

PHYSICAL AND CHEMICAL PROCESSES INVOLVED IN THE PRODUCTION  
AND APPLICATION OF SMOKE

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Abstract - The physical and chemical processes involved in the production and application of wood smoke are reviewed and discussed. Outlines for rendering the production of smoke a more controllable process as well as for estimating the concentration of individual compounds in the vapour phase, are given. Attention is drawn to the fact that conventional smoke contains not only polynuclear hydrocarbons, but also is contaminated with nitrosocompounds. The need for further basic research indispensable for a better understanding of these processes is urged.

Developing and application of smoke to foodstuffs are technological procedures involving several physical and numerous chemical processes linked closely with each other. Comprehensive reviews of these processes were made by Kurko (37, 38), and their physical and engineering aspects were discussed by Adam and Jankovsky (2) and by Adam (3). Recently Gilbert and Knowles (24) reviewed the chemistry of smoke formation on basis of contemporary analytical results published elsewhere. Ruiter (55) and Ziemba (68) gave the foundations of our actual views concerning the formation of "smoked colour" on the surface of smoked goods.

Despite the immense amount of analytical work done within the recent 20 years only few basic facts, pertaining to the processes involved in smoke formation and application are known, whereas the vast amount of details is still obscure. This situation is foremost the result of our limited knowledge concerning both the substrates and the products of oxidative thermodes- truction of the raw materials used for developing smoke.

Wood, the material most widely used for smoke production, consists of many groups of polymers which for sake of simplicity are referred to as cellulose, lignin and hemicellulose. In fact however, there is a variety of cellulose commonly known as the alpha-, beta- and gamma-cellulose. With lignin the situation is even more complicated as there is much uncertainty regarding some of its functional groups (carbonyls, keto-enol forms, etc.) and so the structures proposed for lignin by Freudenberg (23), Forss et al. (21), Goos (25) or Morton (41) differ from each other. Information relating to the structure of hemicelluloses also is not encouraging (see: Björkman (10), Björkman and Person (11), Kawamura and Higuchi (27)). The most widespread opinion is that these three groups of polymers in wood are partially linked with each other by chemical bonds.

While the structure of carbohydrates is a more or less regular repetition of the structure of the respective monosugars, that of lignin is complicated, and - as postulates Freudenberg (23) - is formed at random during its biosynthesis. According to Brown (13) and Neish (47) the biosynthesis of lignin starts from phenylalanine and shikimic, ferulic and p-coumaric acids and yields the respective 4-hydroxy-phenylpropane derivatives (see: Kin (29)). Freudenberg (23) is tracing these derivatives back to p-coumaric, coniferic and sinapic alcohols. The ratio of these derivatives is changing from one wood variety to another as it is exemplified in table no. 1.

TABLE 1. Percentage share of main components in lignin in two varieties of wood (after Freudenberg (23))

Derivatives of	beech	spruce
coniferic alcohol	49	80
sinapic alcohol	46	6
coumaric alcohol	5	14

Concerning the formation of smoke, one is justified in saying that it starts with the breakdown of these bonds where the vibrational energy is equal or almost equal to the bond energy. However the bond energies are depending on the size and shape of the macromolecules and it is impossible to predict their precise value. Therefore - although temperature will be always the decisive factor - the actual path of thermal breakdown of the wooden substance will depend highly on wood variety, and even on the degree of disintegration of wood. All these factors yield a very rich assortment of possible reaction mechanisms or their dominant paths. Some aspects of these processes will be discussed below.

#### 1. PRODUCTION OF SMOKE

As has been pointed out in an earlier paper (see: Miler (43)) the production of smoke from wooden material is a two-step process, wherein the substrate is degraded thermally in the absence of atmospheric oxygen yielding volatiles and charcoal, and the volatiles react in turn with atmospheric oxygen in the adjacent oxidation zone. This zone is forming a layer around the combusted material, most often making itself visible in form of a flame.

The amount of heat evolved during combustion is very high and is dependent on the elemental composition of the combusted material (see: Meunier (42)), for wood it has the value of approx. 4750 kcal/kg. This fact together with the low specific heat of gases causes the temperature of the oxidation zone to attain very high levels. It is known (see: Miler (44)) that under conditions of natural air draft (convection) the temperature of the glowing zone in sawdust is within the range 860-940 °C. Combustion under conditions of forced air draft yields higher temperatures. Borys et al. (15) basing on their recent investigations performed with alder wood (*alnus incana*) found the following

relationship between combustion temperature and air flow rate:

$$T = \frac{y_m \cdot e^{-a^2 \cdot (u - u_m)} - A}{B \cdot u} \dots\dots\dots(1)$$

where: T - temperature of the combustion bed

u - air flow rate

$u_m$  - air flow rate yielding the highest combustion rate of wood ( $y_m$ )

A, B - constants

They present also numerical values for all constants present in the above formula covering the range of air flow rates from 7 cmsec<sup>-1</sup> through 35 cmsec<sup>-1</sup>, moisture contents in the wood from 0 % till 37,24 % and two particle sizes: 0.48 mm and 1.07 mm. Using these data the temperatures corresponding to the highest combustion rates were calculated from equn. (1), and the results are given in table no. 2. As a rule, they exceed 1000 °C.

TABLE 2. Temperatures and air flow rates yielding maximal combustion rates of alder sawdust (calculated from data of Borys et al. (15))

Average particle size of sawdust (mm)	Moisture contents (%)	Optimal temperature (deg C)	Optimal air flow rate (cmsec <sup>-1</sup> )
0.48	0.00	1389	28.8
0.48	6.57	1409	24.5
0.48	31.64	1171	26.2
1.07	0.00	1246	32.7
1.07	14.12	998	28.8
1.07	37.24	1226	26.7

The high temperature of the oxidation zone, its immediate proximity to the degrading wood, and the low amount of heat liberated during thermal degradation (260 kcal/kg - Klason et al. (31)) cause that the temperature of the degradation layer practically to be equal or almost equal to that of the oxidation zone. This fact must of course influence the rate of thermal degradation of wood, which process can be described by the kinetic equation of first order (Stamm (61)). For thermal degradation of beechwood logs Miler (45) found data which can be expressed in form of the following equations:

$$L = L_u \cdot (1 - e^{-k \cdot t}) \dots\dots\dots(2)$$

$$L_u = \frac{8.493 \cdot (T - 453)}{100 + 8.493 \cdot (T - 453)} \dots\dots\dots(3)$$

$$k = \exp \left( 8.3478 - \frac{7401 \cdot 36}{T} \right) \dots\dots\dots(4)$$

where: L - percentage loss of wooden matter

T - temperature of degradation (deg K)

t - duration of the degradation process (min)

The linear forms of equn. (2) and equn. (4) have the following correlation coefficients, respectively:  $r_2 = -0.92107$  and  $r_4 = -0.99983$ . In this respect the pyrolysis of wood is resembling that of hydrocarbons, which also follow first order kinetics (see: Błaszczuk (12)).

Experimental data published by Kuriyama (36) make it possible to have an insight into the degradation kinetics of the main groups of wood components. From the performed calculation follows that cellulose, pentosans, the sum of cellulose pentosans and lignin, the methoxyl groups, and the total mass of the wooden substance degrade in accordance with first order kinetics. In the computations the actual amount of the compound was expressed in percentage of its initial amount. In table no. 3 the values for A and B of the Arrhenius equation

$$\ln k = A - \frac{B}{T} \quad \dots\dots(5)$$

are given alongside with the respective correlation coefficients.

TABLE 3. Values of constants and correlation coefficient for the Arrhenius equn. pertaining to pyrolysis rate of "Konara" wood (calculated from data published by Kuriyama (36))

Process	A	B	r
Losses in total mass of wood	- 2.1468	2006.16	-0.98458
Degradation of total cellulose	5.3891	4692.20	-0.99955
Degradation of pentosans	13.4547	7406.58	-1.00000
Loss of summaric mass of cellulose, pentosans and lignin	- 1.0785	2216.39	-0.96296
Loss of methoxyl groups	1.3400	3063.36	-0.94810

The value of the term B in table no 3 indicates also how susceptible the given component is to thermal degradation. Namely for a first order reaction one can write:

$$\frac{dv}{dT} = v \cdot \frac{B}{T^2} \quad \dots\dots(6)$$

where:  $v = \frac{dm}{dt}$  - reaction rate.

From the data given in table no. 3 one can see that pentosans are most susceptible to thermal degradation, cellulose being in the second, and methoxyl groups in the third place. From Kuriyama's data follows that lignin - when taken alone - does not obey the above mentioned rules. Moreover there is a bidirectional course of its degradation process - first indicating an increase of the amount of lignin, much exceeding its initial amount, and then fol-

lows a decrease well below the initial amount. This reaction rate could be satisfactorily expressed by the following formula:

$$v_L = v_S - (v_C + v_P) \quad \dots\dots\dots(7)$$

where:  $v_L$  - degradation rate of lignin  
 $v_C$  - degradation rate of cellulose  
 $v_P$  - degradation rate of pentosans  
 $v_S$  - degradation rate of the total amount of cellulose, pentosans and lignin

Applying equn. (6) to formula (7) one gets

$$v_S = 2.117 \cdot v_C + 3.342 \cdot v_P \quad \dots\dots\dots(10)$$

This ridiculous behaviour of lignin can be explained by assuming that during degradation of wood there occurs some reaction between the depolymerizing carbohydrates and lignin, which loosing some of its methoxyl groups exhibits some sites in excited states. It follows that the elegant degradation mechanism elaborated for homogeneous polymers, like polystyrene (see: Cameron and McWalter (16)), is not fully applicable to wood. To the two main steps postulated for homogeneous polymers, i.e.: a/ formation of radicals at the chain ends, b/ unzipping of the polymer chains yielding volatile mono- and oligomers (see: Vasile et al. (66)) in wood we have to add one step more, namely the interaction of different kinds of mono- and oligomers to form non-volatile polymers degrading at higher energetic levels along a mechanism path differing from that which the parent polymers are taking.

Gilbert and Knowles (24) suggest an elegant degradation mechanism for cellulose assuming that the initial reaction is an acid-catalysed hydrolysis to glucose. This is in full agreement with the above mentioned step no "a" for degradation of homogeneous polymers, and possibly is true. However, from data presented by Kuriyama (loc. cit.) indicating that there is a conversion of alpha-cellulose into beta-cellulose and gamma-cellulose one is inclined to say rather that unzipping of the aligned polymer chains is the primary process. For such an unzipping can take place at lower energetic levels, as polymer chains usually are aligned in bundles by means of hydrogen bonds. Nevertheless the scission of glucoside radicals takes place although probably this is becoming pronounced at temperatures above 140 °C. At these temperatures there is little chance of having any of the "free water" initially present in the wood. However, there is enough water originating from splitting away hydroxyl groups, therefore there is some chance for acid-catalysed hydrolysis, which probably involves some sort of radical mechanism (OH radicals). The splitting away of hydroxyl groups from cellulose and hemicelluloses to form water is described in literature (e.g. Klason (31), Kuriyama (36)). Nevertheless the detailed mechanism of the pyrolysis of wood still remains unknown, and the theories of Rice and coworkers (52, 53) so fruitfully applied to the pyrolysis of hydrocarbons are not fully applicable here. The presence of oxygen bound with the wood constituents has to be taken in account (see: Meunier (42)), as it alters the reaction mechanism by introducing hydroxyl

radicals which are said to be essential to initiate and propagate chain reactions in combustion processes (see: Lewis and von Elbe (40)). An excellent example of the complexity of reactions taking place during degradation of oxygen-containing organic substances is given by Osman et al. (51) for the case of thermal alkylation of aromatic nuclei with aryl-benzyl ethers.

The results given by Kishimoto and Hirano (30) for thermal degradation of wood in the absence of air are a clear-cut demonstration of the diversity of compounds obtained in this process. These data are a firm basis for stating that already during the first stage of smoke production, i.e. during the degradation process, all hitherto known substances essential for wood smoke, are formed. Hence the oxidative step of smoke production most probably induces only quantitative changes in the initial pattern of volatile degradation products, but will not lead to synthesis of new substances on a bigger scale. Besides, the oxidative step is supplying energy for propagation of the reactions.

The quantitative changes occurring in the oxidative zone seem to be far reaching, as can be deduced from the data collected by Miler et al. (43) for the case of total phenols. The susceptibility of this reaction to changes in oxygen concentration according to these authors can be written as

$$\frac{dC_{ph}}{dC_{ox}} = q \cdot C_{ox} \quad \dots\dots\dots(11)$$

where:  $C_{ph}$  - concentration of phenols as resorcinol  
 $C_{ox}$  - concentration of air oxygen

The susceptibility of this reaction to temperature changes was found to be:

$$\frac{dC_{ph}}{dT} = C_{ph} \cdot \left( \frac{a}{T} + b \right) \quad \dots\dots\dots(12)$$

where: a and b are constants

From the latter follows that there exists a temperature yielding the highest amount of total phenols, namely

$$T_{max} = \frac{a}{b} \quad \dots\dots\dots(13)$$

The above correlates well with the findings resulting from data presented by Borys et al. (15) which indicate also a curvilinear dependence between the amount of the formed individual compounds, and the air flow rate or combustion temperature. Benzo(a)pyrene, which is focussing so much of public interest, also indicates a similar dependence, although its maximum usually is at or above the upper practicable limits of air flow rate or temperature. This is in agreement with results published by Lam (39) and in the majority of cases also with those given by Grimmer et al. (26). The linear correla-

tion between the contents of benzo(a)pyrene and combustion temperature found by Toth and Blaas (65) probably is reflecting the particular conditions under which these authors produced their smoke. Unfortunately they do not give details pertaining to moisture contents in wood, mesh size etc. Moisture contents and particle size of the combusted material have a marked effect on the amount of benzo(a)pyrene and are capable of changing the slope of the curve from positive to negative values (see: Borys et al. (15)). These two factors have also a pronounced influence on the combustion rate of wood. From data published by Borys et al. (15) one can derive that this interdependence has the form of a bell-shaped curve. They enable also to find optimal conditions of burning the sawdust yielding the highest possible combustion rates. These conditions were calculated and are shown in table no. 4.

TABLE 4. Optimal moisture, temperature and air flow rate conditions yielding highest combustion rates of alder sawdust (based on data of Borys et al. (15))

Average particle size of sawdust (mm)	Optimal moisture contents (%)	Optimal air flow rate (cmsec <sup>-1</sup> )	Optimal combustion temperature (deg <sup>C</sup> )	Maximal combustion rate (gmin <sup>-1</sup> cm <sup>-2</sup> )
0.48	0.00	32.64	1322	0.836
1.07	16.18	43.11	942	1.110

As can be seen from these data the coarser grades of sawdust have a higher combustion rate, whereby a definite amount of moisture is indispensable to reach the maximal combustion rate. The moisture enables also to keep the combustion temperature at a lower level although at the expense of a higher air flow rate.

These findings indicate that combustion temperature, moisture contents and grading of the wood as well as air flow rates are means which can be used to control the combustion rate of wood. However, until such functional relationships will be established for any of the major smoke components and also until we get exact knowledge on the contribution of these components to the overall smoke flavour or other important features, we are not entitled to say that this wild process, which the self-propagating combustion of wood indeed is, has been tamed. It is an immense amount of work, which still has to be done, and it must be done if we will deal with a controlled process in future.

In search of methods for controlling the thermal degradation of wood, friction generators were developed some years ago, and relatively new is the method of producing wood smoke by treating the wood with overheated steam. The first method is well described in literature (see: Adam (4), Klettner (32)), while the latter - known as the Fessmann procedure - is covered by numerous patents (see: Fessmann (18, 19), Becker (8)). However, the simple fact that friction generators have not gained any massive industrial application may indicate that among others the flavour of friction smoke is not

fully competitive to traditional smoke. Also experiments performed by Kersken (28) gave no clear evidence for the competitive position of smoke obtained by the Fessmann procedure towards that of traditional smoke. In the majority of cases the scores for salami were inferior to those obtained for the same sausage when smoked traditionally. However, when the Fessmann smoke was produced at 340 °C and the product assessed after five days of storage, the scores for flavour were comparable to those obtained for a traditionally smoked product. The results obtained by Kersken (loc. cit.) indicate also that the higher the temperature of smoke production in the Fessmann procedure, the lower is the acceptance of the smoke flavour. This result is exactly the contrary of that which would be expected from experience with traditional smokes and from experiments with two-stage smoke generators (see: Tilgner et al. (62)). Whatever is the actual situation with the above two methods of smoke production, they allow to obtain smoke with low contents of polynuclear hydrocarbons and hence they deserve more attention and investigations to bring these smokes to the flavour quality comparable with that of traditional wood smoke.

TABLE 5. Average<sup>a/</sup> percentage shares in the total under-peak area found in GIC analyses<sup>b/</sup> for nine phenolic compounds isolated from alderwood smoke (after Olkiewicz (50))

Compound	No. of experimental series <sup>c/</sup>						mean sum
	1	2	3	4	5	6	
Phenol	4.50	3.72	3.70	3.35	3.16	4.33	8.11 ± 0.12
3-methylphenol plus 4-methylphenol	4.88	4.37	4.62	3.20	3.80	5.04	
2-methoxyphenol	5.49	5.01	5.06	3.40	3.97	5.00	18.72 ± 2.28
2-methoxy-4-methylphenol	6.76	6.49	6.93	4.51	4.87	6.29	
2-methoxy-4-vinylphenol + 2-methoxy-4-allylphenol	2.59	4.41	3.07	3.14	4.15	3.46	
2-methoxy-4-transpropenyl- phenol	4.53	4.97	4.99	3.71	4.33	5.16	
2,6-dimethoxyphenol	24.65	21.47	22.82	31.83	29.00	19.55	53.01 ± 6.57
2,6-dimethoxy-4-methyl- phenol	19.73	19.92	22.64	26.10	22.24	16.78	
2,6-dimethoxy-4-allyl- phenol	7.03	8.96	4.85	5.44	6.63	8.43	
Sum	80.16	79.32	78.68	84.68	82.15	74.04	79.84 ± 3.58

a/ average is defined as  $y = \frac{1}{u_{\text{sup}} - u_{\text{inf}}} \cdot \int_{u_{\text{inf}}}^{u_{\text{sup}}} (A_0 + A_1 u + A_2 u^2 + A_3 u^3) du$   
(see: Borys et al. (15))

b/ for analytical details see Borys (15)

c/ for combustion conditions see Borys et al. (15)



The influence of wood variety on smoke flavour, well known from experience and established in experiments (see: Tilgner et al. (63)), may be partially explained on basis of the aforementioned fact that the basic pattern of smoke compounds is formed during thermal degradation of wood, and hence is to some extent reflecting the differences in the chemical constitution of the wood varieties. As the smoke flavour is mostly depending on the pattern of phenolic compounds, so these variations may be traced back to the ratio of phenoxypropane- to methoxy-phenoxypropane- to dimethoxy-phenoxypropane derivatives in the combusted wood. In gaschromatographic analyses of phenols extracted from smoke obtained by combustion of alder wood under various combustion conditions, Olkiewicz (50) determined the average percentage-shares of the under-peak area for the main nine components. The results are shown in table no. 5.

Although these compounds comprise only approx. 80% of the total under-peak area, they are a good representation because the remaining 20% is made up by peaks, from among which none has a percentage share exceeding 2%. These results indicate that the ratio of phenoxypropane- to 2-methoxy-phenoxypropane- to 2,6-dimethoxy-phenoxypropane derivatives is as 10 : 24 : 66. When comparing this ratio with that of another hardwood (beech) given in table no. 1 one can see that most probably the 2-methoxy-phenoxypropane parts of lignin are most liable to demethoxylation, whereas 2,6-dimethoxy-phenoxypropane parts are relatively resistant to this reaction.

Air components when passing through the combustion bed not only take part in reactions with smoke constituents but also can react with each other. The reaction between nitrogen and oxygen is well known in inorganic technology and found its industrial application in the production of nitric acid already some 50 years ago. However, until the excellent work of Möhler (46) nobody was aware of the fact that the same reaction leading in first instance to the formation of nitric oxide, may also proceed during the production of wood smoke. However, if we take in account the temperatures given in table no. 2 and the well known relationship linking Gibbs' free energy with the equilibrium constant, i.e.:

$$G = - RT \cdot \ln(K_p) \quad \dots\dots\dots (14)$$

then we come to the conclusion, that Möhler is perfectly right. The concentrations of nitric oxide (NO) expressed in parts per million can be calculated from the formula (approximation):

$$C_{NO} (\text{ppm}) = 2678.6 \cdot \sqrt{K_p} \quad \dots\dots\dots (15)$$

Inserting the respective data taken from any tables of chemical constants one gets the values given in table no. 6.

TABLE 6. Influence of temperature on the values of  $K_p$  and  $C_{NO}$  for the reaction:  $N_2 + O_2 \rightarrow 2 NO$

Temperature (deg C)	$K_p$ (-)	$C_{NO}$ (ppm)
400	$1.83 \times 10^{-13}$	0.11
600	$3.00 \times 10^{-10}$	4.63
800	$3.11 \times 10^{-8}$	47.28
1000	$7.49 \times 10^{-7}$	231.70
1200	$7.61 \times 10^{-6}$	739.29
1400	$4.44 \times 10^{-5}$	1781.25
1600	$1.78 \times 10^{-4}$	3575.89

Of course, NO is easily oxidized to  $NO_2$  and higher nitrogen oxides, nevertheless it is also eagerly reacting with organic substrates, in this number also with phenols as has been shown in the excellent paper published by Knowles et al. (33). Therefore the results found by Mähler (loc. cit.) must be accepted as a warning that traditional smoke production may lead to the contamination of foodstuffs not only with polynuclear hydrocarbons but also with nitrosocompounds. Among the latter nitrosoamines may be present, as wood contains approx. 0.1-0.32 % of organically bound nitrogen. At the high temperatures existing during smoke production the concentration of low molecular radicals is probably higher than that of higher molecular ones. Therefore one may expect that the amount of low molecular nitrosocompounds will be higher than that of higher boiling ones.

From the above, it follows that the production of smoke is a very complicated process, highly difficult to control and yielding a product which besides desired constituents contains also a vast variety of hazardous compounds. As the list of detected hazardous components is rather constantly enlarging, so methods for producing a safe and though full flavoured smoke are becoming more and more urgent. It can be foreseen that with the advent of such methods the traditional smoke production will be abandoned, although at this moment it is impossible to say when this goal will be reached.

## 2. APPLICATION OF SMOKE

Application of smoke to foodstuffs essentially is a physical process, which is based on such phenomena as diffusion, adsorption, dissolution and deposition in force fields. It is accompanied by chemical processes, wherein smoke compounds interact with food constituents.

The physical properties of wood smoke and the physical factors involved in deposition of smoke on surfaces were extensively studied by Foster 22. The mechanism of smoke deposition is comprehensively described in the paper published by Simpson and Foster (60). From these investigations it became known that the particulate phase of wood smoke, amounting up to 90% of its

organic matter, is depositing only on dry or almost dry surfaces, whereas transport of smoke compounds to wet surfaces is effected by the diffusion mechanism. This has been proved valid in experiments made by Tilgner et al. (50), Rusz et al. (56), and Rusz (57) who used electrostatically filtered smoke for smoking foods. In the traditional draft smoking we usually deal with a wet surface in the beginning of the smoking period, however, with elapsing time this surface loses much of its moisture, and hence we have to say that in such processes probably both forms of mass transfer are active in depositing smoke compounds on the smoked good.

Smoke density is a very important factor determining the rate of smoke deposition. However, we must be aware of the fact that density measurements usually represent only the density of the particulate phase, because they are performed either by measurement of light absorbance or scattering or by some deposition technique (e.g. absorption on filters). Nevertheless these measurements by no means can be regarded as meaningless - on the contrary they are a useful means because under equilibrium conditions Nernst's partition rule

$$\frac{C_{\text{vap}}}{C_{\text{part}}} = K \quad \dots\dots\dots(16)$$

is applicable. In said formula  $C_{\text{vap}}$  stands for concentration of smoke compounds in the vapour phase, whereas  $C_{\text{part}}$  denotes the concentration of these compounds in the particulate phase. The partition rule may be used not only for determining empirically the interdependence between the concentration of smoke compounds in the vapour phase and that of their counterparts in the particles, too, it can be used for assessing - if not exactly determining - the concentration of any compound in the vapour phase, provided its boiling temperature and latent heat of vapourization is known. Namely when in equn. (16) the concentrations are expressed in molar fractions, then we can write

$$K = \exp \left( \frac{\Delta H_B}{R \cdot T_B} - \frac{\Delta H}{R \cdot T} \right) \quad \dots\dots\dots(17)$$

where:  $H_B$  - latent heat of vapourization at the boiling point and atmospheric pressure  
 $\Delta H$  - latent heat of vapourization at the vapourization temperature  
 $T_B$  - boiling point temperature (deg K)  
 $T$  - vapourization temperature (deg K)  
 $R$  - gas constant.

When the latent heat of vapourization is not known for the vapourization temperature, which case usually is encountered as these values are tabularized mainly for the boiling point temperatures, then it can be calculated from the following formula developed by Fish and Lielmezs 20 :

$$S_s = \frac{T_s + T_s^{0.35298}}{1 + T_s^{0.13856}} \quad \dots\dots\dots(18)$$

where:

$$S_s = \frac{\Delta H/T}{\Delta H_B/T_B} \dots\dots\dots (19)$$

$$T_s = \frac{T_c/T - 1}{T_c/T_B - 1} \dots\dots\dots (20)$$

$T_c$  - denotes the temperature of the critical point (deg K).

For the majority of cases, where the value  $\Delta H_B$  is unknown, it may be calculated from Trouton's rule (see: Barrow (7)). The temperatures of the critical point - if not tabulated - can be computed on basis of the structural formula of the compound in question and the correlations given by Ambrose et al. (6).

Of course the above formulae are applicable only then when concentrations are quickly equilibrated and for compounds which have not significant deviations from Raoult's rule in the given range of concentrations.

From equns (16) and (17) it can be seen that the increase of the smoke temperature causes an increase in the concentration of the smoke compounds in the vapour phase. This explains also why hot smoking procedures give a higher "smoking" rate. However, with higher temperatures the amount of adsorbed substances is rapidly decreasing, so as a result there will be always an optimal temperature, at which the "smoking" rate is highest. Probably this does explain the maxima found by Simpson and Foster (loc. cit.) for the deposition of total phenols on wet surfaces.

As pointed out by Adam, in smokehouses filled with smoked goods the flow of smoke is always turbulent - in particular in those smokehouses, where forced draft is applied. Therefore we can take it for granted that mixing effects exist in the smoke stream and concentration gradients will be found only in the nearest vicinity of the smoked surfaces due to their absorption activity. Not trying to go into details of the many existing absorption theories (see: Newsome (48), Bergmann and Antonioni (9)) we can say that it is the amount of the adsorbed smoke compounds at the surface of the smoked goods, which triggers the diffusion mechanism of these compounds into the interior of the smoked goods. The fundamentals of this diffusion mechanism are well known and described elsewhere (see: Crank (17)), however in the case of smoking we have to do with a process, where the boundary concentration, i.e. the concentration of smoke compounds at the surface of the smoked food, is changing with time, and besides at least some of the smoke compounds are partially bound by constituents of the smoked goods. Such interaction has been demonstrated by Kozłowski (34) on the example of guaiacol, phenol and 2-n-propylphenol. This author states that phenols with a blocked para position do not interact with meat. Krylova et al. (35) found in their investigations that phenolic compounds present in wood smoke react with aminoacids, in particular with those which contain sulphur. For the above reasons the time-dependent diffusion equation known also as Fick's second law, hitherto has no ready to use solutions in literature. We deem that this problem deserves more attention from side of investigators, in particular with the ultimate aim to find

simple and though exact solutions of the same type as given by Adam (4, 5) for conduction of heat in smoked sausages.

As is well known, during smoking - depending on the conditions - a more or less pronounced drying effect is obtained. This is connected with the diffusion of water from the inside of the smoked item to its outside, and generally can be said to be covered by the classical solutions of the diffusion equation (see: Crank (17)). These solutions were successfully broadened by Adam and Jankovsky (2) and Adam (4, 5) to include also the effects of changing temperature in the goods. Recently Rotstein et al. (54) extended the classical solutions on the case of non-conventional shapes of the dried goods. It is worth noting that they treated successfully also the case of total moisture diffusion from the solid body, not only the classical concentration distribution. In the cases where steam is used as a direct source of heat, attention should be paid to additional heat transfer resistance on the surface of the heated body due to the formation of a layer of noncondensable gases, escaping from the heated goods (see: Brown (14)).

The problem of colour formation during the application of smoke was extensively studied by Ruitter (loc.cit.) and Ziembra (loc.cit.). As these results are well known, so this problem will not be dealt with here.

Electrostatic deposition of smoke, which was so intensively studied some time ago (see: Sikorski (58, 59), Zander and Metz (67)) now is used sporadically. Most probably this retreat from that procedure can be linked with the growing public awareness of the risks connected with contaminating food with polynuclear hydrocarbons. As was shown by Obiedziński (49), the concentration of these compounds in the particulate tarry fraction of smoke is extremely high, and so this risk is not an imaginary one. This awareness probably is also the causative factor for the growing interest in smoke flavouring, usually called "liquid smokes". Although the vast majority of these flavourings is still of poor quality, there are some which give flavours equivalent to that of traditional smoking. As these products are obtained either by distillation or by extraction or by some combination there of, from the technological point of view there are no hindrances to produce a flavouring with a taylor-cut composition. If then there are so many poor quality products on the market, so the reason has to be sought both in the lack of knowledge concerning the role of the individual components in the overall smokey flavour as well as in bad craftsmanship.

Ending, the authors would be glad if the above presented few remarks on the physical and chemical processes involved in the production and application of smoke will inspire you to join in the efforts to make these processes more understandable and more controllable.

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