to spoilage at ordinary temperature, the period of absolute freshness not exceeding 4 hours, while prompt icing extends the period to 3 - 5 days.]

The prawn fishery is one of the most important fisheries of India. About 25% of the prawn catches is consumed locally in the fresh condition 60% is exported as dried prawn pulp to the Eastern countries and 15% exported frozen to Western countries mainly the U. S. A. The frozen prawn exports, however, fetch more price than the dried product. For the production of high quality frozen and canned prawns the raw material has to be in absolutely fresh condition. In order to assess the quality of the raw material suitable for the processing industry a knowledge of the main biochemical and bacteriological changes which occur in prawns from the time these are taken from the water till they are delivered to the factories is necessary. Considerable attention has, therefore, been given to the study of prawn spoilage.

While the spoilage of fish and prawns does not differ essentially from the spoilage of other protein foods certain features characterise the spoilage of seafoods. Fish spoils far more readily than meat and is probably the most perishable amongst foods. Different keeping qualities of some foods are mainly due to differences in their biochemical compositions; in this way fish spoilage differs from spoilage of meat, spoilage of crustaceans such as prawns, lobsters and crabs differs from fish spoilage, spoilage of teleosts i.e. bony fishes differs from spoilage of cartilaginous fishes such as sharks and rays, and the pattern of spoilage differs even amongst the different species of teleost fishes.

The chemical composition of the flesh in respect of the major constituents such as protein and water does not differ significantly in fishes, crustaceans or land animals but the minor constituents, both organic and inorganic, often differ considerably in the different animals. Marine animals contain about 1% trimethylamineoxide in the muscle unlike land animals or fresh-water fishes which contain very little, if any. Spoilage of marine foods is characterised by the peculiar 'fishy' odour caused by trimethylamine which is produced from the oxide through bacterial action. The sea prawns contain about 1% trimethylamineoxide but prawns taken from the backwaters, even those belonging to the marine spp., contain very little; also its concentration appears to vary with the salinity of the backwaters, being lower when the salinity is low. The trimethylamine spoilage test usually applicable to seafish is not of much value in the case of the backwater prawns. Backwater prawns contribute a large proportion of the total prawn fisheries of the Kerala State. The glycogen content of the

prawns is much greater than that of fishes and enzymatic breakdown of the glycogen, which occurs post mortem, results in the production of glucose to which the characteristic sweet taste of prawn and other crustacean meat is due.

A study made by the author and his associates indicated the presence of free amino acids in considerable quantities in several species of prawns, and in lobsters, crabs and several other invertebrates unlike in the fishes. The free amino acids occur in concentrations of 300 mg. N/100 g. muscle in the prawns and this level is about ten times as high as found in the fishes. This fact raises a new factor to be considered in problems relating to the spoilage of prawns. The amino acids present in free condition might easily provide a ready substrate for the bacteria to grow particularly in the early stage ; bacteria normally are unable to attack protein as such but the free amino acids are easily utilised by the bacteria as food. The fate of these amino acids when attacked by bacteria leads to a diversity in the pattern of the spoilage phenomenon, since the free amino acids undergo various transformations such as deamination, decarboxylation, oxidation and reduction and the synthesis of esters. The fruity or grassy odours which are often noticed before the prawns are really spoiled are caused by these esters. These changes occur fairly early in the process of deterioration, much earlier than the onset of protein breakdown and putrifaction. The flavour of prawn meat is no doubt influenced by these amino acids. An examination of the qualitative nature of the free amino acids present in the different species of prawns showed that some essential amino acids are also present in the free condition. When prawns are held in ice storage considerable losses of the free amino acids occur through leaching by the melting ice. The flat taste encountered in prawns preserved in ice is probably due to the loss of the free amino acids, and possibly other water soluble organic compounds present in the muscle.

The black discolouration of the external surfaces which is peculiar to the prawns and occurs when the prawns are held in storage is known to be caused by an enzymatic reaction which involves the oxygen of the air, copper ions which are present in the blood of the prawns, the enzyme 'tyrosinase' and the substrate tyrosine. When all these factors are present it is inevitable that the blackening should occur. Attempts to remove the copper through chemical combination with other ions have not been successful in preventing the discolouration. Another method which has shown promise is the use of sodium bisulphite in small concentrations, either incorporated in the ice to be used or in solutions applied by initially dipping the prawns in the solution. The use of sodium sulphite is effective in arresting the enzyme reaction. But this treatment requires considerable care in application and handling, for the sodium sulphite might otherwise easily damage the prawns through bleaching and reduce the quality. When prawns are held adequately iced, water which is formed by the melting of the ice covers the prawns and their contact with the oxygen of the air is prevented and this reduces the inside incidence of the blackening. Prawns held in ice storage can withstand blackening much better than prawns held at low temperature without the application of ice.

Experiments in holding the prawns in ice in 'headless' and whole condition respectviely showed that the headless remain comparatively free from discoloration for a longer period. This is due to the fact that removal of the head usually entails removal of the cephalothorax which contains most of the enzymes. In commercial practice whenever the fishing vessels have to stay at sea for several days the prawns are necessarily beheaded before they are kept iced in the hold.

Treatment such as boiling in water or with acids brings about certain changes in prawns and lobsters which are characteristic of the crustaceans. Chromogens i.e. substances capable of producing coloured compounds, initially present in the crustacean flesh are transformed into brightly coloured compounds which impart the bright red colour of cooked prawns. A bright colour of the boiled prawns is to some extent indicative of the freshness of the material.

After this consideration of the peculiar character of the crustacean spoilage it is necessary to consider the normal spoilage occurring in prawns. Spoilage of prawns originates from (i) the external surfaces and (ii) the gut. On account of their relatively small size, prawns have a much higher ratio of surface

body-weight compared with fishes. The external surfaces of all aquatic animals carry large bacterial poulations of the order of several millions per sq. cm. of the surface and it is essentially these bacteria which later attack the flesh of the prawn when the animal is dead. The comparatively quicker spoilage occurring in prawns is probably explained by this fact, since relatively larger bacterial loads would be present compared with fishes. Spoilage from the gut sources is caused both by bacteria and enzymes present in the gut; when the prawns are feeding the gut contains numerous bacteria. When the gut is empty the gut spoilage is mainly due to autolytic enzymes. Autolytic spoilage is usually evidenced by a yellowing of the flesh at the point where the spoilage is advanced.

Investigations were carried out by the author and his associates keeping fresh prawns at ordinary temperatures (80°-90°F) and studying the various changes occurring in the prawns such as formation of trimethylamine, increase in the volatile acids and increase in the bacterial population. The investigations showed that no detectable changes occurred till 4 hours elapsed since the prawns were taken out of the water; after this period all the undesirable changes become perceptible and rapidly attained a logarithmic rate of increase indicating the stage of distinct spoilage of the material. The implication of these observations is that bacterial and enzymatic activities proceed at significant rates almost immediately after the prawns are dead and these have to be arrested by icing the prawns immediately when taken from the sea. Prawns often remain edible for even eight to ten hours after catching but they are not suitable for further processing since they will not have the same quality or adequate shelf life when frozen or canned. Studies carried out with prawns iced immediately on netting showed that they remained excellent for about 5 days and were suitable for processing; the period in ice when the prawns remained edible extended up to 12 days but after the first 7 days the flavour was lost though the prawns were not spoilt. Attempts were made to extend the shelf life of prawns at both ordinary temperatures and in ice storage by application of the antibiotic chlorotetracycline, which is being used to some extent for fish preservation in Canada, Japan, etc. The results indicated that for the first 5 days in ice storage, prawns which were treated with the antibiotic were not better than those which were not treated, but after this period there was a distinct difference, the antibiotic treated prawns showing less bacterial counts than the control. It would appear therefore that since our prawns are taken not far from the port, the maximum storage period in ice may not exceed 3 to 5 days before these are processed in which case the antibiotic is not necessary.

The studies also revealed that the larger size prawns taken by the trawlers from deeper waters keep better than the smaller size prawns such as are caught in the backwaters or near the shore in the sea.

The investigations have shown that our prawns have as good keeping quality as the prawns spp. which constitute the fishery in the U. S. A. The use of adequate quantities of ice in handling the prawns from the time these are netted till they are finally processed should ensure a product of unquestionable high quality.

Discussion

The formation of red colouration in cooked prawns and the grading of prawns based on colour came up for a detailed discussion. Mr. John P. George pointed out that different varieties gave different colours. He mentioned the existence of some varieties of prawn which do not give any colour on blanching. Shri Velankar said that the difference is only in the degree of intensity and in every case heat converts the colourless compounds into coloured compounds. Acids also bring about the same change. Copper ions influence the formation of discolouration. The Chairman observed that on blanching prawns on the whole do change colour, perhaps with the exception of the species mentioned by Mr. George. Shri Velankar agreed that the absence of colour in certain species may have to be attributed to the differences in the compounds present in such species. A lot of research has to be done on this aspect of the subject.

During further discussion pointed reference was made to the changes in flavour occurring in prawns under different conditions of preservation and processing. On the basis of the statement by Shri Velankar that the sweetness of prawns is due mainly to the glycogen content, Shri M. R. Nair pointed

out that recent experiments in his laboratories have shown that amino acids like glycine are far more important than glycogen. He also pointed out that the glycogen level in ice-stored prawns remains almost steady for the first seven days, while most of free glycine is lost with the melt water. This change in glycine level is closely followed by significant loss in the flavour of the prawns. Shri Velankar thereupon agreed with the "assumption" and mentioned that biochemical changes occur always together and it is very difficult to isolate one reaction from the other. The glycogen content is very high and studies have also shown that prawns kept in ice gradually lose their sweetness. This is perhaps the reason why prawns on ice storage develop a flat taste. Of course glycogen is not the only compound, but, there are other compounds like anserine, inosine monophosphate etc. and several other nucleotide compounds responsible for the changes. All these changes occur simultaneously.

Mr. John P. George enquired whether a yardstick for the measurement of spoilage in prawns can be suggested and emphasised that there is urgent need for intensive work on evolving a quick test for spoilage in prawn. Shri Madhavan Nayar stated that the blackening of the shell of prawns is a very important problem that experiments in other countries had shown that sodium bisulphite mixed in the water used for washing and for making ice had prevented the blackening. The general opinion was that it is very unsafe as bisulphite might bring in other changes in fish tissue which may have an adverse effect. The use of sodium bisulfite, if at all to be advocated, should be done under very strict supervision. It may produce a bleaching effect also. The texture of the tissue may be also affected.

Shri Nayar requested the scientists and technologists to give top priority to this problem and find an early solution so that the tremendous wastage of prawns now experienced by the processors on this ground could be avoided.