The Distribution of Gases within the Combustion Coal of a Cigarette*

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INTRODUCTION

There have been many studies of the composition of the vapour phase from a burning cigarette (1), but these investigations took samples from the exit gas stream of the cigarette and so could give no indication of the gas-phase composition within the cigarette. As far as is known, only one previous study has taken samples from inside the cigarette (2), using a syringe to sample the gases for analysis by gas chromatography. In the present study a mass spectrometer coupled to a sampling probe within a cigarette has been used to provide a direct estimate of the distribution of low molecular weight gases in the combustion coal of the cigarette.

EXPERIMENTAL DETAILS

The non-filter cigarettes used in this study contained a typically English-type Virginia blend tobacco, and were 68 mm long and 8 mm in diameter. They were selected for weight (0.99 ± 0.02 g) and pressure drop (9.25 ± 0.25 cm water gauge), and conditioned at 21° C and 60% relative humidity.

Mass Spectrometer

Gas samples from within the cigarette were continuously sampled through the probe into an A. E. I. type MS 2 mass spectrometer. Direct entry of the gas samples into the mass spectrometer source was obtained by removing the standard four-way valve system and using a modified A. E. I. continuous inlet system, originally designed for use on the MS 10 mass spectrometer. The sample from the probe was drawn along a stainless steel capillary tube ($2 \text{ m} \times 0.3 \text{ mm i. d.}$) by a rotary pump (model GDR 1, with a displacement of 1 litre s^{-1}) and two diffusion pumps. In the interspace, part of the gas sample diffused into the mass spectrometer through a porous ceramic leak. The pumping system produced an ultimate pressure of 6×10^{-7} torr ($1 \text{ torr} = 133 \text{ N m}^{-2}$) with the capillary inlet closed by a screw plug; with the capillary inlet open to the atmosphere, a pressure of 8×10^{-7} torr was obtained. The response time of the inlet system was about 0.5 s: when a gas was introduced at the capillary inlet, the recorder monitoring the mass spectrometer output obtained its maximum deflection in less than 0.5 s. This time lag was, in fact, due mainly to the response time of the recorder.

The Probe Assembly

Since it was required to sample gases from a small section within the cigarette, the probe should have as small a diameter as possible. However, tarry material produced by the cigarette very readily condensed in the probe, and the smallest diameter probe that could be used without blocking with condensates was of 1.0 mm internal diameter. The efficiency of the probe in collecting condensates produced by the burning cigarette (defined as the weight of condensate collected on the probe/total weight of condensate on probe and Cambridge filter placed behind the probe) can be used to provide a rough estimate of the diameter of the particles in the condensate (3). It is found that the particles have diameters in the range 7 to 25×10^{-7} cm, which are very small for aerosol particles and are of almost molecular magnitude. It is therefore concluded that a large proportion of the material trapped in the probe condensed from the vapour phase.

The probes used were quartz tubes of 1.0 mm internal diameter. It was necessary to filter the smoke before it reached the stainless steel capillary inlet to the mass spectrometer, since unfiltered smoke would very quickly block the capillary with condensate. A microfilter unit (with a dead volume of 0.12 cm^3), containing a 13 mm diameter Cambridge filter, was placed just behind the probe. A water manometer was incorporated in the circuit in order to check that the filter and/or probe did not block with condensates.

The quartz probes were made with a platinum/platinum-13% rhodium thermocouple (0.05 mm diameter wire) mounted at the mouth of the probe, with one side of the thermocouple insulated with fine quartz tubing (0.3 mm outside diameter). The probe was inserted into the cigarette either from the side or the "mouth" end. For sideways entry, a hole was drilled into the cigarette with a size 14 hypodermic needle, the probe inserted to the required distance from the centre of the cigarette, and a small portion of latex solution was used to seal the hole in the cigarette paper. Entry from the end of the cigarette was accomplished by drilling a size 14 needle along the cigarette axis, inserting the probe into the needle from the opposite end of the cigarette, and then withdrawing the needle to leave the probe in the required position. The cigarette was squeezed to remove the remaining hole along the axis.

Within the limits of precision in measuring the intensity of a given mass number with the sample obtained from the cigarette ($\pm 10\%$), the results were independent of the position of entry of the probe into the cigarette (axial or from the side). The temperature-time

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and concentration-time relationships were determined at a fixed point 20 mm from the lighted end of the cigarette, and distances of 0, 2, and 3 mm from the central cigarette axis, using the combined quartz probe/thermocouple, with the cigarette smoked at a continuous draw of $2.0 \text{ cm}^3 \text{ s}^{-1}$. A constant draw smoking regime was used since it considerably simplified the collection and interpretation of the experimental data.

The flow rate through the probe, which was governed by the flow rate through the capillary to the mass spectrometer, was $0.1 \text{ cm}^3 \text{ s}^{-1}$.

General Procedure

The mass spectrometer could be locked onto any required mass number using the manual sweep to lock onto the mass approximately, and adjusting the accelerating voltage for fine control. Optimisation of a given mass number was obtained by adjusting the first slit control, the ion repeller, focus, and beam centering controls. The output from the mass spectrometer for a given mass number was monitored either on a Rikadenki two-channel recorder (model number 241X), or on a Dynamco one-channel data logger type DM2022S, used in conjunction with the programme timer (type DS-0413-1), punch drive unit (type DM5021), and teletype paper tape punch unit (type BRPE11). The second channel of the recorder monitored the thermocouple output.

The cigarettes were smoked at a constant draw of $2.0 \text{ cm}^3 \text{ s}^{-1}$, obtained by adjusting a needle valve coupled to a rotameter and rotary pump, all protected by a Cambridge filter. Each experiment was started by igniting the cigarette with an electrically heated wire. Weighing the probe and Cambridge pad in the micro-filter assembly before and after each experiment gave the weight of condensates produced.

Calibration of Mass Spectrometer

The mass spectrometer output was adjusted to zero with pure helium admitted into the inlet capillary. The spectrometer was calibrated for a given gas by locking onto a principal peak in the mass spectrum of the gas, and measuring the peak height of different percentages (volume/volume) of the gas in helium, under flow conditions. Both the gas being calibrated (via a needle valve and bubble meter) and the helium (via a needle valve and rotameter calibrated for helium) flowed into a gas diluting vessel where the gases mixed, and the outlet of the vessel was connected directly to the mass spectrometer inlet.

Corrections to Mass Spectrometric Data

Most of the peaks monitored in the probe work using the low resolution MS2 mass spectrometer were due to contributions from more than one compound.

A high resolution mass spectrum of filtered (Cambridge filter) mainstream smoke of the cigarettes was obtained by collecting the smoke of four cigarettes smoked in parallel under continuous draw conditions ($2 \text{ cm}^3 \text{ s}^{-1}$)

when approximately one third of the cigarette length was consumed. Table 1 gives the spectrum obtained on an A.E.I. type MS9 mass spectrometer at the Physico-Chemical Measurements Unit, Aldermaston, for the peaks up to $m/e = 44$. Only part of the mass spectrum was scanned under high resolution conditions.

It should be noted that the relative intensities in Table 1 were obtained from the mainstream smoke of four cigarettes using an MS9 mass spectrometer, whereas the internal cigarette gas concentrations in the major part of this study were obtained from a small volume within one cigarette, using the MS2 mass spectrometer. Peaks with relative intensities less than about 0.1 in Table 1 could not be detected in the probe study.

With the low resolution mass spectrometer used in the probe work it was not possible to resolve m/e values less than an integer apart. Consequently, most of the peaks monitored were multi-component peaks. For instance, the peak $m/e = 16$ was due to CH_4^+ as well as O^+ and O_2^+ , produced from oxygen, carbon dioxide, and water. However, due to the low concentration of water vapour in the filtered smoke, its contribution to $m/e = 16$ is negligible. Carbon monoxide does not give a peak at $m/e = 16$ under the conditions used in the present study.

Based on the relative intensities given in Table 1, and the sensitivities of different gases at various m/e values on the MS2 mass spectrometer, the contributions of the various components in filtered smoke to the peaks monitored in the probe study, are given in Table 2.

The concentration profiles for oxygen and carbon dioxide were obtained by monitoring peaks of m/e value 32 and 44 respectively, with no corrections applied, and Table 2 suggests that other substances contribute 0.4% and 0.8% respectively to the observed intensities. Since the carbon monoxide profiles could only be obtained mass spectrometrically by a series of corrections to the peaks at m/e 28, 14 and 16, they were obtained directly using a Bosch carbon monoxide meter (type EFAW215). This instrument measures the carbon monoxide concentration by the absorption of infra-red radiation at a wavelength of $4.7 \times 10^{-6} \text{ m}$. Since the Bosch meter measures a maximum concentration at 10% v/v carbon monoxide, the filtered smoke from the probe was diluted with air prior to entering the meter. The instrument itself was slightly modified so that the diluted, filtered smoke was passed directly into its detection cell. This reduced the dead volume of the meter so that the overall response time of the system was of the order of 0.5 s.

All the other concentration profiles presented in this paper were either obtained by applying corrections to the mass spectrometric peaks, or they involve some appreciable error. For example, the methane profiles were obtained at $m/e = 16$, and at a given point in the profile:

$$\begin{aligned} X_{16} &= X_{\text{CH}_4} + X_{\text{CO}_2} + X_{\text{O}_2} \\ &= C_{\text{CH}_4} S_{\text{CH}_4} + C_{\text{CO}_2} S_{\text{CO}_2} + C_{\text{O}_2} S_{\text{O}_2} \end{aligned}$$

where X_{16} is the experimental peak height (mV) and

Table 1. High resolution mass spectrum of filtered, mainstream cigarette smoke †.

Identification of ion	Relative intensity*	Measured mass (m ₁)	Calculated mass (m ₂)	m ₁ - m ₂
H ₂ ⁺	0.21	2.0156	2.0156	0.0000
C ⁺	0.09	12.0000	12.0000	0.0000
¹³ C ⁺	0.001	13.0034	13.0034	0.0000
CH ⁺	0.03	13.0077	13.0078	0.0001
N ⁺ , N ₂ ⁺⁺	0.96	14.0029	14.0031	0.0002
CH ₂ ⁺	0.06	14.0155	14.0156	0.0001
CH ₃ ⁺	0.50	15.0232	15.0235	0.0003
O ⁺ , O ₂ ⁺⁺	0.25	15.9951	15.9949	0.0002
CH ₄ ⁺	0.74	16.0314	16.0313	0.0001
OH ⁺	0.01	17.0031	17.0027	0.0004
NH ₃ ⁺	0.01	17.0260	17.0265	0.0005
H ₂ O ⁺	0.02	18.0106	18.0106	0.0000
Ar ⁺⁺	0.04	19.9813	19.9812	0.0001
Ne ⁺	0.03	19.9924	19.9924	0.0000
CO ₂ ⁺⁺	0.10	21.9952	21.9949	0.0003
C ₂ H ₂ ⁺	0.14	26.0158	26.0156	0.0002
HCN ⁺	0.02	27.0106	27.0109	0.0003
C ₂ H ₃ ⁺	0.26	27.0236	27.0235	0.0001
CO ⁺	11.9	27.9950	27.9949	0.0001
N ₂ ⁺	100.0	28.0061	28.0062	0.0001
C ₂ H ₄ ⁺	0.60	28.0313	28.0313	0.0000
¹³ CO ⁺	0.10	28.9983	28.9982	0.0001
CHO ⁺	1.14	29.0032	29.0027	0.0005
¹⁴ N ¹⁵ N ⁺			29.0033	0.0001
C ₂ H ₅ ⁺	0.32	29.0392	29.0391	0.0001
NO ⁺	0.014	29.9991	29.9978	0.0013
CH ₂ O ⁺	0.004	30.0105	30.0106	0.0001
¹² C ¹³ CH ₅ ⁺	0.002	30.0424	30.0424	0.0000
C ₂ H ₆ ⁺	0.18	30.0469	30.0469	0.0000
CH ₃ O ⁺	0.08	31.0185	31.0184	0.0001
¹² C ¹³ CH ₆ ⁺	0.002	31.0510	31.0503	0.0007
O ₂ ⁺	16.3	31.9899	31.9898	0.0001
CH ₄ O ⁺	0.07	32.0263	32.0262	0.0001
¹⁶ O ¹⁸ O ⁺ , H ₂ S ⁺	0.06	34**	34	—
H ³⁵ Cl ⁺ , C ₃ ⁺	0.02	36**	36	—
C ₃ H ⁺	0.03	37**	37	—
H ³⁷ Cl ⁺	0.06	38**	38	—
C ₃ H ₂ ⁺				
C ₂ N ⁺				
C ₃ H ₃ ⁺ , C ₂ HN ⁺	0.37	39**	39	—
Ar ⁺	2.1	39.9625	39.9624	0.0001
C ₂ H ₂ N ⁺	0.4	40.0187	40.0187	0.0000
C ₃ H ₄ ⁺	0.14	40.0311	40.0313	0.0002
C ₂ HO ⁺	0.02	41.0030	41.0027	0.0003
C ₂ H ₃ N ⁺	0.06	41.0266	41.0265	0.0001
C ₃ H ₅ ⁺	0.61	41.0394	41.0391	0.0003
C ₂ H ₂ O ⁺	0.03	42.0109	42.0106	0.0003
C ₃ H ₆ ⁺	0.26	42.0472	42.0469	0.0003
C ₂ H ₃ O ⁺	0.08	43.0187	43.0184	0.0003
C ₃ H ₇ ⁺	0.32	43.0547	43.0548	0.0001
CO ₂ ⁺	17.2	43.9904	43.9898	0.0004
C ₂ H ₄ O ⁺	0.09	44.0266	44.0262	0.0004
C ₃ H ₈ ⁺	0.04	44.0625	44.0626	0.0001

† MS 9 mass spectrometer, resolving power (M/ΔM) = 10,000; electron energy of 70 eV; ion source at 150°C.

* Expressed relative to the base ion (N₂⁺), and corrected for the instrument background spectrum.

** Low resolution data only is available for these peaks.

Table 2. Contribution of filtered smoke components to various mass spectrometric peaks.

m/e	Ions	Contributing molecules
14	N ⁺ , N ₂ ⁺⁺ , CH ₂ ⁺ , C ₂ H ₄ ⁺⁺	94 % N ₂ , 6 % (CH ₄ , C ₂ H ₄)
16	O ⁺ , O ₂ ⁺⁺ , CH ₄ ⁺	75 % CH ₄ , 25 % (O ₂ , CO ₂)
28	CO ⁺ , N ₂ ⁺ , C ₂ H ₄ ⁺	89 % N ₂ , 10.6 % CO, 0.4 % C ₂ H ₄
30	NO ⁺ , C ¹⁸ O ⁺ , C ₂ H ₆ ⁺ , CH ₂ O ⁺	90 % C ₂ H ₆ , 7 % (NO, NO ₂), 3 % CH ₂ O
32	O ₂ ⁺ , CH ₄ O ⁺	99.6 % O ₂ , 0.4 % CH ₃ OH
42	C ₂ H ₂ O ⁺ , C ₃ H ₆ ⁺	83 % C ₃ H ₆ , 7 % C ₃ H ₈ , 10 % (R-CO-CH ₃)
43	C ₂ H ₃ O ⁺ , C ₃ H ₇ ⁺	80 % C _n H _m (n ≥ 3), 20 % RCOCH ₃
44	C ₂ H ₄ O ⁺ , C ₃ H ₈ ⁺ , CO ₂ ⁺	99.2 % CO ₂ , 0.5 % CH ₃ CHO, 0.3 % C ₃ H ₈

X, C and S refer to the peak height, concentration (% v/v), and sensitivity factors (mV %⁻¹) for the subscripted gases.

The values of C_{CO₂} and C_{O₂} were obtained from the concentration profiles for carbon dioxide and oxygen respectively. Therefore the concentration of methane is given by:

$$C_{CH_4} = \frac{X_{16} - (C_{CO_2} S_{CO_2} + C_{O_2} S_{O_2})}{S_{CH_4}}$$

Table 3 gives a list of the gases which have been determined by the probe technique, the m/e peak on which they were monitored, the applied correction, and an estimate of the error in the concentration profiles. The quoted errors are the maximum cumulative errors, and further refinements to the concentration profiles are not possible without the use of high resolution mass spectrometry.

Table 3. Estimated errors in the gas concentration profiles.

Gas	m/e peak monitored	Corrections applied to the monitored peak	Probable error in profile (%) due to other components
Oxygen	32	none	0.4 %
Carbon dioxide	44	none	0.8 %
Carbon monoxide	Bosch meter	none	0.0 %
Methane	16	oxygen, carbon dioxide	2 %
Higher hydrocarbons*	43	none	25 %
Propene	42	higher hydrocarbons	20 %
Ethane	30	none	10 %
Nitrogen	28	carbon monoxide	0.5 %

* The peak of m/e = 43 is due mainly to the propyl radical, which is produced by propane and higher hydrocarbons. Propane was used to calibrate the m/e = 43 peak.

Figure 1. Temperature-length profiles.

Figure 2. Oxygen-length profiles.

RESULTS AND DISCUSSION

It was assumed that neither the temperature profile nor the concentration profiles changed as they move down the cigarette rod, and that the function-distance profiles could, therefore, be deduced from the function-time profiles and the burn rate. Under the continuous draw conditions used in the present study the length of burn was directly proportional to the time of burn, giving the burn rate as 0.20 mm s^{-1} .

The function-distance profiles for temperature, and the concentrations of the gases oxygen, carbon monoxide and carbon dioxide, are shown in Figures 1–4. Since the temperature and concentration distributions are symmetrical about the central axis, three dimensional contour distributions can be obtained from the profiles in Figures 1–4, and these are shown in Figures 5 and 6.

Figure 3. Carbon monoxide — length profiles.

Temperature Distribution

The temperatures within a burning cigarette have been determined previously [e.g. (4–6)] although only two studies have reported the actual temperature distribution within the coal (5, 6). However, the present temperature contours (Figure 5 [a]) are similar to those obtained during a puff using thermocouples, with the highest temperatures occurring in the centre of the interior of the coal, and the coal cooling towards the exterior regions. In contrast, temperature measurements obtained using optical pyrometry and X-ray photography of the melting of added metal particles within the cigarette (6) indicate that the highest temperatures occur at the exterior of the coal. The metal particles used in the X-ray technique were of similar volume and heat capacity to the thermocouple junction of the present study, and so should indicate the same temperature. However, with a thermocouple, heat losses by conduction along the leads become quite large if there is a steep temperature gradient in the immediate vicinity of the thermo-junction. Applying a lead-conduction correction to the present results increases the highest recorded temperature in the centre of the coal from

Figure 4. Carbon dioxide — length profiles.

Figure 5. Temperature ($^{\circ}\text{C}$) and gas concentration (% v/v) contours.

800° to 868°C , and increases the 400°C contour at the periphery of the coal to 560°C , but it does not affect the relative temperature distribution within the coal.

Laszlo et al. (4b), using a non-contact scanning infrared camera to measure the surface temperature at the exterior of the coal, have recorded surface temperatures of about 850 – 920°C during a puff and 700°C (below the ash) during smoulder. An optical pyrometer study by Egerton et al. (6) has found spots on the coal's surface with temperatures as high as 1200°C , which is more than 300°C higher than the temperatures measured by thermocouples or the X-ray technique. A possible explanation is that thermocouple junctions and the metal particles of the X-ray method measure mainly the gas temperatures within the cigarette whereas the non-contact radiation methods measure the temperature of the solid tobacco bed. Since thermal equilibrium is unlikely to be established, the solid and gas tempera-

tures are thus understandably different. In the present study, the thermocouple temperature distribution (uncorrected for conduction errors) in Figure 5 [a] is used merely as a useful reference point in defining the position of the combustion coal.

Combustion Reactions inside the Coal

The oxygen contours (Figure 5 [b]) show that the interior of the coal is effectively an oxygen-deficient region, in agreement with the results of Newsome and Keith (2) and a prediction of Hobbs (7) made earlier on thermodynamic grounds. Thus oxygen in the air is unable to penetrate into the region of carbonised tobacco in the interior of the coal. This is confirmed by studies of the cross sections of quenched cigarettes (6), which have shown that the influx of air during a puff is confined to the periphery of the coal. The interior of

Figure 6. Hydrocarbon contours (% v/v).

the coal is thus largely a pyrolytic or oxygen-sensitised pyrolytic region. Consequently, a large proportion of the organic products found in tobacco smoke are probably produced by pyrolytic reactions rather than combustion reactions. It would appear that the major quantitative effect of oxygen intake during smoking is probably to produce carbon dioxide, carbon monoxide, water, and therefore heat, by combustion on the hot surface of the coal.

Examination of the contour diagrams for carbon dioxide, carbon monoxide, oxygen, and temperature (Figure 5) reveals that in the high temperature ($> 750^\circ\text{C}$), low oxygen ($< 0.2\% \text{ v/v}$) region of the coal carbon monoxide production reaches a maximum, while the carbon dioxide contours indicate a fairly constant production. This is illustrated more clearly in Figure 7, which shows that as air is drawn through the cigarette coal (from right to left in the contour diagrams), oxygen is consumed, the

products of combustion are formed, and the temperature of the coal rises due to the heat released by the combustion reactions. The distance origin in Figure 7 is at a point in the ash, and the distance axis is related to the length of burn axes in the contour diagrams by the relationship $\text{distance} = 46.5 - \text{burn length}$.

The oxygen balances *due to the combustion in the coal*, expressed as $([\text{O}_2] + [\text{CO}_2] + \frac{1}{2}[\text{CO}])/20.946$, are given in Table 4 at various extents of reaction (concentrations are in $\% \text{ v/v}$ and 20.946 is the $\% \text{ v/v}$ of oxygen in air). It is shown later that about 21% and 5% of the carbon monoxide and carbon dioxide respectively produced *in the coal* are formed by thermal degradation of the tobacco, and so the figures given in Table 4 have been corrected to include only the carbon oxides produced by combustion. Three of the five oxygen balances 2 mm from the central axis of the cigarette are greater than 100% reflecting the cumulative errors of

Table 4. Oxygen balance (due to combustion through the coal.

$$\text{Oxygen balance} = \frac{[\text{O}_2] + [\text{CO}_2]^* + \frac{1}{2} [\text{CO}]^*}{20.946} \cdot 100\%$$

Oxygen balance at r mm from central axis of cigarette			O ₂ consumed (% v/v)
r = 0	r = 2	r = 3	
95	107	92	4
91	106	88	8
81	102	81	12
68	94	81	16
59	87	86	20

* Concentration due to combustion reactions only.

three independent measurements. The oxygen balances at 0 and 3 mm from the central axis indicate that a large proportion of the oxygen-containing products of combustion are accounted for by the two oxides of carbon. The deficiency is most probably due mainly to water produced during the reaction.

A volume element of the coal can receive heat in two ways: either from the chemical reactions occurring within it, or by heat transfer from hotter regions of the coal. The point of inflexion on the temperature profile (occurring when $d^2T/dx^2 = 0$, at a distance of 8 mm in Figure 7) separates two heat zones. At temperatures lower than the point of inflexion d^2T/dx^2 is positive, and since the heat flow into any volume element in the + x direction is given by:

$$\left(\frac{dH}{dt}\right)_{\text{in}} - \left(\frac{dH}{dt}\right)_{\text{out}} = k \frac{d^2T}{dx^2}$$

where dH/dt is in $\text{J cm}^{-3} \text{ s}^{-1}$ and k is the thermal conductivity of the coal ($\text{J s}^{-1} \text{ cm}^{-1} \text{ K}^{-1}$), then $(dH/dt)_{\text{in}}$ is greater than $(dH/dt)_{\text{out}}$. At temperatures greater than the point of inflexion, the converse is true and $(dH/dt)_{\text{out}}$ is greater than $(dH/dt)_{\text{in}}$. However, at these temperatures the chemical reaction rate will be sufficiently high for the rate of heat production by the exothermicity of the overall reaction to be significant. The temperature therefore continues to increase through the coal although at a progressively slower rate (d^2T/dx^2 is negative), and reaches a maximum when all the oxygen has been consumed (at about 13 mm in Figure 7). That part of the ash up to the point of inflexion on the temperature profile can be considered a preheating zone for the incoming air, while the main reaction zone is beyond that point.

Similar behaviour also occurs in the concentration profile for oxygen, with the point of inflexion occurring at 7 mm. The major loss of oxygen, and formation of the combustion products carbon monoxide and carbon dioxide in the preheating zone, is controlled by diffusion into this coal peripheral zone (for oxygen) and out of the zone (for the oxides of carbon). Most of the transport into and out of the preheating zone will occur radially, since the radial concentration gradients are much larger than the axial gradients.

In the reaction zone of the coal, the radial distribution of gases will be controlled mainly by the chemical

Figure 7. Combustion products on the central axis, in the coal region.

reactions occurring. The radial distribution as a function of oxygen consumed at a distance of 14 mm in Figure 7 is shown in Figure 8. The broken portions of the plots in Figure 8 are extrapolations of the plots containing the experimental points, and no experimental points are available in the extrapolated regions because of the very large extent of reaction for very small radial distances at the radial periphery of the coal. However, within the accuracy of the extrapolations, the productions of both oxides of carbon are directly proportional to the amount of oxygen consumed, until about half the oxygen is consumed. In this part of the coal, the carbon oxides are produced solely by reaction of tobacco with oxygen. Chemical analysis has shown that 27.4% of the cigarette coal is inorganic, and 66% of the combustible part of the coal is carbon, compared to 47.5% for the original tobacco (8). Kinetic considerations indicate that, within the limits of the precision of available literature data, the surface oxidation of impure carbon can account for the observed burn rate of the cigarette (9). Thus, representing the coal as a carbon substrate,

Figure 8. Radial distribution of products in the coal (at an axial distance of 14 mm, cf. Fig. 7).

the main reactions occurring in this part of the coal are:

At intermediate levels of oxygen consumption both oxides of carbon are formed at rates greater than the linear dependence on oxygen consumption, and under these conditions a proportion of the carbon oxides is probably produced by decomposition reactions of the tobacco substrate. For large consumptions of oxygen the carbon dioxide concentration goes through a maximum and decreases, while in the same region carbon monoxide increases very sharply. In this high temperature, low oxygen part of the coal, the endothermic reduction of carbon dioxide is a predominant reaction.

Thus the cigarette coal acts very much as a classical oxidising graphite or coal bed (10).

Formation of the Carbon Oxides behind the Combustion Coal

Inspection of Figure 5 [c] indicates that immediately behind the coal the carbon monoxide concentration begins to decrease. In this region, the production of the gas by combustion has ceased (since the oxygen concentration is almost zero) and the decrease in concentration is purely a dilution effect, caused partly by the carbon monoxide diffusing out of the cigarette and partly by air flowing in behind the coal. The concentration of carbon dioxide, however, continues to increase behind the coal (Figure 5 [d]). The maximum in the carbon dioxide concentration, and a second maximum in the carbon monoxide concentration, occur at a burn length of 18 mm. Since the oxygen concentration in this region is still very low (less than 0.5% v/v, Figure 5 [b]), this further production of the oxides in this relatively low temperature region (about 150 to 400°C) must be due to thermal decomposition of the tobacco. Pyrolysis of 1 g of tobacco in a stream of pure nitrogen (3.3 cm³ s⁻¹) and heated at a rate of 1.2°C s⁻¹ confirms that both carbon monoxide and carbon dioxide are produced by direct pyrolysis of the tobacco at 150°–350°C (Figure 9). Further, studies in which a cigarette is smoked in an atmosphere of nitrogen and oxygen-18 (11) have established that about 40% of the carbon dioxide and 53% of the carbon monoxide present in mainstream smoke at the butt of the cigarette are formed by decomposition of the tobacco.

Thus, there are two regions of formation of the oxides of carbon: a high-temperature (400–800°C) combustion region in the coal, and a low-temperature (150–400°C) pyrolysis region behind the coal. In addition, studies in which the tobacco is heated in nitrogen (Figure 9) and compared to the equivalent results when heated in air (9) indicate that about 21% of the carbon monoxide, and 5% of the carbon dioxide produced in the high-temperature region are also formed by pyrolytic reactions.

Figure 9. Production of the oxides of carbon by pyrolysis of 1 g of tobacco in nitrogen.

Transmission of Carbon Monoxide down the Tobacco Rod

Extrapolation of the carbon monoxide decay profile at the back of the coal down to the low-temperature region (Figure 3) indicates that about 50% of the carbon monoxide in the low-temperature region has been transmitted from the high-temperature region. The remainder of the carbon monoxide formed in the coal must escape in the sidestream gases. Due to radial diffusion of carbon monoxide out of the tobacco rod, together with a small contribution from dilution with air entering through the paper, the concentration of carbon monoxide behind the low-temperature region towards the butt falls approximately exponentially.

Formation of Hydrocarbons inside the Burning Cigarette

Figure 6 indicates that the gases methane, ethane, higher hydrocarbons and propene, all have maximum concentrations occurring at about 17–18 mm, corresponding to temperatures around 200°C. The effect on the methane concentration profile of smoking the cigarette in an atmosphere containing 1% nitrogen dioxide is small. Since nitrogen dioxide reacts very rapidly with methyl and other radicals (12, 13), it follows that methane cannot be formed via alkyl radicals. Rather, it would appear that methane is produced as a molecular product by thermal degradation of the tobacco itself.

Of the hydrocarbons determined, ethane is unusual in that some is formed in the high-temperature region, possibly by dimerisation of methyl radicals. However, it was not possible to test this hypothesis by experiments with the cigarette smoked in an atmosphere containing nitrogen dioxide, because of excessive interference to the mass spectrometric peak at m/e 30 (used to monitor ethane) by nitrogen dioxide.

SUMMARY

Measurements have been made of the distribution of temperature and low molecular weight gases within a burning cigarette, using a sampling probe coupled directly to a mass spectrometer (or Bosch carbon monoxide meter).

The interior of the combustion coal is effectively an oxygen-deficient pyrolytic region. The oxides of carbon are produced in two distinct regions: a high-temperature (about 400–800°C) combustion region and a low-temperature (about 150–400°C) pyrolysis region. In the high-temperature coal the carbonised tobacco acts very much as a classical oxidising solid fuel bed of carbon to give the two carbon oxides (and water). In the low-temperature region behind the coal tobacco decomposes to give a substantial proportion of the carbon oxides and a major proportion of the hydrocarbons found in mainstream smoke.

ZUSAMMENFASSUNG

In einer brennenden Cigarette wurde die Verteilung der Temperatur und der niedermolekularen Gase unter Verwendung einer unmittelbar mit einem Massenspektrometer (oder einer Kohlenmonoxid-Meßapparatur von Bosch) gekoppelten Analysensonde gemessen.

Im Inneren des Verkohlungsgebietes befindet sich faktisch eine sauerstoffarme Pyrolysezone. Die Kohlenoxide bilden sich in zwei verschiedenen Regionen: in einer Verbrennungszone mit hohen Temperaturen (etwa 400–800°C) und in einer Pyrolysezone mit niedrigen Temperaturen (etwa 150–400°C). In dem Bereich der Kohle mit hohen Temperaturen wirkt der karbonisierte Tabak in starkem Maße als klassisches festes oxydierendes Medium, in dem sich die beiden Kohlenoxide (und Wasser) bilden. In dem hinter der Kohle befindlichen Bereich niedriger Temperatur finden die Zersetzung des Tabaks und die Bildung eines wesentlichen Anteiles der Kohlenoxide und des Hauptanteiles der Kohlenwasserstoffe des Hauptstromrauches statt.

RESUME

On a procédé à des relevés de distribution de température et de gaz à bas poids moléculaire dans une cigarette brûlante, au moyen d'une sonde reliée directement à un spectromètre de masse (ou un compteur Bosch de monoxyde de carbone).

L'intérieur de la partie de carbonisation est effectivement une région pyrolytique pauvre en oxygène. Les oxydes de carbone proviennent de deux régions distinctes: une région de combustion à haute température (environ 400–800°C) et une région de pyrolyse

de basse température (environ 150–400°C). Dans la partie de carbonisation à haute température, le tabac carbonisé se présente de façon très similaire à un lit classique oxydant de carburant carboné solide, donnant les deux oxydes de carbone (et de l'eau); dans la partie à basse température, derrière le charbon, le tabac se décompose de façon à donner une proportion importante des oxydes de carbone et une majeure partie des hydrocarbures présents dans le flux de fumée principal.

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