Effect of Cigarette Circumference on Formation Rates of various Components in Mainstream Smoke *

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SUMMARY

Using cigarettes of different circumference but a constant packing density, the effect of circumference on the rate of formation (ratio of total delivery to the weight loss of tobacco during puffs) of various components was investigated. The rates of formation of CO and HCN increased and that of B[a]P decreased with decreasing circumference, while those of CO₂, NO and vapour phase CH₃CHO were independent of circumference. The differences in the effect of circumference on the rate of formation of CO, B[a]P and HCN can be explained by differences in their thermal formation during puffs.

RESUME

En utilisant des cigarettes de même densité de remplissage mais de diamètres différents, on a étudié l'effet du diamètre de la cigarette sur le taux de formation (rendement total par rapport à la perte de poids du tabac pendant les bouffées) de différents composés. Lorsque le diamètre diminue, il se forme davantage de CO et de HCN et moins de B[a]P tandis que les quantités de CO₂, NO et de CH₃CHO contenues dans la phase gazeuse sont indépendantes des modifications que subit le diamètre. Les différences observées en ce qui concerne la formation de CO, B[a]P et HCN peuvent s'expliquer par le fait que les divers composés sont produits pendant les bouffées par des processus thermiques différents.

ZUSAMMENFASSUNG

Unter Verwendung von Zigaretten gleicher Füllichte und verschiedenen Umfangs wurde untersucht, inwieweit die Bildung einiger Rauchinhaltsstoffe (d. h. die Gesamtausbeute im Verhältnis zum Gewichtsverlust des Tabaks während der Züge) quantitativ durch den Zigarettenumfang beeinflusst wird. Verringerte sich der Umfang, so bildete sich mehr CO und HCN und weniger B[a]P, während die Mengen an CO₂, NO und an in der Gasphase befindlichem CH₃CHO von Veränderungen des Umfangs unabhängig waren. Die bei der Bildung von CO, B[a]P und HCN zu beobachtende unterschiedliche Einwirkung des Umfangs könnte damit erklärt werden, daß die einzelnen Verbindungen während der Züge durch verschiedenartige thermische Prozesse entstehen.

INTRODUCTION

In the previous paper, it was reported that the total delivery of tar and nicotine (i.e. the sum of the amount in mainstream smoke and that trapped on the filter and the tobacco column) changed proportionally with the loss in weight of the tobacco during puffs (1). This finding implies that the rate of formation (i.e. the ratio of total delivery to weight loss of tobacco during puffs) is independent of the circumference of the cigarette. Since the weight loss during puffs was proportional to the cross-sectional area of a cigarette with a constant packing density, it became possible to estimate the amount of tar and nicotine in mainstream smoke from the weight per unit length of cigarettes with different circumferences.

The rate of formation of a smoke component during a puff is an important factor in estimating the amount of

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Table 1.
Physical variables of tobacco columns and acetate filters.

Circumference (mm)	Tobacco column (65 mm)		Filter (20 mm)		
	Weight (g)	Pressure drop (mm H ₂ O)	Weight (g)	Pressure drop (mm H ₂ O)	Fractional volume
21.1	0.682 ± 0.01	79.9 ± 3	93.7	66 ± 2	0.087
22.9	0.797 ± 0.01	66.4 ± 3	117.6	66 ± 2	0.093
25.0	0.948 ± 0.01	53.9 ± 3	149.2	66 ± 2	0.101
25.8	1.010 ± 0.01	50.5 ± 3	164.0	66 ± 2	0.103

Packing density of each tobacco column is 0.281 g/cm³.

that component in mainstream smoke. The present paper describes the effect of circumference on the rate of formation of carbon oxide (CO, CO₂), nitric oxide (NO), vapour phase acetaldehyde (v.p. CH₃CHO), benzo[*a*]pyrene (B[*a*]P), and hydrogen cyanide (HCN), which will be discussed in relation to differences in their thermal formation during puffs.

MATERIALS AND METHODS

Cigarette Samples

The cigarettes used were of a Virginia blend type and were the same as those used in the previous study (1). The physical variables of the tobacco column and the acetate filter (2 cm length) are shown in Table 1. The sample cigarettes were smoked, their weight and pressure drop measured and their smoke components analyzed at 22 °C and 60% relative humidity.

Determination of Smoke Components

Cigarettes were smoked on a smoking machine (Filtrona, model 302) under standard smoking conditions. The total particulate matter (TPM) was trapped on a Cambridge filter pad and the gas phase, which passed through the filter pad, was collected in a bag. The gas phase was introduced into a non-dispersive infrared analyzer, and the concentrations of CO and CO₂ were measured. Vapour phase CH₃CHO was determined by gas chromatography, as reported previously (2). The NO_x concentration in the mainstream smoke was determined on a chemiluminescence analyzer (Yanaco, ECL-77(v) type). Since the NO_x in mainstream smoke is almost all nitric oxide (NO), hereafter NO_x will be referred to simply as NO. The amount of B[*a*]P in the TPM trapped on the Cambridge filter pad was measured by means of fluorescence HPLC with a Nucleosil® 7C₁₈ column (Macherey-Nagel) using benzo[*k*]fluoranthene as internal standard (3).

HCN in mainstream smoke, in both the vapour and the particulate phases, was trapped in 75 ml of a 0.5% NaOH solution. An aliquot of the solution was mixed

with an equal amount of isoamyl alcohol. After being shaken, the mixture separated into two portions: an NaOH solution containing HCN and an isoamyl alcohol solution containing substances which prevent analysis. The concentration of HCN in the solution was colorimetrically determined by the pyridine-pyrazolone method (4).

Total Deliveries of Smoke Components

Total deliveries of the gas components CO, CO₂ and NO were determined by considering the loss due to diffusion through the cigarette paper. Generally, the equation $C_1 = C_0 e^{-D_i L}$ has been used when the linear gas velocity in a cigarette with ordinary cigarette paper can be considered constant (5–8), where C_0 and C_1 are the concentrations of the gas at the inlet and outlet of the cigarette, respectively, L is the length of cigarette in contact with the air, and D_i is the coefficient of diffusion per unit length of the cigarette. In the present experiment, a cigarette was puffed when the normal cone was formed after ignition. After some static burn, the cigarette was again puffed. This procedure was repeated four times per cigarette. The length of the butt in contact with the air after completion of each puff was measured with a vernier caliper. The concentrations of CO, CO₂ and NO corresponding to each puff were measured. As a typical example, the relationship between the logarithmic values of the concentration of components in the gas and the length of the butt (L) is shown in Figure 1. From the linear relationship between them, equation $C_1 = C_0 e^{-D_i L}$ was verified for cigarettes of each circumference. The concentration of components in the gas formed during a puff (C_0) was obtained from the intercept of each regression line. Strictly speaking, the amount of components in the gas during a puff (C_p) which is calculated from C_0 is not considered to be quite constant as burning progresses, even in a cigarette with ordinary cigarette paper, because of a slight difference in the air inflow through the burning cone during a puff and the combustion of TPM accumulated on the tobacco of the butt. However, the values of C_0 and C_p can be regarded as average values per puff. Therefore, the total delivery of gas compo-

Figure 1.

A typical relationship between the logarithmic value of gas concentration and the butt length in contact with air (cigarette circumference: 25 mm).

nents per cigarette can be expressed as nC_p , where n is the puff count. The total delivery of vapour phase CH_3CHO was considered to be almost equal to that in the mainstream smoke, because, in the vapour phase, it neither diffuses through the cigarette paper nor is retained by the filter. The total delivery of $B[a]P$ was obtained from the sum of the amount in the mainstream smoke and that retained by the filter which was measured directly. The total delivery of HCN was taken to be the same as that in the mainstream smoke of a non-filter cigarette which was smoked up to a butt length of 1 cm. In that case, the amount of HCN retained by the tobacco column could be ignored, because the retention of HCN in the particulate phase by the tobacco column was very small.

RESULTS AND DISCUSSIONS

Amount of Components in Mainstream Smoke

Figure 2 shows the amounts of CO , CO_2 , NO and vapour phase CH_3CHO in mainstream smoke. With increasing circumference, each component increased. In the range from 21 mm to 26 mm, the increase was about 20% for CO , 40% for CO_2 , 43% for NO and 57% for vapour phase CH_3CHO . On the other hand,

Figure 2.

The amounts of CO , CO_2 , NO and vapour phase CH_3CHO in mainstream smoke vs. cigarette circumference.

* (value determined) $\times 10$

as shown in Figure 3, the effect of circumference on the amounts of $B[a]P$ and HCN was found to be different from that on the components shown in Figure 2. With increasing circumference, not only did the amount of $B[a]P$ increase, but the rate of increase also became higher. The amount of HCN was almost constant, not depending on changes in circumference. To clarify the reason for these different patterns, the following experiments were carried out.

Total Deliveries of Smoke Components

Table 2 shows the amounts of CO , CO_2 and NO formed during a puff (C_p), which were derived from C_0 . The total deliveries of these gas components can be expressed as nC_p , where n is the puff count. The total delivery of vapour phase CH_3CHO is almost equal to that in the mainstream smoke as described in the section Materials and Methods. Figures 4 and 5 show the total deliveries of these gas components (nC_p), and those of $B[a]P$ and HCN vs. the weight loss of tobacco during puffs which can be expressed as nW_p , where W_p is the weight loss during one puff (1). The total delivery of tar and nW_p were already reported to be proportional to the square of the radius of a cigarette (1). The total deliveries of CO_2 , NO and vapour phase

Table 2.
Concentration and amount of gas components during a puff.

Circumference (mm)	Concentration of gas formed during a puff (C_0)			Amount of gas formed during a puff (C_p)		
	CO (%)	CO ₂ (%)	NO (ppm)	CO (mg)	CO ₂ (mg)	NO (μ g)
21.1	6.20	10.88	489.4	2.51	6.92	21.22
22.9	6.15	12.10	504.7	2.49	7.70	21.89
25.0	6.67	12.87	574.0	2.70	8.19	24.89
25.8	6.68	13.40	595.8	2.70	8.52	25.84

Figure 3.
The amounts of B[a]P and HCN in mainstream smoke vs. cigarette circumference.

Figure 4.
Total delivery of CO, CO₂, NO and vapour phase CH₃CHO vs. weight loss of tobacco during puffs.

* (value determined) $\times 10$

Figure 5.
Total delivery of B[a]P, HCN and tar vs. weight loss of tobacco during puffs.

Table 3.
Effect of cigarette circumference on the diffusion of gas components.

Circumference (mm)	Amount lost through diffusion			Diffusion rate		
	CO (mg/cig.)	CO ₂ (mg/cig.)	NO (μg/cig.)	CO (%)	CO ₂ (%)	NO (%)
21.1	4.24	11.10	39.81	19.9	18.9	22.1
22.9	6.14	20.20	40.99	25.4	27.0	19.7
25.0	7.60	22.56	66.69	27.1	26.5	26.3
25.8	8.93	27.07	76.03	30.1	28.9	27.5

CH₃CHO were found to be proportional to nW_p (Figure 4). The plot of CO did not fall on a straight line passing through the origin, showing that the rate of increase decreased slightly with increasing nW_p . As shown in Figure 5, the total deliveries of B[a]P and HCN were not proportional to nW_p , i.e. the rate of change in B[a]P became greater and that of HCN lower with increasing nW_p .

From the total delivery of gas components and the amount in the mainstream smoke, the loss through diffusion from the cigarette paper was estimated. These data are shown in Table 3. The amount lost through diffusion increased with increasing circumference. The diffusion rate, which was calculated from the ratio of the amount lost through diffusion to the total delivery, also increased with increasing circumference. The diffusion rate of NO remained almost equal to that of CO for the various circumferences.

Figure 6 shows a decrease in the retention of B[a]P and HCN by the filter with decreasing circumference. The retention of these components was lower than that of tar obtained from the same cigarette samples (1). The decrease in HCN retention with decreasing circumference was sharper than that for tar or B[a]P. It is well known that HCN formed during puffs is distributed in both the vapour and particulate phases (9, 10). The sharp decrease in HCN retention is thought to be a result of a decrease in the condensation of gaseous HCN which, in turn, is due to an increase in the velocity of air in the tobacco filter when the circumference is reduced.

Formation Rate of Smoke Components

Figures 4 and 5 show the difference in the effect of circumference on the rates of formation of these components, since the gradient at each point corresponds to the formation rate. The rates of formation of CO₂, NO and vapour phase CH₃CHO, as well as tar, were found to be almost constant and independent of circumference. On the other hand, the rate of formation of CO increased slightly, HCN increased considerably, and B[a]P decreased with decreasing circumference. The results can be attributed to the difference in the formation mechanisms of these components during puffs. NO and vapour phase CH₃CHO in mainstream smoke

are mostly formed from the thermal decomposition of tobacco during puffs, the former from nitrate (11–14), the latter from skeleton substances such as cellulose (15–17). The independence of circumference of the rates of formation of NO and vapour phase CH₃CHO can be explained by the fact that formation of these components by thermal decomposition occurs in the range of temperatures below about 400 °C, which coincides with the loss in weight of the tobacco. The independence of the rate of formation of CO₂ of circumference seems to be due to the fact that CO₂ is a primary product formed by both thermal decomposition and combustion of tobacco, and that an endothermic reduction of CO₂ to CO occurs in the range of combustion temperatures.

The formation of HCN from nitrogen substances, such as protein, amino acids and nitrate, is known to be promoted by an increase in temperature (18, 19). With increasing combustion temperature, the ratio of CO to CO₂ becomes higher owing to enhancement of the carbonaceous reduction of CO₂ to CO (20–23), and to higher activation energy for CO formation than that

Figure 6.
Effect of circumference on retention of tar, B[a]P and HCN by the filter.

Figure 7.

Effect of circumference on total delivery of CO/CO₂.

for CO₂ formation in oxidative reaction (21, 22). In the present experiment, the ratio of total delivery of CO to that of CO₂ increased with decreasing circumference (Figure 7). This is thought to be caused by the following phenomenon: with decreasing circumference the ratio of air inflow through the burning cone to the amount of tobacco consumed during a puff becomes higher, because the weight loss of tobacco during a puff changes proportionally with circumference (1). Consequently, it seems reasonable to conclude that the increase in the rate of formation of CO and HCN resulted from an increase in the combustion temperature due to a decrease in circumference. In addition, there seems to be some connection between the rate of formation of B[a]P and the combustion temperature. An increase in the concentration of B[a]P (the ratio of B[a]P to tar) has been found in cigarettes with a vented filter (24). Increasing the ventilation of a cigarette can reduce the maximum solid-phase temperature at the base of the cone (20, 25), and decrease the ratio of CO to CO₂ (22, 26). Hence, the increase in the formation rate for B[a]P is thought to be due to a decrease in the temperature of the burning cone during puffs. From these results and discussion, we can ascribe the reason for differences in the effect of circumference between the amounts of B[a]P and HCN in the mainstream smoke (Figure 3) to distinction in their formation rate during puffs and retention by the filter. The increase in the amount of B[a]P in mainstream smoke as well as its ascending rate of change with increasing circumference can be explained by an increase in the rate of formation which results in a sharp increase in total delivery. The almost constant amount of HCN in mainstream smoke in the range from 21 mm to 26 mm of circumference can be explained by a sharp decrease in retention by the filter and an increase in the rate of formation of HCN with decreasing circumference.

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