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Research on the composition of wood smoke

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INTRODUCTION

Curing of meat is an age-old traditional process, which has by now grown out into an important technological operation.

In the earliest stages of mankind's existance, at the time when its food supply system was organized along the lines of hunting and fishing, one of the findings of those days was the remarkable favourable influence of the woodfire-smoke on keepability and organoleptic qualities of foods.

The amazement on this wonderful feat of cultural development, however, seems to have had a continuing stupefying effect on the interest in the real happenings of this process. And whilst technologically many improvements were made, only perhaps 25 years ago, when Pettet and Lane (8) did their introductory work on the chemical composition of wood smoke, a real interest awoke in an understanding of this important industrial operation.

According to the published material on this subject, we may underscribe the statement of Tilgner (47) that, what was once a haphazard process, must now be closely controlled (40). A scientific base has to take the place of an empirical one, if mechanisation and automatization in an increasing mass-production should be succesful. Also is it clear that the basic scientific rules of smoke-curing should be valid for both the meat- and fish-smoking industries.

Therefore our Institute, aiming at contributing to this effort, has taken in hand a.o. the work involved in answering one of the basic questions, i.e. the actual composition of wood smoke.

DEFINITIONS

Smoke-curing may be defined as the combined actions of components, obtained by partial thermal decomposition of vegetable material mostly wood, on food-products, under suitable conditions of temperature and humidity, with the aim to influence favourably colour, taste and flavour, as well as consistency and keepability.

Physically a smoke-composition can be considered as a polydisperse system of single, charged, colloidal particles and their aggregates, consisting of solid, fluid and dissolved components, in a mixed air-gaseous components medium. The particle radii vary between 0.01 and 8 μ (10^{-4} cm), with an average radius of 0.1 μ. The distribution of the components between the colloidal particles and the dispersing medium will be governed by a dynamical equilibrium between both and show a temperature dependance and connected with respective charging conditions. The variation in particle range as well as the above mentioned distribution will be controlled in the first place by the conditions under which the thermal decomposition has taken place (33,36,40,48).

Chemically smoke is as yet a very much undefined matter. One should be ready to expect any compound, combined out of C-, H- and/or O-atoms. The presence of the following homologuous groups can be accepted as probable: aliphatic and aromatic hydrocarbons, the lower representatives of the aliphatic alcohols, aldehydes and ketones, branched and unbranched mono- and dicarboxylic acids, phenolic compounds with carbonyl-, alkyl-, (esp. C_{1-3}), carboxyl- and methoxyl-substituents, furan- and cyclo-pentane derivatives and polycyclic compounds. As individual compounds may be mentioned: formaldehyde, acetaldehyde, acetone, formic acid, acetic acid, propionic acid, phenol, creosol, guaiacol, vanilline, catechol, 2.6.-di-methyl-pyrogallol and their 4-methyl-,4-ethyl- and 4-propyl-derivatives, furfural, methyl-cyclo-pentenolon. Under smoke-curing conditions reactivities between several compounds may be high (3,4,7,8,20,26,30-35,40,148).

CRITERIA OF QUALITY OF SMOKE

When faced with this intricate physical and chemical structure of smoke, one may expect smoke curing to be a very complicated process.

Methods in practice in industry are based upon trial and errof, procedures depending very much on the human factor and climatic conditions, causing great variations in product quality and material requirements.

Efficient measures of control have to based on a thorough understanding of the curing process itself.

In cold- as well in hot-smoking (for meat up to 25 ° and 45 to 75 ° respectively) partial drying of the product and denaturation of the proteins occur, influencing product consistency and palatability. These factors are controlled mainly by technical procedures.

Other objective indices of quality of smokes may be classified according to their effect on colour and gloss, taste and odour, anti-oxidant properties, bactericidal and bacteriostatic activity, besides carcinogenic or toxic properties.

a. Colour and gloss. In a review by Tilgner (1) he mentions that the required surface-colouring does not depend upon the amount of phenols present (4), but on the presence of chemical compounds of a neutral nature, mainly resins (60). Ziemba (61) finds that these neutral compounds possess a distinctive colour, which deepens readily, probably due to polymerisation or auto-oxidation. There seemed, however, to exist a correlation between the amount of these neutral compounds and that of the phenols, hence the percentage of phenols in smoke should be considered as a measure of its colouring properties (53,62).

In connection of our own observation that the absence of aldehydic reacting compounds deprives a smoke-condensate of its meat-colouring properties, these facts point to the possibility that resins and tannins may be considered to be colouring agents in some curing. Reactions between proteinic amino-groups and carbonyl-compounds in smoke should not be left out of consideration.

Whilst salting may have its affect on the deposition of colouring agents (40,63), artificial colouring remains open.

b. Taste and odour. Tilgner (1) considers only those smoke components which are readily volatile in steam (aldehydes, ketones, acids, phenols) responsible for the specific flavour of smoked products. In contrary to Guinot (2,27), who prepared a so called "liquid smoke" by subjecting a smoke condensate to steam distillation in order ro remove undesirable components (2,26,27). Acids are considered undesirable in great quantities (2,47), phenolic compounds are probably important (2,34,40). Interesting are the identification of methyl-cyclopentenolone believed to cause the formation of the tangy flavour (64) and the non-enzymatic formation at 196 °C of maltol out of maltose (65).

Faulkner and Watts note the oxydative destruction of the red-coloured compound astaxanthin in shrimps during smoke-curing (18).

c. Anti-oxidants. A conserving effect by smokecuring is in particular to be expected of phenolic compounds, which are known anti-oxidants.

Watts and Faulkner (18) found positive results with several liquid smokes and a synergetic effect between smoke components and ascorbic acid (20, 21). Their results are supported by Erdmann (15)and Rideal (6).

The importance of phenolic compounds as anti-oxidants has been recognized by English workers (31-35,50). A systematic investigation on the anti-oxidant properties of the homologuous groups of the phenols, carboxylic acids, alcohols, aldehydes and ketones has been carried out by Kurko (64). He found activities comparable with that of BHT with the phenolic compounds, boiling at 119-126 °C/4 mm Hg, which are supposed to be methyl-ethers of pyrogallol and their ethyl- and propyl- derivatives. Such compounds have been identified by Fusako as well (66).

Kurko a.o. (64) performed also microbiological studies and found the strongest bactericidal effect with phenols and acids.

d. Carcinogenic and toxic substances. While in electrostatically smoked sausages 1.9 to 10.5 µg of 3.4.-benzpyrene has been found (67), while Tilgner and Müller (47) showed the presence in 1 m^3 of dense smoke of 5.6 µg of 3.4.-benzpyrene and 7.1 µg of 1,2,5,6-dibenzanthracene. According to their opinion the main factor contributing to the formation of these compounds is a too high temperature in smoke generation, which should be kept below 300 °C.

The increased frequency of stomach cancer by manifold use of smoked foods according to a Leningrad investigation is mentioned by Tilgner (47) and is ascribed by Dungal (68) to home-cured Iceland mutton and trout. Results of investigations on tobacco-smoke may be useful in this respect.

Attention to toxic substances is drawn by Watson (69) and (38), who estimate up to 25 p.p.m. of arsenic in smoked fish when arsenicum treated wood was used as a smoke source.

METHODS OF COLLECTING AND ANALYSIS OF SMOKE-COMPONENTS

Analytically a wood smoke tends to be both a fascinating and a frightening proposition. Analysis afterwards, i.e. by study of smoked products of important compounds may prove to be an unhappy business. However, there is no indication at all to show the necessity of 200 or more compounds to be present in a smoke-curing process. On the contrary in future simple synthetic "liquid smokes" may prove to be sufficient for a excellent, rapid cure.

Directing chemical analysis of smoke to the investigation of compounds present and their properties will lend the basis for a systematic research on the smoke-curing process, which may lead to new processing methods (72).

To collect a representative smoke condensate 5 methods are available:

a. Gravimetric precipitation on mechanical filters
b. Impinger interception
c. Thermal precipitation (8,11,54)
d. Absorption (64,70)
e. Electrostatic precipitation.

Any collecting system used has to possess the capacity to diminish effectively mutual reactions between individual compounds- which seem to be light - and acid-catalysed and optimal at a acidity of pH 4 to 5-. Losses may otherwise be heavy (61,71). Cooling, dilution, use of suitable absorbing reagents apart as well as combined methods, are needed.

Consideration of the factors particle diameter-range, presence of compounds in solid, liquid and gaseous phases, partly as colloidal, charged, aggregates, the handling of large volumes of gas, analytical handling possibilities, method characteristics and last, but not least the aim at 100 % efficiency, leads to the application of electro-static precipitation, aided by thermal precipitation, with the simultaneous absorption of of gaseous components by continuously spraying in and removing out of the collecting system of a suitable absorbing liquid.

Further analytical handling of this smoke condensate might have to encompass any known separating or identifying method or apparatus.

CONSIDERATION OF PROCESS-COLLECTING METHODS

Indications regarding the lines along which a systematic investigation on the composition of smokes could be run may be found in the results of two modern smoke-curing processes: the use of "liquid smokes" and the electrostatic curing.

a. <u>Liquid smokes</u>

The trade products belonging to this group (51,56) have a common origin in the condensates of traditionally generated smokes. These condensates are subjected to refining and concentrating operations, as a result of which neither gaseous, nor in lesser degree, volatile components are contained.

Known are several U.S.A. products, one prepared out of hickory wood, others used by Watts and Faulkner (20,21) or Erdman (15).

The method of Guinot (2,27) who refines by subjecting his condensate to steam distillation and extraction by ethylacetate of essential components, seems a bit odd in view of Tilgner's opinion on the steam volatile components being responsible for the specific smoke-aroma (1). However, Guinot reports a strong and desirably smelling extract , reacting positively with phenol-reagents.

Lapshin (57) concentrates and distills off unwanted components by heating up to a headtemperature of 135-140 °C. The diluted rest, containing 0.96 % volatile acids, 1.67 % total acids with a trace of formic acid, 0.1 % carbonyl-compounds, 0.84 % phenols and no alcohols or furfural, flavoured perhaps not quite as strong or as pleasant as normal smoke.(40)

Toriyama (28,44) prepares liquid smokes by precipitating components in a high tension electric field at 10 kV and uses it, after diluting with water, as a filling liquid with tinned fish. Gaseous smoke components won't be present therein, as those are not precipitated electrostatically.

b. Electrostatic smoking

In this method, similar to the industrial Cottrell process, smoke components are transferred on the products by the action of a 20 to 60 kV high-tension field.

The products may either act themselves as earthed electrodes (40,63,70) or the smoke particles are charged by passing a corona field before entering the smoking-chamber, where they precipitate by actions of their own space charge.

Although the colour developed seems to be darker than traditionally (34,40), fish smoked by this method tasted a little more acrid. Relatively volatile phenolic anti-oxidants were less deposited (35).

However, these results do not prove the components in the gaseous phase to be inactive in regard to the curing process (50,54).

SMOKE-COMPOSITION AND GENERATION

According to their respective principles methods of generating smokes can be divided into 4 types:

a. Traditional. Great variations in air speed, temperature and humidity are reported by Tilgner (47). In a systematic test on 21 charges room temperatures were found to vary between 86 and 200 °C and estimated curing times between 23 and 80 minutes.(59). It seems therefore improbable that any consistency of smoke-composition can thus be found.

b. Mechanical smoke-generators, of which at least 26 types have been developed, operate in a much more controlled way (47).

c. In friction generators smoke is produced by the friction heat when a block of wood is pressed against a serrated steel surface revolving at a high speed. Several types are known (40,41,54).

d. A generator operating on the principle of the fluidized bed, has been developed at Torry Research Station (30,35,50).
The temperature of the very finely divided wood can be regulated quite accurately in a variable air speed. Constancy of composition of the smoke produced seems to be satisfactory. No figures are, however, yet available.

A comparison between types b and c may be found in Table 1, containing figures of Husaini and Cooper (7) and of Tilgner (54). A collection of literature data is compiled in Table 2.

Table 1. Comparison of different types of smoke

	sauwdust smoke				friction smoke			
	cond. -78°	cond. in water	condensed at -80°		cond. at -78°	cond. in water	condensed at -80°	
Total acids	317 mg	346 mg	1.28 %	0.183 %	422 mg	402 mg	4.98 %	0.209 %
Total carbonyls	229 mg	216 mg	0.63 %	0.164 %	352 mg	320 mg	4.78 %	2.79 %
Phenols	156 mg	127 mg	0.07 %	0.007 %	197 mg	194 mg	0.217%	0.067 %
Free bases	226 mg	135 mg	------	-------	257 mg	211 mg	------	-------
	steam volatile			non-steam volatile	steam volatile			non-steam volatile
	(54)		(7)		(54)		(7)	

Table 2. Comparison of smoke-compositions

Author	Type of wood	Type of smoke generator	% or g/m^3	formaldehyde	total aldehydes	total carbonyls	formic acid	other acids	total acids	phenols	furfural
Pettet and Lane (8)	oak	open fire 400	%	0.12	0.69	1.36	0.38	1.71	2.09	0.07	-
		800		0.06	0.25	0.56	0.43	1.80	2.23	0.12	-
		1200		0.24	0.51	0.59	0.36	1.69	2.05	0.06	-
Rusz a.o.(70)	beech	electric burner 300±20 °C	%	1.10	3.80	8.69	-	-	5.24	0.30	0.69
	oak			1.04	4.30	8.05	-	-	5.14	0.30	1.57
	alder			0.87	3.10	7.47	-	-	3.88	0.20	0.66
	fir			1.43	5.22	10.84	-	-	3.74	0.25	1.03
	birch			0.96	3.31	8.71	-	-	4.57	0.19	0.75
	poplar			0.78	3.08	7.06	-	-	2.23	0.60	0.47
Tilgner (54)	beech	mechanical burner	gr/m^3	-	-	±0.13	-	-	±0.20	±0.12	-
	oak			-	-	0.09	-	-	0.26	0.13	-
	alder			-	-	0.16	-	-	0.21	0.15	-
	fir			-	-	0.02	-	-	0.33	0.23	-
	birch			-	-	0.12	-	-	0.20	0.17	-
	plane			-	-	0.26	-	-	0.25	0.21	-
	pine			-	-	0.01	-	-	0.61	0.17	-
	lime			-	-	0.23	-	-	0.29	0.18	-
	aspen			-	-	0.25	-	-	0.45	0.25	-
Ziemba (61)	beech	mechanical burner	gr/m^3	-	-	0.05	-	-	0.04	0.02	-
	beech			-	-	0.11	-	-	0.20	0.09	-
	oak			-	-	0.02	-	-	0.06	0.01	-
	oak			-	-	0.07	-	-	0.33	0.07	-
	oak+beech			-	-	0.20	-	-	0.16	0.09	-
Rusz a.o. (70)	beech	electric burner 400±20°C (furfural spent wood)	%	0.69	3.32	9.03	-	-	3.65	0.25	0.63
	oak			0.70	3.26	8.56	-	-	3.34	0.22	0.95
	alder			0.57	2.45	7.56	-	-	2.45	0.19	0.50
	fir			1.07	3.73	10.55	-	-	2.11	0.23	0.69
	birch			0.91	3.10	7.73	-	-	2.81	0.15	0.56
	poplar			0.59	2.49	7.38	-	-	2.04	0.42	0.45
	aspen			0.90	3.31	8.01	-	-	3.32	0.27	0.66

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By A.S.J. Koole, M.Sc.

(Summary)

Curing of meat by smoking is an age-old traditional process, which by now has grown into an important technological operation.

Its purpose is to exert a favourable influence on colour, taste and flavour as well as on consistency and keepability. Good advances have been made in the technological developments during the last 25 years but only in the last few years research has become actively engaged in trying to understand the process itself.

Results (Pettet, Husaini, Tilgner, Rusz, Fusako, a.o.), not yet being intercomparable, do show complicated physical and chemical structures of smokes, both being affected by many factors. Mentioned are a.o. type, particle diameter and condition of the wood used, way of generating and life-time of smoke, as well as temperature and humidity. The method of depositing smoke-components on and in the products to be cured must be supposed to play a role.

As for the composition of the smoke, the-accepted-presence of aldehydes, ketones, carboxylic acids, phenols and furans besides "extraneous" components such as methyl-cyclo-pentenolone, phenyl-dioxane and carbon dioxide cannot be considered as a sufficient description.

About 200 primary and probably a greater number of secondary components can easily be considered to be present in the gaseous, liquid and solid phases.

As to their individual or combined physical and chemical activities in the curing process one can only guess up to now. Simplifications such as considering groups of compounds have their use, but do call for a more detailed description.

Future research on the nature of the smoke curing process and the development of new lines will have to be basic as well as applied, aided by modern instrumentation and carried out by coordinated teams of specialists.

Based on this conception the Central Institute for Nutrition and Food Research T.N.O. has recently started research on the analysis of smoke by means of modern physical and chemical methods.

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