DEPENDENCE OF THE GAS PHASE COMPOSITION OF SMOKE ON THE COMBUSTION TEMPERATURE OF TOBACCO PRODUCTS

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On the basis that the measurement of carbon monoxide and carbon dioxide in the gas phase of smoke may be a method of estimating combustion, it was proposed to correlate these parameters with combustion temperatures as measured by the thermocouple technique. A method of determining carbon monoxide, carbon dioxide, oxygen and nitrogen in the gas phase of a single puff is described and the following empirical equation developed:—

$$T = 785\,\gamma^{-0.06}$$

where T = Thermocouple temperature in °C

and $\gamma = \frac{O_2}{N_2} \times \frac{CO_2}{CO}$ measured in volume %

of the gas phase of a single puff.

Several hundred samples have been tested and there is good agreement over the range 750-1000°C; over 80% of the results lying within 10-15°C of the measured thermocouple temperature. These techniques have been used to estimate combustion temperatures of a range of smoking products and the following pattern has been found:—

Pipe tobaccos ∠ hand rolled cigarettes ∠ machine made cigarettes ∠ cigars. The effect of varying rod lengths of products on combustion temperatures, as measured by this technique is also reported.

INTRODUCTION

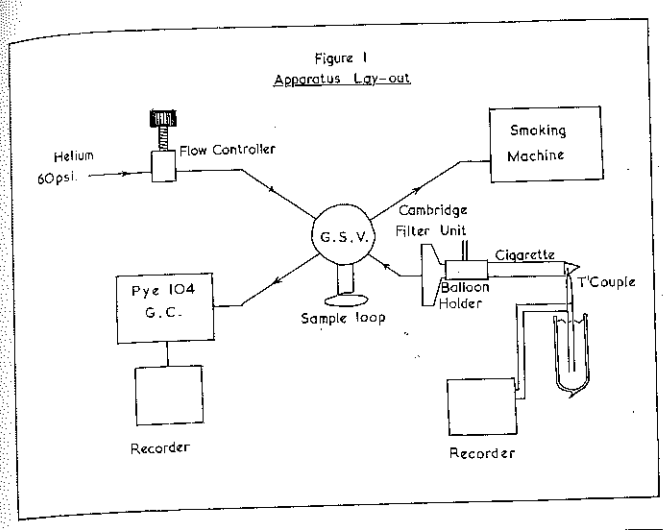
The temperature at which tobacco combusts could be an important factor in determining the quantity and nature of smoke components; for instance the yield of polycyclic hydrocarbons is suggested as being dependent on the combustion temperature (5, 12, 16, 17). As part of a long-term project designed to elucidate the mechanism of the formation of biologically active smoke components, with subsequent modification of tobacco to eliminate these, we were interested in measuring a realistic combustion temperature. The problems of measuring combustion temperatures directly using a thermocouple are well documented (7, 10, 11, 13, 14). Because of these problems and limitations of this technique we decided to follow-up the suggestion made by Wynder (18) that amounts of carbon monoxide and carbon dioxide in smoke could be used to indicate the completeness of tobacco combustion. Since carbon monoxide and carbon dioxide are smoke components it seemed logical to suppose that in addition to being a possible function of degree of combustion, they could be used as a function of combustion temperature. We were therefore particularly interested to see whether there was a correlation between carbon monoxide, carbon dioxide yields and combustion temperature as measured by the thermocouple, so that carbon monoxide and carbon dioxide could be used as a measure of combustion temperature; the latter technique may be more accurate and less open to criticism than thermocouple measurements. Much of the literature on combustion temperature of cigarettes and cigars is misleading since too thick thermocouples have been used to measure the temperature. It is not proposed in this paper to review all the literature and the paper of Adams (1) has already covered this thoroughly.

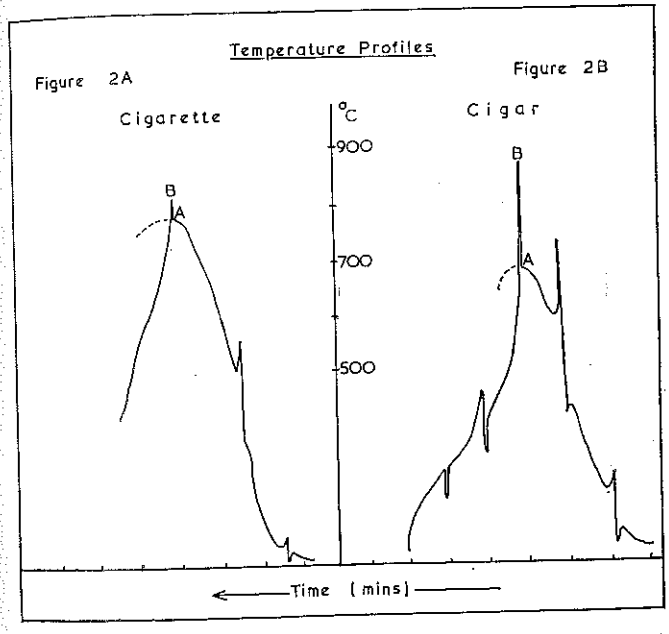
This paper describes the simultaneous determination of oxygen, nitrogen, carbon monoxide, carbon dioxide in smoke by gas chromatography and the measurement of combustion temperature with a thermocouple. An empirical relationship between the gas phase composition and combustion temperature is derived which is valid for pipes, cigarettes and cigars (and even non-tobacco products).

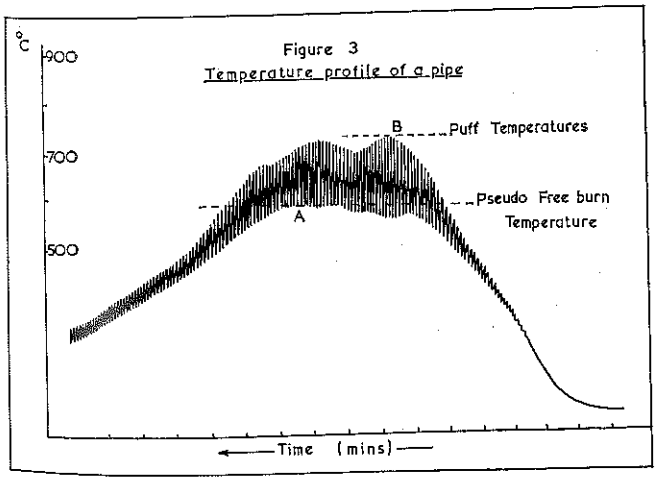
EXPERIMENTAL AND RESULTS

General

The tobacco products investigated were smoked using a single channel smoking machine designed and built in the Gallaher Laboratories. In this instrument the puff volume was accurately maintained by a differential flow controller and the puff duration and timing by an electrically operated timer. The smoking machine and the cigarette, with the thermocouple inserted at the given point were connected by means of a balloon holder to a Cambridge filter unit to remove particulate matter and hence to a 2-way gas sampling valve (**Figure 1**) from which an aliquot of the vapour phase was sampled for analysis by gas solid chromatography for oxygen, nitrogen, carbon monoxide and carbon dioxide (QV). In all experiments using cigarettes and cigars smoking conditions were, 25 ml puff, 2 second duration, 1 puff per minute. For pipes we used the conditions described by Darby and Wilson (3) as they were sufficient to keep the pipe lit. They were, 35 ml puff, 2 second duration, 10 puffs per minute.







TEMPERATURE MEASUREMENTS

Experimental

The thermocouple wires used were supplied by Johnson, Mathey & Co. Ltd., of London, and were made of platinum and platinum: 13% rhodium of 0.002" diameter. The thermocouple junction was made manually by twisting the two wires together to form a junction approximately 2 mm in length. The thermocouple was inserted into the cigarette or cigar by means of a fine sewing needle. The cigarette was then connected to the smoking machine and smoked down towards the position of the thermocouple. In the case of pipes the thermocouple was placed at the centre of the pipe bowl. The wires from the junction were led downwards from the centre to the side of the bowl and then upwards along the edge and over the top of the bowl so that the leads were not subjected to high temperatures.

When the thermocouple was inserted into the cigarette, difficulty arose in making the cigarette puff at the exact time when the junction was in the free burning cone of the cigarette. The most practical way of overcoming this was to stop the smoking machine as the cone approached the junction, allowing the cigarette to free burn until the cone was just about to pass through the thermocouple position, then restarting the smoking machine and taking a puff so that the regression of the cone passes through this junction during the particular puff. We do not believe that this significantly influenced the burning characteristics of the cigarette.

Five readings were taken, the mean of which was taken as the thermocouple temperature and is quoted in subsequent sections.

Results

Typical temperature profiles for a cigarette and cigar are given in **Figures 2A** and **2B**. When the thermocouple temperature reached a maximum (i.e. Point A) this corresponded to the free burning temperature of the product. On puffing at this point a "spike" was produced giving a puff temperature (i.e. Point B). For normal flue cured cigarettes free burn temperatures were usually in the range 780-810°C, and puff temperatures 800-840°C, hence this gave a spike of 20-40°C, (i.e. the difference between free burn and puff temperatures).

However, cigars had much lower free burn temperatures 650-750°C and much higher puff temperatures i.e. 850°C-950°C. This resulted in a large spike i.e. 100-250°C.

Figure 3 gives a typical temperature profile of pipe tobacco in a pipe. The shape of the profile is completely different to that of the cigarette or cigar due to the different smoking conditions used. The top of the zigzag line represents the puff temperature while the bottom of the zigzag line we have termed the "pseudo free burn temperature." If the smoking machine is shut off completely the pipe goes out immediately, hence in reality pipes have no free burn temperature.

Figure 4 shows the relative temperature ranges of pipes, hand rolled cigarettes, machine made cigarettes and cigars.

GAS ANALYSIS

Experimental

The analysis of the vapour phase of smoke for oxygen, nitrogen, carbon monoxide, carbon dioxide, was achieved by gas solid chromatography, using a Pye Model 44 Chromatograph equipped with a heated Katharometer Detector. The gases were separated using columns of silica gel and Linde molecular sieve 5A in series, with one arm of the detector at the exit to each column. Column 1 containing activated silica gel separated carbon dioxide from the rest of the smoke vapor phase. The 2 peaks were measured by Arm I of the detector. On passing into column 2 containing the molecular sieve the carbon dioxide was absorbed but the remainder of the gaseous phase was separated in the order—oxygen, nitrogen, methane and carbon monoxide and these were measured by

Arm II of the detector. All the organic compounds were retained in one or other of the columns and did not interfere with the chromatograms.

The chromatograms were recorded on a Honeywell Electronic 15 Potentiometric Recorder (−0.1 to + 1.0 mV). The experimental procedure was as follows: A puff was taken so that the cone regressed through the thermocouple wires during that puff as described above. At the exact moment when that puff ceased the gas sampling valve was turned to inject a 1 ml. aliquot of the vapour phase of smoke into the gas chromatograph for analysis. The gas sampling valve was turned back to its original position after 30 seconds in readiness for the next sample.

Five readings were taken for each sample the mean of which was taken as the gas analysis subsequently quoted in Sub-Sections. The gas chromatograph was calibrated for each component by introducing known volumes of air, carbon monoxide and carbon dioxide via the gas sampling valve.

Columns were reconditioned at regular intervals by heating the Silica Gel column to 220°C and the molecular sieve column to 400°C for 16 hours in a stream of helium.

Results

Table 1 shows the gas analysis for a wide range of tobacco products (and one non-tobacco product). For pipe smoke, the carbon monoxide value is very low at approximately 1% by volume but carbon dioxide is higher at 6%. This produces a very low carbon monoxide/dioxide ratio. The oxygen value however, is high i.e. 13-14%.

Cigarettes produce greater amounts of carbon monoxide and carbon dioxide i.e. 4-7% and 11-14% respectively. Oxygen values on the other hand are at 9%, much lower than that for pipes. Cigars produced the greatest amounts of carbon monoxide and carbon dioxide i.e. 9-13% and 16-18% respectively. Carbon monoxide/dioxide ratios for cigars are also high i.e. 0.6-0.8 compared to cigarettes of 0.3-0.5. Oxygen values for cigars are much lower than for cigarettes or pipes i.e. 3-5% which in turn produces very low oxygen/nitrogen ratios. Hand rolled cigarettes produce an inorganic gas phase composition intermediate between that of pipes and machine made commercial cigarettes, while that of liquorice paper cigarettes lies between cigarettes and cigars. (The rayon filter rod has a carbon monoxide value similar to that of cigar but the carbon dioxide level is much lower producing a very high carbon monoxide/dioxide ratio).

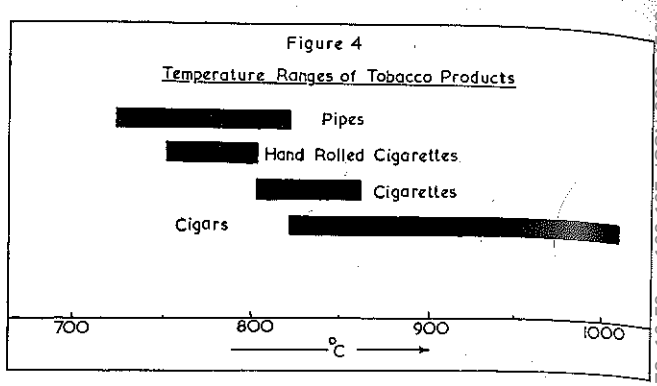
Correlation of gas phase and thermocouple combustion temperatures

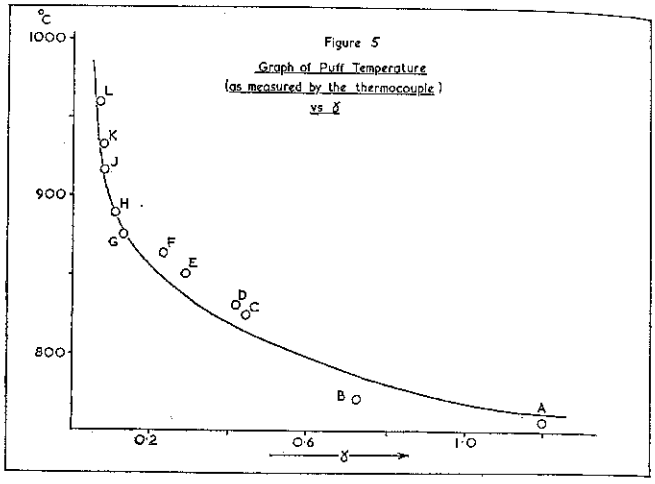
As stated before the object of this work was to attempt to correlate carbon monoxide and carbon dioxide with combustion temperatures. The carbon monoxide values in Table 1 show a general increase with increasing thermocouple puff temperatures. Carbon dioxide values on the other hand do not show as clear a trend with considerable fluctuations. Carbon monoxide/dioxide ratios which could also be considered as a measure of combustion temperatures were also subject to considerable variations between different products (not shown in that table).

We then considered the other components measured by the gas chromatograph, i.e. oxygen and nitrogen. As thermocouple temperatures increase, oxygen values as expected decrease. However, the values were subject to the same variations as those of carbon dioxide. Nitrogen values too show a general decrease but this is probably due to the large increases in carbon monoxide and carbon dioxide. The ratio of oxygen and nitrogen was studied, but again there were some fluctuations. The most promising method was to take a ratio of the oxygen/nitrogen and carbon monoxide/dioxide ratios, this factor we call δ-(Gamma) for simplicity, i.e.—

$$\delta = \frac{\text{oxygen/nitrogen}}{CO/CO_2} \text{ In volume \%}$$

Using over 100 samples and taking the mean of 5 thermocouple and 5 gas phase analysis figures for each point, a graph was plotted to establish a correlation between δ and the thermocouple puff temperature (**Figure 5**). The approximate statistically calculated mathematical relationship of this graph is—





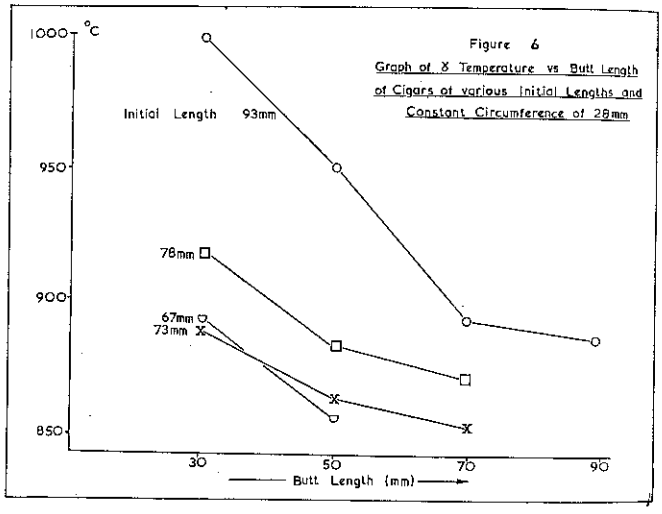


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Table 1. Preliminary comparison of three analytical methods for TDE and DDT in tobacco

Table 1. Combustion temperature and gas analysis for a wide range of tobacco products

Sample	Length (mm)	Butt Length (mm)	Percentage Volumes CO	CO_2	O_2	N_2	CO/CO_2	O_2/N_2	δ	Temp °C T'CFB	T'C Puff	Puff
A Pipe	—	—	0.9	6.0	13.3	74.0	0.15	0.18	1.2	636	752	756
B Hand Roll Cigarette	70	40	1.9	6.9	14.3	71.7	0.28	0.20	0.73	620	770	789
C Cigarette (Filter)	84	50	4.6	13.6	9.9	65.8	0.34	0.15	0.44	787	824	819
D " (Plain)	70	40	4.7	12.9	9.8	65.4	0.36	0.15	0.42	790	830	820
E " (Filter)	72	40	6.3	13.0	9.2	67.0	0.48	0.14	0.29	785	850	847
F Liquorice Paper	80	45	7.2	12.2	8.6	63.6	0.59	0.14	0.23	770	862	862
G Cigar	82	50	9.7	16.7	4.1	56.0	0.58	0.07	0.13	680	875	895
H "	96	60	11.5	16.0	4.2	54.0	0.72	0.08	0.11	600	890	895
J "	77	45	12.7	15.5	3.5	51.8	0.82	0.07	0.08	680	917	930
K Cigarillo	83	40	13.3	15.8	4.0	56.5	0.84	0.07	0.08	748	932	919
L Rayon Filter Rod	90	50	13.0	10.7	5.2	66.5	1.17	0.08	0.07	650	958	940

$$T = 785\ \delta^{-0.06}$$

Where T = thermocouple puff temperature in degrees centrigrade. A statistical analysis of this formula also showed that we could predict combustion temperatures of a product using the mean of 5δ determinations with an accuracy of approximately $\pm$ 10°C with 95% confidence. This is far better than one can expect from a similar number of thermocouple measurements. Hence we feel that this method of temperature measurement is less tedious and more dependable than thermocouple measurements.

At this point several important factors should be considered Egerton et al (4) have shown that cigarettes burn more at the outer annulus of the cone, than at the cone tip on puffing: during the free burn time equilibrium is restored by the cone tip regressing at a faster rate than the periphery. This would suggest that during the puff the main stream carbon monoxide and carbon dioxide originate in this annular region and not at the center of the cone where the thermocouple is placed.

Also Baxter and Hobbs (2) have shown that only 60% of the carbon dioxide and 47% of the carbon monoxide are derived from the oxidation of carbon in the glowing cone. Experiments carried out recently in these laboratories using pyrolysis techniques have indeed shown that considerable amounts of carbon dioxide are evolved from tobacco at temperatures far below those in the burning cone of a cigarette. From these observations it would follow that the thermocouple is placed at a point from which a large part of the gas phase of cigarette smoke does not originate, so it could be that this relationship is somewhat fortuitous. Although we cannot explain the reason for the relationship, we have found this correlation workable and it is now used for all our temperature measurements instead of the thermocouple.

Egerton et al found transient puff temperatures of 1,000-1,200°C in this annular region using radiation pyrometers. Adams (1) too using extremely fine thermocouple wires was able to detect very high puff temperatures of 1,050°C occasionally. From Adams' results it would appear that such temperatures are only transient, otherwise the cigarette would probably burst into flames on puffing. These higher transient temperatures would be recorded when a sensitive thermocouple happens to be placed in that discrete position where the transient effect occurs. We therefore believe that our own temperatures which incidentally agree with those of Kobashi (7), and Touey and Mumpower (14) are realistic in that they give a measure of the mean temperature for the whole cone during puffing.

Table 2. Combustion temperatures and gas analysis of different tobacco products at various butt lengths

Sample	Length (mm)	Butt Length (mm)	Percentage Volumes CO	CO_2	O_2	N_2	δ	Temps °C T'CFB	T'C Puff	δ Puff
C CIGARETTE filtered	84	80	2.1	7.0	16.2	71.8	0.75	782	808	787
		55	3.4	10.8	12.9	69.1	0.59	788	812	802
		25	5.8	16.3	6.9	62.5	0.31	794	835	834
D CIGARETTE plain	70	55	3.9	11.5	11.8	67.1	0.52	785	824	807
		25	5.5	14.3	7.8	63.6	0.32	796	835	832
H CIGAR panatella	106	90	6.9	15.4	8.1	64.6	0.28	581	812	838
		70	10.8	17.4	4.6	60.7	0.12	615	870	888
		50	11.4	18.2	3.7	58.9	0.10	607	890	901
J CIGAR	75	30	12.7	19.0	2.8	56.9	0.07	585	894	930
		65	12.2	15.3	4.0	52.4	0.10	682	882	905
		45	12.7	15.4	3.4	51.6	0.08	673	913	918
		25	13.2	15.8	2.9	50.3	0.07	675	952	934

Application of graph

Variations of δ Temperature with Butt Length of Cigarettes

All samples tested to date have shown that combustion temperatures are dependent on butt length. As the butt length decreases, thermocouple puff temperatures increase. This is accompanied by an increase in carbon monoxide and carbon dioxide and a decrease in oxygen and nitrogen. The results of this are a decrease in δ and hence an increase in puff temperatures. **Table 2** gives results for several samples of cigarettes and cigars.

In cigarettes this increase is only 20-30°C but in the case of cigars the range can be as great as 150°C. Carbon monoxide and oxygen values show the greatest changes whereas carbon dioxide and nitrogen only exhibit small changes. In general free burn temperatures tend to increase also with decreasing butt length.

Touey and Mumpower (14) using a similar thermocouple to our own found that temperatures did not vary with the length of the cigarette, but Pyriki (11) found that with long cigarettes there was a slight increase in temperatures with decreasing butt length. Although our thermocouple results do show up this butt length effect we feel that the gas analysis is more sensititive to such small variations and hence more useful. Reasons for this increase in combustion temperature with decreasing butt length may be complex. Jarrell et al (6) and Newsome and Keith (9) have shown that there is considerable dilution of the gas phase by air entering through the cigarette paper. As the cigarette burns down the area of paper decreases and hence less air can enter through the paper and more enters through the cone. Thus combustion temperatures may be increased slightly.

Variation of Temperature with Length and butt length of Cigars

As shown above, temperatures of a cigarette vary by 20-30°C along its length but in cigars this range is much greater i.e. 100°C (**Table 2**). The temp. range of cigars in general is much greater i.e. 850-1000°C, than for cigarettes 800-840°C. However, it has also been found that the longer the cigar the higher the combustion temperature at the same butt length (see **Figure 6**). Four cigars were chosen with