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Abstract : This review discusses the use of direct wood fire as a source of energy and smoke to dry and preserve fish in the developing countries. It covers various treatment and handling methods as well as the physical and chemical nature of the smoke. It points out that the present traditional methods are inefficient and wasteful of energy and smoke and cites attempts made to improve on them.

It discusses the dynamic equilibrium that exists between the particulate and gaseous smoke fractions. The compounds in the gaseous fraction are stated to be more directly involved in the development of colour, odour and flavour while those of the particulate fraction serve as a reservoir. Phenolic compounds are found to be particularly active in the smoking process.

The nutritional and health effects of the use of high temperatures in the smoking process are also discussed.

1. Introduction

The use of direct wood fire as a source of energy to dry fish dates back into history. There was certainly no fire without smoke ; as the fish dried it also became smoked. It is believed that as the special organoleptic and preservative properties of the smoke-dried fish became evident, the fish was deliberately smoked. In tropical Africa and Asia, fish smoking as a means of fish preservation is extensively practised.

Though smoking has been practised over many centuries in various parts of the world, it has been done empirically and it is only recently that the mechanism of the process is being elucidated and the advantages and limitations of current methods being appraised. This report discusses some of the current methods and ideas relating to fish smoking.

2. Traditional methods of fish smoking

Methods in use vary with local customs, species of fish and product keeping-time desired. These include hot smoking, smoke drying, combined smoke/sun drying, boiling and smoke sun drying [1].

2.1. Initial handling

The fish to be smoked are usually washed descaled but may or may not be gutted. They may also be brined or left unbrined. Where the fish are brined, they may either be immersed in brine (70 to 95% solution) or packed in dry salt for periods

ranging from 5 min to 12 h depending on the size of fish, fat content and local taste. After this treatment, the flesh of the fish may reach a salt concentration of up to 3%. When the fish are heavily salted, as when they are packed in dry salt, they are usually desalted by immersion in fresh water for periods of up to 24 h.

Whether brined or merely washed in water, excess surface moisture on the fish is evaporated prior to the actual smoke treatment by exposing either to the atmosphere or predrying for a short period at a low temperature (30 °C) in an oven. This surface evaporation may last from 30 min to 4 h and it results in a firm, shiny surface especially when the fish have been brined in 70 to 80% salt solution.

2.2. Smoke curing units and processes

In many developing countries, the fish are smoked on home-made wooden slats placed on wooden supports. A smouldering type fire is lit directly below the rack and the fish are cooked, dried and smoked for several days. In other methods, the fish are laid or hung on metal grills over shallow, open-top, circular, earthen or metal structures with fire and smoke generated directly below the grill. Thus in some areas, the fish are cooked and smoked simultaneously, while in others they are cooked prior to exposure to smoke. While lying or hanging on grills or on wooden slats, the fish are normally arranged and turned periodically to obtain a uniform cure. The drying and smoking treatments may last from a few hours to several weeks in some instances.[11] When dried for long periods, the purpose is to reduce the fish to a very low moisture to prolong its keeping qualities.

These traditional smoking structures and procedures, commonly used in developing countries, are highly inefficient and wasteful of energy and smoke. There is, for example, an unrestricted escape of smoke, heat and moisture from the open tops of the grill supports.

Recently, attempts have been made to improve on the design of these traditional smoke units.[11,3] These designs have, to a limited extent, succeeded in increasing the volume of fish cured but have not significantly controlled such important factors in hot smoke fish curing as smoke density, humidity, temperature and air velocity.

In developed areas of Europe and America, the fish are usually heavily salted before smoking. The smoking is usually carried out in ovens with temperature, draught and smoke density controls and the fish are normally smoked lightly at moderate temperatures. In these areas, hot smoke curing of fish for preservation is unimportant due to the availability of freezing and cold storage facilities; instead smoke is applied for the flavouring it imparts to the fish.

Recent studies have improved our understanding of the factors involved in hot smoke fish curing; this is necessary for future improvements on any primitive traditional techniques. These factors are discussed briefly below.

3. Factors in hot smoke fish curing

3.1. Wood suitable for generating smoke

Generally resinous wood is not recommended for smoking fish because it imparts an unpleasant flavour to the smoked product. Soft wood is also undesirable as it produces too much soot. Best results are generally obtained with hardwoods.[32] It is, however, recommended that they be tested before they are used as some of them may impart dark colour and bitter taste to the smoked fish. Maize cob,[32] sugar cane pulp and coconut fibre are some of the non-resinous materials used in fish smoking in some developing countries.

Experiments in Canada[29] indicate that white fish with a good flavour may be produced from smoke generated with red maple, red oak, trembling aspen, white ash, balsam poplar and birch. Diamond willow and burr oak gave objectionable flavours; hickory wood was marginally acceptable.

3.2. Method of smoke generation

Methods for generating smoke vary from place to place. In the United States, three methods are in use[9]: smoke may either be generated by burning dampened sawdust, or by burning dry sawdust continuously, or by the method of friction. In the latter method, smoke is generated by pressing the end grain or hardwood block against a rotating carbide-tipped disk. The commonest method of generating smoke in other parts of the world, however, is to burn hardwood in a smouldering type flame at temperatures which may reach between 682 and 966 C.[40]

3.3. Smoke as a gas liquid system

When wood or any plant part is burnt, a large number of carbonyl and phenyl compounds are released. The less volatile of these compounds, usually the large molecular weight compounds, upon mixing with colder air, condense into visible light scattering liquid smoke particles while the more volatile fraction remains in the vapour state. There exists, therefore, minute light scattering particles suspended in a medium of air and invincible vapours which together constitute a gas liquid partition system.[13,14]

3.4. Composition of wood smoke

The composition of wood smoke is highly complex. It depends on the type of wood, type of smoke generator, moisture content of the wood, temperature of combustion and on air supply. Acids, alcohols, carbonyls and many other neutral compounds have been identified as constituents of smoke by various authors.[12,17,30,34,5]

3.5. Distribution of smoke in a closed chamber

The disperse phase of wood smoke has a relatively large surface area compared to its volume and in such a system equilibrium between the particle and vapour phases is expected to be reached almost instantaneously.[14] This means that, in a fixed volume of smoke, the vapour absorbed by the fish tissue is replaced almost instantaneously from the particle phase. In practice, however, it appears that the attainment of equilibrium is not so fast and a non-uniform distribution of carbonyl and phenol compounds has been shown[36] to exist in smoking chambers. This non-uniform distribution does not only occur in the vertical cross section but in various sections of the chamber as well. This distribution pattern results in active and passive areas in the smoking chamber. This problem may be overcome with good controls over airflow, relative humidity, temperature and in the design of the smoking chamber.[36]

3.6. Smoke absorption

Experiments by Foster and Simpson[13] show that smoking does not depend so much on the direct deposition of smoke particles on the fish as on the absorption of the gaseous constituents of the vapour phase of the smoke. This is indicated by their finding that fish cured in vapours which remained after the visible smoke particles had been precipitated electrostatically were indistinguishable in colour, flavour and keeping quality from normally smoked fish.

When smoke vapours are absorbed by the fish tissue in a closed chamber, the gas liquid partition equilibrium is disturbed. The equilibrium may also be disturbed by admitting air or raising the temperature of the smoking chamber. In either case, the equilibrium is restored by the liquid phase releasing a part of its content into the vapour phase. It is clear from this that during smoking, if the more volatile compounds absorbed by the fish are not replaced from the point of generation, the vapour phase gets enriched with less volatile larger molecular weight compounds. In this connection it has been observed[14] that vapour absorption is greatest when the moisture content of the fish is high and that as it dries there is very little absorption.

3.7. Smoke colour and its uses in foods

Of the constituents of wood smoke, phenols are considered the most important because they are believed to contribute most to the development of flavour and colour and to the general stability of the smoked fish.

The colour of a typically smoked fish is believed to be developed from a non-enzymatic interaction between polyhydric phenolic[43] and carbonyl[47,23] compounds of smoke vapour with collagen of the surface connective tissue. The belief is that not all the phenolic groups in the smoke vapour can interact with collagen. The

phenols involved in the reactions are the large phenolic compounds (> 500 g M W) with sufficient hydroxyl groups to link adjacent collagen sites at several points through hydrogen bonds.

The cross linkages that result from the interaction between protein and phenyl compounds impart to surface tissues great stability to heat, enzymes, water abrasion and to microorganisms. Indeed, when these linkages are formed, very large molecular weight constituents of wood smoke may fail to penetrate the surface.[40,42] A case-hardening effect results, with the sub-surface tissue left unspoiled and susceptible to the effects of heat such as gelatinisation or the breakdown of collagen. This case-hardened layer on the skin surface shows final values for smoke constituents 10 to 20 times higher than in the underlying flesh.[5]

3.8. Smoke-flavour and odour

The overall odour and flavour of smoked products are created, according to Daun[7] by: (1) food constituents changed during processing, (2) products of combined food and smoke constituents, and (3) uncombined smoke constituents. The phenol fraction of the wood is believed to contribute most to flavour and odour, and the total phenol content of fish has often been used as an index of the degree of fish smoking.[15,43]

Available evidence indicates that most of the flavouring components of smoke are to be found at or near the surface of the smoked product. By pressing NaOH treated paper against the cut surfaces of sausages and developing the papers chromatographically with 2,6 dichloroquinone-chlorimide, Kurko[21] found indications of phenols only at or near the surface of the smoked product up to 48 h. Shewan[35] found 60 mg% total phenols at the surface, 16.25 mg% in the flesh immediately below the surface and 2.15 mg% at the centre of the fish fillet. Tucker[41] also found phenolic compounds concentrated at the surface.

The phenol guaiacol, 4-methyl guaiacol and syringol (2,6 dimethoxy phenol) have been found[35] to be the major phenols of wood smoke vapour phase. Wasserman[42] found the same phenols to be present in largest concentrations in wood smoke condensate. Taste panelling subsequently showed that the guaiacols had a more smoky-taste while the 2,6 dimethoxy-phenol or syringol had a smoky-odour. Daun[7] similarly observed three gas chromatographic peaks of three unidentified phenolic compounds associated with odour and taste. Like Wasserman[42] he found one of the compounds associated with "smoke cured" odour and the remaining two associated with "smoke cured" taste.

It is clear from this discussion that the efficiency of the smoking process may be determined by the relative contribution of flavour and colour forming compounds. The absorption of these compounds, we have noted, is greatest when the moisture content of the fish is high. This suggests that the fish must not be dried

too quickly to enable the greatest amount of vapour constituents to be absorbed. It also means that the initial smoking temperature must not be too high to cause rapid drying. Clearly, vapour absorption will be favoured by conditions of high humidity and low temperature.

4. The effect of heat on smoked fish

Fish smoking does not only involve exposure to smoke, it also involves drying and baking as well. In developed countries, fish are smoked principally for the colour and flavour the process imparts to fish. In developing areas, on the other hand, fish are smoked principally for preservation. Whatever the aims for smoking fish, they are best served by exposing the fish to some degree of heat treatment which helps the development of both flavour and colour.[40,2]

4.1. Textural problems

The drying, and at times the baking which follows, often causes textural problems in smoked fish. By texture is meant the retention of good microstructure of fibre and fibre substance expressed in terms of softness, juiciness, fibrousness and glutinousness.[6] This is important with respect to reconstitution ability of the dry fish which refers to the extent to which the dried fish fibre returns on addition of water, to a state indistinguishable from the undried fibre. This depends on the structural properties of collagen or fibre connective tissue.

As the fish dries under excessive heat treatment, the increased concentration of tissue solutes may denature its proteins. Indeed, during heat treatment of fish, Hughes[19] found that there was a degradation of connective tissue or collagen, especially of the skin, to gelatin and other smaller peptide fragments. The fish flesh is held together by connective tissue and the breakdown of the latter should render the fish soft and liable to break upon handling.

Since absorbed smoke constituents may cross link with fish surface tissue proteins under mild heat conditions to form a firm, stable surface,[43] it would appear a good smoking practice to develop this firm outer surface before raising the heat to dry the fish. Mann[32] recommends that during the smoking process more smoke and less heat must be applied in the initial stages.

As a general recommendation the FAO,[11] however, states that the initial pre-drying must be carried out and maintained at 80°C for 2 to 4 h, depending on the size of fish being cured. For the following 2 h, the temperature must be raised to between 90 and 110°C to cook the flesh. After the cooking, it is recommended to return the temperature to 80°C for the rest of the smoke drying process.

4.2. Nutritional losses

Foster and Simpson[13] are of the opinion that the hot-smoke curing temperature must be between 32° and 82°C. Temperatures in excess of this either during the initial smoking period or during the later baking process is believed to result in some unfavourable nutritional effects on the smoked product. This conclusion appears to agree with Duckworth and Woodham[10] who found that vegetable proteins heated beyond 82°C suffer a loss in nutritive value; soybean heated to this temperature[31] is seen in the loss of digestibility of its proteins. Halevy and Goggenheim[10] demonstrated this loss in digestibility by autoclaving wheat gluten/glucose mixture. They found that with such treatment the *in vitro* digestibility of essential amino acids was reduced. However, Yanez *et al*[45] working with hake fillets observed a negligible change in Net Protein Utilization (NPU) up to 105°C but Net Sulphur Utilization (NSU) suffered some losses at this temperature. Heating at 170°C considerably reduced Nitrogen and Sulphur Utilization—NPU fell from 79 to 41 and NSU from 89 to 60.

Lysine, the most abundant amino acid in fish is also considered[28,31,29] to be the most labile amino acid. A major part of lysine losses undoubtedly results from reaction of the ε-amine group with reducing carbohydrates followed by a series of rearrangements and dismutations that lead to brown-coloured polymers and evolution of carbon dioxide. These reactions referred to collectively as non-enzymatic or Maillard reactions are known to form complex linkages which are very resistant to digestive enzymes and are therefore not metabolized.[31]

Greaves *et al*[15] have reported that even in the absence of the Maillard reaction, heating alone is sufficient to render lysine unavailable. Chen and Issenberg[5] have reported a 44% loss of available lysine after a 10 h exposure of beef to wood smoke; heating alone at 65°C for 10 h, on the other hand, caused a loss of 15% in available lysine. These results indicate that smoke components may account for some of the amino acid losses in smoked products.

The rate at which fish protein may be rendered unavailable may also depend on the moisture content at which the fish are dried. This is indicated by the results of Lea and Hannan[27] who heated a casein/glucose mixture in excess sugar and found marked loss of amino group up to a peak value at 70% RH with a minimum loss at the wet and dry extremes. Lobuza *et al*[24] similarly found the rate of browning in a pea-soup mix increasing to a peak value at 70% RH and thereafter falling. Livingston *et al*[29] have also found the retention of lysine, methionine, cystine, arginine, histidine and aspartic acid during alfalfa dehydration to correlate well with meal moisture and dehydration outlet temperature.

5. Preservative action of wood smoke

Smoke does more than provide desirable flavour and colour to smoked products. It contributes substantially to their preservation by acting as an effective antioxidant, microbiostatic and microbiocidal agent.

Phenols are again reported by Kurko[22] to be the effective antioxidants in smoked products. He found neutral compounds (alcohols, carbonyls), organic acids and bases ineffective as antioxidants. The highest boiling phenols composed of pyrogallol ethers were slightly more effective than lower boiling ones. Foster and Simpson,[13] however, found no difference in antioxidant properties between normally smoked products and those smoked with gases left over after the high boiling phenols, wood resins and tars were removed by electrostatic precipitation. In support of reports[35,41,21] that most smoke constituents are concentrated in the surface tissues, Lee[26] had previously observed very low peroxide values in the surface tissues of smoked bacon, whereas in the unsmoked bacon the peroxide values were very high but decreased to a negligible value only a short way below the surface tissues.

Generally smoke components, for example, formaldehyde, acetic acid and creosote, which concentrate in the surface tissues are not toxic to bacteria, fungi or viruses below a concentration of 1%.[43] Above this concentration, however, they have been found to prevent spore germination and growth of many bacteria, fungi and certainly inhibit the activities of a wide range of viruses.[8]

Since smoke constituents are concentrated in the surface layers, their antimicrobial activities will not affect microorganisms in the sub-surface layers and therefore those microorganisms (especially in the gut) which may survive heat treatment during smoking may grow if the moisture content of the smoked fish is kept low enough.

6. Wood smoke and carcinogens

In addition to flavouring, colour and antiseptic compounds, wood smoke may contain potent carcinogenic polycyclic aromatic hydrocarbons.[39] The generation of these compounds is influenced by the parameters that govern smoke generation which include the type of wood, type of generator, moisture content and degree of contamination of the wood, temperature of combustion and air supply.[40,9]

Burning dampened hardwood sawdust in a heated atmosphere, White *et al.*[44] identified the following polycyclic aromatic hydrocarbons: anthracene, phenanthrene, pyrene, fluoranthene, triphenylene and 4-methyl-benzo (a) pyrene. The latter substance is considered to be the most carcinogenic and levels greater than 7.2 μg/Kg have been recorded in hot smoked fish.[40]

Tilgner[18] was of the opinion that the formation of 3,4 benzo pyrene in wood smoke may be eliminated by generating smoke at a low temperature (400 C). Indeed, carcinogenic substances have been detected most in smouldering type smokes. Solinck[17] found that smoke condensate and tars decreased with increasing moisture content of the wood used to generate the smoke. Indeed, to the extent that moisture content affects the smoke temperature it could be expected to affect its composition and yield as well.

7. Conclusion

From the smoke curing mechanism [illegible] it is apparent that the most important [illegible] temperature control within the smoking chamber. For effect [illegible] the smoking chamber must be initially kept below [illegible] moisture content long enough to absorb the [illegible] necessary for the development of texture, [illegible] to smoke and dry the fish. The [illegible] level (< 400 C) [illegible]

[illegible] by lack temperature [illegible] Furthermore, [illegible] by [illegible] drying [illegible] smoking technology, [illegible]

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