Effect of Chemical Constituents on the Formation Rate of Carbon Monoxide in Bright Tobacco*

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SUMMARY

From cigarettes made of different bright tobaccos but with a constant fractional volume, the following results were obtained. The rate of formation of CO was a more influential factor determining the amount of CO in mainstream smoke than the weight loss of the cigarette during puffs. From a stepwise multiple regression analysis it was found that the rate of formation of CO was mainly dependent on the potassium content of the tobacco and could be estimated from the amounts of potassium, total carbon, and lignin. The rate of formation of CO increased with a rise in combustion temperature, which in turn rose as the potassium content of the tobacco decreased.

ZUSAMMENFASSUNG

Eine Untersuchung von Zigaretten mit einem konstanten Anteil an verschiedenen hellen Tabaksorten erbrachte folgende Ergebnisse: Die Geschwindigkeit der Bildung von Kohlenmonoxid hatte einen größeren Einfluß auf die im Hauptstromrauch enthaltene Menge an Kohlenmonoxid als der Gewichtsschwund der Zigarette während der Rauchzüge. Eine stufenweise durchgeführte multiple Regressionsanalyse ergab, daß die Geschwindigkeit der Kohlenmonoxidbildung vor allem eine Funktion der im Tabak enthaltenen Kaliummenge ist und sich aus den Kalium-, Gesamtkohlenstoff- und Ligningehalten abschätzen läßt. Die Geschwindigkeit der Bildung von Kohlenmonoxid erhöhte sich mit ansteigender Verbrennungstemperatur, welche wiederum mit abnehmendem Kaliumgehalt des Tabaks zunahm.

RESUME

Une étude effectuée sur des cigarettes ayant une proportion constante de différentes variétés de tabac blond a conduit aux résultats suivants: la quantité de monoxyde de carbone contenue dans la fumée du courant principal dépend davantage de la vitesse de formation du monoxyde de carbone que de la diminution de poids de la cigarette pendant les bouffées. Une analyse de régression multiple réalisée par étapes a montré que la vitesse de formation du monoxyde de carbone était avant tout fonction de la quantité de potassium contenue dans le tabac et qu'il était possible de l'estimer à partir des teneurs en potassium, carbone total et lignine. La vitesse de formation du monoxyde de carbone augmente avec la température de combustion laquelle s'élève lorsque la teneur en potassium diminue.

INTRODUCTION

It is well known that the amount of carbon monoxide in mainstream smoke decreases as the ventilation of the filter and the permeability of the cigarette paper increase (1, 2). As for the effect of the kind of tobacco on CO delivery, several investigations have been carried out with cigarettes made of various tobaccos which differed with respect to cultivar and stalk position (3–5), and correlations were demonstrated between the smoke components, including CO, and various chemical constituents of the tobaccos (6). However, there has as yet been no report on the interrelation between the amount of CO in mainstream smoke, the chemical constituents of the tobaccos, and the burning characteristics, i.e. the rate of formation of CO (the ratio of CO delivery to the weight loss of tobacco during puffs)

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and the amount of tobacco consumed during puffs. The amount of CO in mainstream smoke (A) can be expressed by the following equation:

$$A \text{ [mg/cig.]} = n W_p F D ,$$

where n is the puff count, W_p is the weight loss during a puff, F is the rate of formation of CO, and D is a factor relating to the loss of CO through the cigarette paper by diffusion. The product of n and W_p , nW_p , is regarded as the quantity of tobacco burned during n puffs, and F as a qualitative factor concerning the burning of tobacco during a puff. D is considered to be constant under standard smoking conditions when the lengths of the cigarettes in contact with air are constant (7–9).

We investigated the importance of the rate of formation of CO for the amount of CO in mainstream smoke and the effect of chemical constituents on the rate of formation of CO.

EXPERIMENTAL

Cigarette Samples

Unblended non-filter cigarettes were made of the leaf and cutter of five kinds of bright tobacco cultivars. The width of the cut shreds was 0.8 mm, and ordinary cigarette paper (permeability: about 10 ml/cm²/min/100 mm w.g.) was used. The length and circumference of the cigarette were 70 mm and 25 mm, respectively. After conditioning at 22 °C and 60% relative humidity, cigarettes were selected at the weight and pressure drop shown in Table 1. The weight of each sample was selected to keep the fractional volume of the cigarette constant (0.30). The apparent density of the shreds, which was necessary for deciding the fractional volume, was measured by a mercury displacement method (10).

Table 1.
Weight and pressure drop of cigarette samples.

Tobacco	Weight (g)	Pressure drop (mm w.g.)
A Cutter	0.939	51–56
	0.963	38–43
B Cutter	0.872	32–34
	0.924	28–30
C Cutter	0.901	31–33
	1.001	28–30
D Cutter	0.909	65–71
	0.926	40–45
E Cutter	0.834	58–64
	0.929	34–36

Fractional volume of cigarettes : 0.30.

Smoking Conditions and Measurement of Formation Rates of CO and CO₂

The cigarettes were smoked to a 30 mm butt length on a smoking machine (Filtrona, model 302) under standard smoking conditions. The methods of determining the amount of tar and carbon oxides in the mainstream smoke were the same as those in previous studies (9, 11). The weight loss of a cigarette and the delivery of carbon oxides during a puff were measured simultaneously with the shortened tobacco column as reported previously (11, 23). In this case, the delivery of carbon oxides can be regarded as the amount formed during a puff, because the loss through the cigarette paper by diffusion is negligible. Therefore, the rates of formation of CO and CO₂ were obtained from dividing the weight of CO and CO₂ in the mainstream smoke during a puff by W_p measured on the shortened tobacco column, respectively.

Measurement of Peak Temperature

All temperature measurements were made with a Pt/Pt(87%)-Rh(13%) thermocouple of 0.05 mm in diameter. Two thermocouples were inserted perpendicular to the longitudinal axis of a cigarette at points 15 mm and 25 mm from the front end so that the thermocouple junctions were located at the center of a cross section of the cigarette (13). After ignition, the electromotive force was recorded. When the paper burn line of static burn reached the first thermocouple, the temperature increased to the range of 640 °C–680 °C. At this point, one puff was taken by a syringe-type smoking machine which draws 35 ml of air over a period of two seconds. The same procedure was carried out when the paper burn line reached the second thermocouple. From twelve preliminary tests the coefficient of variation of the peak temperature measured during a puff was found to be less than 5%. Generally, the temperature of the gas phase is measured by a thermocouple, and that of the solid phase by an infrared probe. The two phases are in near equilibrium in the period between puffs. During a puff, the two phases have very different temperature distribution near the surface of the burning cone. However, they are similar in the central region, where the temperature of the gas phase is highest (14–16). Therefore, the peak temperature measured by the present method can be regarded as an index which is representative of the combustion temperature of the burning cone during a puff.

Analysis of Chemical Constituents of Tobacco

After being powdered in a mill, all the tobacco samples were analyzed by the following conventional method. Total carbon was determined by a CHN recorder (Yanaco, MT-2 type), and water-soluble sugars by a colorimetric procedure involving a Technicon AutoAn-

alyzer. The ethanol-benzene(1:2)-soluble portion was extracted from 5 g of tobacco powder for 48 h in a Soxhlet extractor. Then the portion of the residue soluble in hot water was extracted, and the remaining insoluble portion was regarded as cell-wall substances. The lignin content was obtained from the weight of the insoluble residue after hydrolysis of the cell-wall substances with 72% H_2SO_4 . The cell-wall substances were put through the extractor separately using 0.05 M EDTA- Na_2 (pH 4.5). The amount of pectin in the extract was calculated from the galacturonic acid content, which was determined colorimetrically. The insoluble fraction was treated with glacial acetic acid and sodium chlorite to remove lignin; holocellulose was obtained as the residue. Hexane extracts were determined gravimetrically after the desiccation of substances extracted with *n*-hexane for 40 h in a Soxhlet extractor. The nicotine content was determined by spectrophotometric analysis of the steam distillate. To determine the potassium content, 1 g of tobacco powder was stirred in 100 ml of 2 N ammonium acetate solution (pH 6.9–7.1) containing 0.2 N magnesium acetate. The amount of potassium in an aliquot of filtered solution was determined by flame photometry using a Technicon AutoAnalyzer.

Multiple Regression Analysis

A stepwise multiple regression analysis was performed with a BMDP program on a Digital Equipment Corporation (DEC) VAX 11 computer using the RS/1 system (BBN Software Products Corp.).

RESULTS AND DISCUSSION

Burning Characteristics and Smoke Components

The amounts of CO, CO_2 and tar in the mainstream smoke and the burning characteristics measured with the shortened tobacco column are shown in Tables 2 and 3, respectively. As shown in Table 3, large variations were observed in the rate of formation of CO among the different kinds of tobacco, while the variations in the rate of formation of CO_2 were found to be small. On the other hand, little variation in the weight loss of the cigarettes during a puff (W_p) was observed. Figure 1 shows the relationships between the weight loss of a cigarette during *n* puffs (nW_p) and the amounts of CO, CO_2 and tar in the mainstream smoke. The slopes of the straight lines for CO, CO_2 and tar correspond to the mean values shown in the legend. The relationship among the variables given by the equation in the Introduction can also be applied to CO_2 and tar. In this case, the term *D* must be replaced by the term *R*, which concerns the retention of tar by the butt. *R* is considered to be almost constant for cigarettes with a given fractional volume. Therefore, the

Figure 1.
Smoke components vs. tobacco weight loss during puffs.

	$\bar{x}$	<i>s</i>	C.V.
CO/nW_p	0.092	0.011	0.120
tar/nW_p	0.150	0.015	0.100
CO_2/nW_p	0.225	0.014	0.062

slope of a line through the origin for each point in Figure 1 is an index of the rate of formation of each component. As can be seen, there are large variations in the slopes for CO, CO_2 , and tar, although these compo-

Figure 2.
Formation rates of carbon oxides vs. their amounts in mainstream smoke.

	$\bar{x}$	<i>s</i>	C.V.
CO/F	138.6	6.20	0.045
CO_2/F	146.8	8.47	0.058

Table 2.
Carbon monoxide, carbon dioxide and tar in mainstream smoke.

Tobacco	Puff count (n)	CO	CO ₂ (mg/cigarette)	Tar	CO/CO ₂	CO/tar
A Cutter	7.7	19.4	42.9	27.2	0.452	0.713
	9.1	22.9	48.7	31.9	0.470	0.718
B Cutter	7.0	17.8	39.6	25.7	0.449	0.693
	7.6	18.3	41.0	29.9	0.446	0.612
C Cutter	8.0	18.8	40.8	29.3	0.461	0.642
	8.8	19.4	44.4	33.2	0.437	0.584
D Cutter	7.2	13.9	41.4	22.9	0.336	0.607
	8.0	16.7	45.7	34.3	0.365	0.487
E Cutter	6.9	13.9	40.2	21.4	0.346	0.650
	7.8	15.7	44.0	32.0	0.357	0.491

Table 3.
Burning characteristics.

Tobacco	W _p (mg)	nW _p (mg)	Formation rate (F)	
			CO	CO ₂
A Cutter	24.40	189.7	0.136	0.291
	23.80	216.6	0.152	0.304
B Cutter	23.50	164.5	0.132	0.286
	25.23	191.7	0.136	0.285
C Cutter	25.67	205.4	0.139	0.281
	24.28	213.7	0.137	0.289
D Cutter	24.27	174.7	0.102	0.303
	24.11	192.9	0.116	0.296
E Cutter	24.86	171.5	0.108	0.298
	25.16	196.2	0.114	0.288
Mean	24.53	191.7	0.127	0.292
Coefficient of variation (%)	2.8	9.1	12.7	2.7

Table 4.
Peak temperature during a puff.

Tobacco		Mean (°C)	Coefficient of variation (%)
A Cutter		872	2.7
	Leaf	922	3.0
B Cutter		877	4.1
	Leaf	896	4.2
C Cutter		928	5.0
	Leaf	902	5.0
D Cutter		802	1.9
	Leaf	860	0.9
E Cutter		824	1.1
	Leaf	886	4.5

W_p : Weight loss during a puff measured on a shortened tobacco column.

n : Puff count (values shown in Table 2).

nents increased on the whole with increasing nW_p . The coefficient of variation was the highest for CO, that for tar was next (legend of Figure 1). The precise effect is shown in Figure 2. All the points for CO fell nearly on a straight line passing through the origin. Some difference was observed between the mean values of the slopes for CO and CO₂, which is reasonable because the term D is smaller for CO than for CO₂ (8, 9, 17). The coefficient of variation for CO/F (Figure 2) was smaller than that for CO/ nW_p (Figure 1). Hence, it can be concluded that the amount of CO in mainstream smoke is more dependent on the rate of formation of CO than the weight loss of a cigarette during puffs. On the other hand, from the fact that the coefficient of variation for CO₂/F was almost equal to that for CO₂/ nW_p , it can be concluded that the rate of formation of CO₂ made about the same contribution to the amount of CO₂ in mainstream smoke as did nW_p .

Peak Temperature and Formation Rates of CO and CO₂

Table 4 shows the peak temperatures of the central region of a burning cone during a puff. The variation in temperature among the different kinds of tobacco was in the range 802 °C to 928 °C. It was larger than the data measured for cigarettes made from different cultivars of tobacco (18, 19). This difference seems to be due to a large variation in the chemical constituents of the tobaccos used in this study, as will be discussed later. The relationship between the peak temperature and the rates of formation of CO and CO₂ is shown in Figure 3. The rate of formation of CO increased with increasing temperature while that of CO₂ remained almost constant. It was known that CO is formed by the pyrolysis of tobacco, the combustion of char and the carbonaceous reduction of CO₂, and that the rate of CO₂ formed by combustion and the rate of CO₂ reduced to CO both increase with increasing temperature (16, 20, 21). Therefore, one of the reasons for the increase in the rate of formation of CO shown in Figure 3 is considered to be an enhancement of the carbonaceous reduction of CO₂ to CO, which is promoted by higher combustion temperatures. The almost zero slope for the rate of formation of CO₂ seems to be due to the fact that the increase in CO₂ formation during combustion is compensated for by the decrease in CO₂ as a result of carbonaceous reduction.

Effect of Chemical Constituents

The levels of several chemical constituents of the tobaccos are shown in Table 5. These tobaccos separate naturally into two groups because of considerable differences in their composition, i.e. into the group A, B, C, and the group D, E. The former contained somewhat smaller amounts of potassium, hexane extracts and cell-wall substances, and larger amounts of water-soluble sugars and ethanol-benzene extracts than did

Figure 3.

Formation rates of carbon oxides vs. peak temperature.

the latter. There was little difference in the total carbon content between the two groups, although a slightly higher content was observed in the leaf of D and E. As is well known, the potassium content is lower in leaf

Figure 4.

CO/tar values in mainstream smoke vs. hexane extract contents of tobacco.

* Significant at the 1% level.

Table 5.
Chemical constituents of various bright tobacco leaves (percentage of total tobacco weight).

Tobacco	Total carbon	Water-soluble sugars	Holo-cellulose	Pectin	Lignin	Ethanol-benzene extracts	Hexane extracts	Nicotine	Potassium
A Cutter	39.1	30.5	11.8	4.1	3.4	49.2	3.43	1.23	1.73
Leaf	38.9	27.9	10.8	4.4	4.1	47.9	3.73	1.65	1.28
B Cutter	38.8	32.2	10.8	3.5	3.7	53.9	3.66	0.94	1.82
Leaf	39.8	30.8	11.2	3.7	3.8	44.8	4.08	1.21	1.51
C Cutter	38.4	26.8	11.0	4.7	4.0	50.9	4.35	2.22	1.59
Leaf	41.0	27.8	10.6	3.7	3.8	52.2	4.61	2.41	1.40
D Cutter	39.4	17.3	13.9	4.9	4.8	38.3	4.76	1.33	2.98
Leaf	42.3	15.6	14.3	5.5	6.9	34.6	6.03	2.38	2.40
E Cutter	39.2	17.6	14.3	5.6	5.5	39.3	4.79	1.27	2.86
Leaf	42.3	15.3	14.0	5.7	4.1	43.6	5.99	2.10	2.10

Table 6.
Simple correlation coefficients.

	Total carbon	Water-soluble sugars	Holo-cellulose	Pectin	Lignin	Ethanol-benzene extracts	Hexane extracts	Nicotine	Potassium	Rate of CO formation
Total carbon	1.00	-0.59	0.49	0.44	0.45	-0.45	0.84	0.61	0.16	-0.37
Water-soluble sugars	-0.59	1.00	-0.93	-0.93	-0.75	0.83	-0.88	-0.37	-0.78	0.83
Holo-cellulose	0.49	0.93	1.00	0.88	0.74	-0.89	0.75	0.08	0.89	-0.91
Pectin	0.44	-0.93	0.88	1.00	0.69	-0.76	0.78	0.35	0.67	-0.68
Lignin	0.45	-0.75	0.74	0.69	1.00	-0.85	0.69	0.31	0.65	-0.59
Ethanol-benzene extract	-0.45	0.83	-0.89	-0.76	-0.85	1.00	-0.68	-0.10	-0.77	0.75
Hexane extract	0.84	-0.88	0.75	0.78	0.69	-0.68	1.00	0.63	0.51	-0.66
Nicotine	0.61	-0.37	0.08	0.35	0.31	-0.10	0.63	1.00	-0.18	0.06
Potassium	0.16	-0.78	0.89	0.67	0.65	-0.77	0.51	-0.18	1.00	-0.95
Rate of CO formation	-0.37	0.83	-0.91	-0.68	-0.59	0.75	-0.66	0.06	-0.95	1.00

Significance levels of correlation coefficients ($n = 8$): 0.632, 5%; 0.765, 1%.

Figure 5.
Peak temperature vs. potassium content of tobacco.

than in cutter tobacco, and there is an opposite tendency with regard to hexane extracts. Figure 4 shows a high negative correlation between hexane extracts and the CO/tar ratio in mainstream smoke. Since hexane extracts contain terpenoid and carotenoid compounds, which are considered desirable for the aroma of the smoke, it is suggested that the CO/tar ratio might be an index of the strength of the aroma inherent in tobacco cultivars.

Table 6 shows the coefficients of simple correlations. Of the coefficients for chemical constituents vs. the rate of formation of CO, the highest was potassium. In addition, it was found that the rate of formation of CO was negatively correlated with the cell-wall substances, and positively correlated with the water-soluble sugars. Based on these simple correlation data, several chemical constituents were selected and computations were performed on the rate of formation of CO [F]. The following are the equations and multiple regression coefficients for these computations:

step 1:

$$F' = 0.1775 - 0.0256 \times (\text{potassium}) \quad [r^2 = 0.912],$$

step 2:

$$F' = 0.2758 - 0.0246 \times (\text{potassium}) - 0.0025 \times (\text{total carbon}) \quad [r^2 = 0.961],$$

step 3:

$$F' = 0.3053 - 0.0284 \times (\text{potassium}) - 0.0035 \times (\text{total carbon}) + 0.0036 \times (\text{lignin}) \quad [r^2 = 0.987].$$

From the equations, it is concluded that the rate of for-

Figure 6.
Amount of CO in mainstream smoke vs. potassium content of tobacco.

mation of CO depends mainly on the potassium content and can be estimated from the amounts of potassium, total carbon and lignin. A multiple regression analysis of the peak temperature [T] yielded the following equation:

$$T' = 945.5 - 80.0 \times (\text{potassium}) + 19.4 \times (\text{pectin}) \quad [r^2 = 0.951].$$

Table 5 shows a significance of 0.5% in the simple correlation between potassium and pectin. Therefore, the peak temperature seems to be mainly dependent on potassium. Peak temperature vs. potassium content is shown in Figure 5. As the potassium content increased from 1.3% to 3.0%, the peak temperature decreased almost linearly from 928 °C to 802 °C. As shown in Figure 3, the rate of formation of CO increased with increasing peak temperature. These results lead to the conclusion that enhancement of the rate of formation of CO is due to a rise in burning temperature resulting from a decrease in the potassium content of the tobacco.

Figure 6 shows the relationship between the amount of CO in mainstream smoke and the potassium content. The amount of CO in mainstream smoke decreased sharply in the low range of potassium content (1%—2%), and decreased gradually in the range of from 2% to 3%. The curve in Figure 6 was obtained from a regression equation of the logarithmic values for both the variables. To clarify the effect of potassium on the combustion mechanism, further experiments are being performed in our laboratory.

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