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I. I. Lapshin

LIQUID SMOKE USED FOR PROCESSING FOOD PRODUCTS

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I.I.Lapshin, Candidate of Technical Sciences.
The Moscow Institute of National Economy named after Plekhanov.
U S S R

Modern technology of smoking food products is based on the use of air-smoke mixture giving characteristic smoked flavour, aroma and colour. This technology has some essential shortcomings.

Firstly, processes of smoke formation can not be exactly regulated as the character and succession of chemical reaction occuring in this case depend on a great number of various factors: therefore it is impossible to achieve constant chemical composition of smoke, generated from wood or sawdust.

Secondly, it is a very long process not yeilding to intensification.

Thirdly, it has been found out recently, that multinuclear cancerogenic carbohydrate —3,4-benzpyrene penetrates into meat products processed by smoke. The latter especially induces to search for an improved technology of smoking food products and semi-prepared products for canning industry.

Analyses show that 1 kg of a smoked product contains about 4-6 γ of 3,4-benzpyrene and its content in some other products (depending on smoke generation) exceeds several doses of gammas.

3,4-benzpyrene found in smoke products is a most drastic cancerogenic substance which undoubtedly causes malignant tumour in a man's organism.

The Moscow Institute of Experimental and Clinical Oncology has established that cancerogenic effect of 3,4-benzpyrene depends on its dose injection into an animals' organism. Thus injection of 2.0-2.5 mg of 3,4-benzpyrene into rats' stomaches caused development of stomach cancer in 7% of rats, and injection of 6-10 mg of 3,4-benzpyrene caused stomach cancer in 30% of the experimental animals.

As, at present, it is impossible to exclude 3,4-benzpyrene directly from air-smoke mixture we have been searching for a liquid smoke which might completely or partially replace smoke during food products processing.

After a long search we decided to use as raw material for liquid smoke a by-product of woodchemical industry, so called sour water, which is a water extract obtained at thermal decomposition of wood in the energochemical unit of Pomerantsev's system.

Analyses showed the following chemical composition of this water: phenols, fatty acids, alcohol, ethers, aldehydes, ketones, lactones, hydrocarbons, etc. and cancerogenic carbohydrate 3,4-benzpyrene.

It was established that "water insoluble" resins forming is sour water at heating, absorb 3,4-benzpyrene from the environment.

This property of "water insoluble" resins was considered by us while preparing smoke liquid.

The smoke liquid production results in excluding from the latter undesirable and harmful substances such as: cancerogenic carbohydrates, methyl alcohol, a considerable number of volatile acids and other substances.

For this purpose sour water is steamed to the specific weight 1.27-1.3. Temperature of such water in the tank with this specific weight reaches 125-130°. At steaming condensation and polymerization of certain chemical constituents, which are included in the liquid smoke occur, cold water insoluble resins being formed. Phenols, fatty acids, aldehydes, ketones, methyl alcohol and other volatile constituents, which give unpleasant flavour and odour to products, partially volatile. The steamed liquid which we call a "smoke preparation" is 7-10 times diluted with water according to its application. "Water insoluble" resins which contain 3,4-benzpyrene are filtrated and thrown off at dilution.

To achieve a better separation of "water insoluble" resins the smoke preparation diluted by 7-10 times with cold water is kept for about 2 days before filtration. The filtrate obtained is used as liquid smoke in food products manufacture.

Chemical composition of the smoke preparation and liquid smoke is shown in Table 1.

After a through separation of "water insoluble" resins by the above mentioned method 3,4-benzpyrene has not been observed by the fluorescent spectral analysis (7). The absence of cancerogenic substances in smoke liquid was proved by biological experiment on animals made by the Leningrad Institute of Oncology of the AMS of the USSR.

Table 1

Chemical composition of the Smoke Preparation and Liquid.

Indices	Smoke preparation	Smoke preparation diluted by 7-10 times with water. (operating liquid smoke)
Specific weight	1.27-1.318	1.041-1.050
Total acidity (calculated as acetic acid) %	7.7 - 9.82	1.41-2.10
Volatile acids (calculated as acetic acid) %	3.45-4.64	0.70-0.86
Formic acid, %	0.04-0.06	traces
Ethers (calculated as methylacetate), %	0.43-1.12	0.06-0.1
Alcohols (calculated as methanol), %	0.05-0.06	none
Aldehydes and ketones (calculated as carbonyl group CO),%	0.22-0.27	0.03-0.10
Furfurol, %	none	none
Phenols, %	5.67-6.42	1.17-1.38
Insoluble resins, %	7.06-10.0	none
Dry residue, %	75.3-83.5	15.04-15.23
Water, %	16.5-24.7	84.96-84.77
Reducing substances (gr of Glucosa/100 g)	21.0-52.0	3.70-5.63

It is important to state that moisture and kind of the fuel, burnt in the energochemical units of Pomerantsev's system effect greatly chemical composition and quality of the liquid smoke. Fuel, used in the energochemical unit of Pomerantsev's system(coniferous stubs[x)] with 6% moisture content and 20-25% of asp addition with 30-35% moisture content, extracted by "Galosha" type benzene) and work rate (11) allow to produce liquid smoke of satisfactory properties.

Asp burning alone (with the above mentioned moisture content) doubles the level of volatile fatty acids and changes chemical constituents of the smoke preparation which makes liquid smoke properties much worse.

From the economic point of view production of smoke liquid is not completely finished at wood-chemical plants; there sour water alone is obtained and steamed to the specific weight 1.3. All the other operations on smoke liquid production are carried out at food industry plants.

Such separation allows to store and transport liquid smoke in winter without heating, reduces by 7-10 times its transportation volume, allows to use wood barrels for transportation and storage instead of glass containers, the necessity of large stores being excluded. There are some other advantages. Smoke preparation storage is accompanied with its condensation polymerization and oxidation processes, which are proved by chemical analyses (Table 2). These changes, however, don't effect smoke properties of the preparation.

x) Those coniferous stubs are used which having been stayed after cutting for 10-15 years.

5.

Table 2

Changes of the Smoke Preparation Chemical Composition at Storage

Indices	Specific weight	Total acidity (calc. as acetic acid) %	Volatile acids (calc. as acetic acid) %	Alcahols content (calc. as methanol) %	Aldehydes + Ketones (calc. as carbonyl groups)	Ethers (calcul. as methylacetate) %	Phenols content %	Water content %	Dry residue content %	Insoluble tars content %	Reducing substances (I gr of Glucosa per 100 gr.)
1. Smoke preparation at the beginning of storage	1.314	7.730	4.41	0.18	0.25	1.12	6.42	16.44	83.56	9.6	46.0
2. Smoke preparation after 2 month storage	1.316	9.350	5.16	0.05	0.12	0.40	4.82	16.42	83.58	12.8	47.0
3. Difference in indices:											
increase	0.002	1.620	0.74	–	–	–	–	–	0.02	3.2	1.0
decrease	–	–	–	0.13	0.13	0.72	1.6	0.2	–	–	–

The smoke preparation ought to be stored in wooden barrels or glass bottles. Such containers do not react with the smoke preparation constituents and do not catalyze oxidative processes.

Smoking products by means of liquid smoke consists in distribution on the initial raw meat surface with subsequent thermal treatment by different heat-carriers. To produce fish of "hot smoking" it is baked by infrared rays or gas after treatment with liquid smoke (9.11).

For production of cooked and semi-smoked sausages, fresh sausages surface is processed with the liquid smoke, then are smoked by hot air and infrared rays or gas and then cooked by steam. Cooked sausages in addition, are dried a little when producing semi-smoked sausages (3,4).

The production of fish of"cold smoking" by means of smoke liquid alone results in slighter smoke flavour and odour as compared to processing with smoke; this is the main reason why a combined method is used at "cold smoking": the surface distribution of liquid smoke prior to drying and after that - extra smoking for 12-18 hrs (instead of 36-56 hrs which are common to the conventional air-smoke processing).

Fish, processed with liquid smoke acquires smoked colour, flavour and odour at drying already, thus, the subsequent extra smoking time is sharply cut.

A smoke liquid film appearing at drying on the fish surface does not prevent accumulation of phenols and other aromatic substances of air-smoke mixture in fish skins and their diffusing into meat.

Food products surface is treated with smoke liquid either by their immersion into it for 5-30 sec., or by its spraying.

Liquid smoke expenses, according to our observation are about 1.5-2.0% as compared to the processed products weight.

To intensify smoked flavour liquid smoke is added directly into minced meat of semi-smoked sausages (to about 0.4% of the minced meat weight).

To intensify smoked flavour and odour of fish products it is recommended to add liquid smoke into curing brine or water (at soaking) (0.5% of the latter weight).

We carried out a number of investigations to reveal substances taking part in the development of smoked flavour and odour and of the processes, occuring in this case.

First of all, phenols, carbohydrates, fatty acids, aldehydes, ketones and other substances were removed from liquid smoke by sulphuric ether or ethyl-acetate extraction.

Processed by such liquid smoke products acquired smoked colour but had neither smoked flavour nor odour. It means that the substances formimg smoked flavour and odour are in the ether or ethyl-acetate extracts.

It is of interest to note, that the residue obtained after distillation had a strong characteristic flavour and none of the smoked one.

Summary phenols, carbohydrated and oxy compounds separated from this residue had no smoked flavour. But phenols

2.5 mm Hg vacuum-distilled and distinguishing from each other in boiling temperature of about 5°, have already had the odour from a pleasant, tar-spicy, flower and fruit to a coal-tar one.

Odour differences are caused by unequal phenols qualitative and quantitative content in individual fractions.

It is obvious from this example that a certain odour of wood pyrolysis products depends on definite combination and co-relation of chemical constituents included into these products.

We established that fresh tissues immersed into liquid smoke selectively extract from it substances giving smoked flavour and aroma chemosobtion occurs.
(Table 3).

Observations show that smoked flavour, odour and colour of food products are not achieved immediately at liquid smoke treatment. They are developing gradually and are influenced greatly by subsequent chemical changes of smoke liquid constituents both on the surface and inside products while heating or drying.

Phenols and other constituents of the liquid smoke on the products surface are partially oxidized, condensed and polymerized like at its storage. It is proved by a golden film appearance on the fish surface, accompanied with phenols content reduction.

The same is observed at heating liquid smoke in autoclaves and under atmospheric pressure (11).

The difference lies in the fact that physico-chemical changes of liquid smoke on the food products surface occur

Table 3

Changes of the Liquid Smoke Chemical Composition According to the Quantity of Fish Processed with it.

Samples No.	Liquid smoke	Specific weight at 20°	pH	Total acidity (calc. as acetic acid) %	% of the initial ~~volatile~~ acids content	Volatile acids (calc. as acetic acid) %	% of the initial volatile acids content	Phenols %	% of the initial phenols content	Methoxyl groups (OCH_3) content in phenols, %	Phenols refraction coefficient, at 20°	Colour change in the relative units
1.	The initial sample	1.0419	3.04	1.41	100	0.755	100	1.38	100	6.4	1.5666	70.0
2.	After treatment of 40 fishes	1.0376	3.10	1.17	83.7	0.600	79.5	1.22	88.4	7.00	1.5680	69.2
3.	After treatment of 160 fishes	1.0311	3.50	0.94	66.7	0.357	47.3	0.74	53.7	4.3	1.4928	74.8
4.	After slime addition into liquid smoke (50 ml per 500 ml)	1.0397	3.09	1.38	97.9	0.74	98.0	1.26	91.1	6.4	1.5600	70

Note: pH of the liquid smoke deluted with water by 10 times is not changed with the oxygen present and in a thiner layer, and therefore deeper, which is proved first of all by the dissapearance of a better flavour of liquid smoke.

The rest of the phenols and other liquid smoke constituents penetrate inside food products.

A.I.Juditskaya using chromatographic separation found in the liquid smoke pyrocatechol, pyrogallol and one non-indentified phenol, and in the products processed by this liquid she found other phenols: guaiacol, phenol, m- and O-cresols(14). Phenols found in the food products are included into the liquid smoke, possibly, in other compounds, therefore we cannot manage to reveal them by chemical separation and subsequent paper chromatography.

It is quite possible that phenols of the liquid smoke penetrating into food products become oxidized, interact with each other and with product tissues formimg other phenols and compounds.

This explanation is quite possible because the majority of phenols are known to be easily oxidized even in the air, being subjected in this case to different conversions. Thus, oxidation of ordinary phenols with hydrosulphate oxide results in obtaining pyrocatechol, a small amount of pyrogallol and hydrochinon traces.

Under certain conditions dinuclear phenol with hydroxyl groups in O- or P-positions to each other are oxidized to compounds of deketones type, O- and P-chinons (8).

Bocuchava and Popov found that chinons, resulting from oxidation of tanned substances of the tea-leaf oxidize other constituents of the tea-leaf, forming aromatic products during fermentation. They established by model experiments that the oxidative interaction of tanned tea-leaf substances with various amino acids causes deamination of the latter and formation of corresponding aldehydes which give a certain characteristic odour to products (from the pleasant one, like that of roses, to unpleasant ones) (1).

According to N.N.Krylova's data phenols at smoking interact with sulfhydryl groups of protein.

Application of liquid smoke permits to introduce quickly smoke substances into a food product and control the rate of smoked flavour and aroma acquiring by the products.

The analyses show that the development of smoked aroma and flavour depends on temperature of smoking, drying and consequently, on the rate of the chemical processes, as these factors, according to Vant-Goff are directly related.

At hot smoking with liquid smoke and infrared rays used fish acquires smoked colour, odour and flavour for 15-30 min. The surface temperature was 140-150^{o}, in the muscles - 90^{o}.

At cold smoking with liquid smoke used smoked flavour and aroma are acquired during drying at 26-36^{o}. The colour of the skin appears in 4-10 hrs, flavour and aroma being developed for 2-3 days (10).

As low temperatures cause a somewhat different current of flavour development it results in a faint flavour and odour; extra smoking is necessary.

Some constituents of food products are still being changed at storage. For the first days of storage phenols diffusion from the skin into the muscle tissue is noted, which increases phenols content in smoked fish.

Further storage results in phenols content reduction both in the fish skin and tissue accompanied by weakening smoked aroma and by surface colour reducing intensity of fish(12).

At storage phenols change not only quantitatively but qualitatively which are proved by A.I.Juditskaya's data. According to her data, the content of guaiacol, phenol, m- and O-cresol in hot smoked sprats during storage at 15° for 1 month is reduced and the content of derivative phenols, namely.: methyl ethers, pyrogallol and 2 unidentified phenols increases. All mentioned changes in smoked fish are mainly used by oxidative processing occuring at storage. It is proved by the fact that smoked products in hermetically sealed containers like caus isolated from atmospheric oxygen preserve their original qualities unchanged by dosens of times longer as compared to those of not isolated ones.

As for the quality of the products, processed with the liquid smoke, it is considered by manufacturers and consumers quite satisfactory.

Sausage products smoked with liquid smoke did not differ at tasting from the sausage smoked with air smoke mixture.

It is important to pay attention to other advantages of liquid smoke. Liquid smoke possesses bacterial and fungicidal properties due to which the initial microbe-load of processed products is significantly reduced and microbe growth at storage is inhibited (2). It also possesses antiooxidative properties related both to autooxiadtion and to fat catalised by hemiglobin (13). Owing to the above stated properties, products processed with liquid smoke are preserved at storage much better than those processed with smoke.

The above said results of our investigations are of definite theoretical and practical interest.

They permit to conclude that smoked flavour and odour are developed not only by the mere mechanical deposition of smoke on products and their subsequent diffusion into products, but by selective chemosorbtion of liquid smoke or smoke substances by a product, followed by their complex conversion, caused by oxidation, reduction reactions, condensation and polymerization, etc.

These reactions result in substances with new organoleptic characteristics, which combined with odourous substances of food products and liquid smoke, give specific smoked flavour and odour.

The liquid smoke and a new technology, suggested by us, are at present applied at more than 35 meat packing plants of the USSR.

It is now introduced in sausage production. The plants, using this technology receive considerable technological advantages.

The new technology, first of all, reduces production cycle of fish and sausages smoking and consequently increases worker's labour productivity. Thus, at the manufacture of hot smoked products (by means of the liquid or infrared rays) smoking operation time is reduced by 3-4 times.

At cold smoking under commercial conditions this time is cut by 30-35%.

Technological losses of fish hot smoking are reduced approximately by 5-7%, and at cold smoking by 1-2% of the raw material weight.

Total economy from this technology at the Moscow and Leningrad plants alone constituted 150.000 roubles in 1960.

Commercial application of the liquid smoke makes it possible to completely mechanize and automate production processes.

No less important advantage of this liquid smoke is a complete exclusion of cancerogenic substances from hot smoked products (fish and sausages) and to minimize the risk of getting these substances into products of combined smoking which is proved by physical research and biological experiments on animals.

Reduction to the minimum and especially a complete elimination of the cancerogenic substances from food products are of great practical importance for prophylaxes of cancer deseases.

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