Cigarette Smoke Formation Studies

V. The Effects of the Cigarette Periphery on Mainstream Smoke Formation*

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INTRODUCTION

In a recent report, recommendations for the standardized preparation of carbon-14 labelled cigarettes were made (1). It was shown that the error generated in uniformly placing the radioactive label axially within the rod is also the degree of error reflected in the radioactivity recovered from total smoke. Cigarettes with large variations in the axial placement of the label would require the smoking of a large number of such cigarettes to determine the total smoke distribution. The data thus generated are reflective of the average values, but with a large experimental error. The more uniformly labelled the cigarette, the smaller the error in the total smoke distribution.

When the radioactivity is not uniformly distributed radially within the cigarette, the smoking of a large number of cigarettes might not overcome any bias imparted to the data. Egerton (2), Keith (3), Wakeham (4) and Osden (5) have all theorized about the effects of the periphery on mainstream smoke formation. To date, there is very little experimental evidence to support these hypotheses. In order to empirically ascertain the importance of the tobacco periphery to smoke formation, carbon-14 labelled cigarettes have been prepared with uniform and non-uniform radial labelling. Effects of radial positioning on the total smoke distributions were measured.

MATERIALS AND METHODS

Preparation of Labelled Cigarettes

The carbon-14 labelled cigarettes were fabricated by the procedures recommended for the standardized preparation of labelled cigarettes (1). The cigarettes were prepared by three basic incorporation methods:

1. *Syringe-Spiking*: This procedure was used to add the labelled compounds primarily to the central portion of the cigarette rod (1).
2. *Spraying*: This procedure was employed when solubility permitted, and produced cigarette filler uniformly labelled with the carbon-14 compounds. Cigarettes were then handmade as previously described (1).

3. *Sheetcasting-Blending*: This procedure was used when materials were insoluble in desired solvents. The labelled sheet materials were then either uniformly blended into normal University of Kentucky 1R1 reference filler or were added at discrete radial positions within the cigarette rod (1).

Radiochemicals

Dotriacontane-16,17-¹⁴C was purchased from Malinkrodt Nuclear and proline-¹⁴C (U) from New England Nuclear. Nicotine-¹⁴C (U) and cellulose-¹⁴C (U) were obtained from biosynthesized Bright tobacco-¹⁴C (U) (6). Invert sugar (U) was prepared by the treatment of glucose-¹⁴C (U) (New England Nuclear) with invertase. Radiochemical purities in all cases were better than 98% before application.

Radioactivity Determinations

Appropriate aliquots of the extracted or combusted samples were counted in a Packard Model 3390 scintillation spectrometer (Packard Instrument Company) with optimized gain and window settings. The procedures and cocktails used have been previously described (7).

Cigarette Smoking

The procedures and smoking machine instrumentation were described previously (7) and were used to obtain the ¹⁴C-activity distributions in the total cigarette smoke.

RESULTS AND DISCUSSION

Keith (3), Wakeham (4) and Osden (5) have each theorized about the effects of the tobacco cigarette periphery on mainstream smoke formation. They reasoned that the major pathway of air into the cigarette during puffing is between the junction of the paper and the coal, referred to by Wakeham as the "bypass zone" (Figure 1). The low air permeability of the paper and the high resistance of the coal combine to bring about a preferential passage of air through the bypass zone. The cigarette during puffing would burn the tobacco more rapidly around the periphery than in the center. Hence, the periphery should play a larger proportionate role in mainstream smoke formation than the center sec-

* Presented, in part, at the 27th Tobacco Chemists' Research Conference, Winston-Salem, North Carolina, U.S.A., in October 1973.
Received for publication: 5th July, 1977.

Figure 1.

tion. When viewed from the coal end, a convex zone of unpyrolyzed tobacco behind the coal is created by the peeling back of the peripheral paper and burnt tobacco during the puffing, leaving a distorted center zone (Figure 1). During the static burn between puffs, the inner portion of the convex coal becomes more linear in shape. The restoring of this center zone should thus contribute a larger proportional share of smoke formation products to sidestream smoke.

With these conjectures in mind, the data from various cigarettes labelled uniformly and non-uniformly in the radial axis can be interpreted. Cigarettes labelled with nicotine- ^{14}C (U) were prepared by spraying (uniform) and syringe-spiking (non-uniform). Nicotine is a compound capable of migration within the cigarette and tends to equilibrate throughout the rod. However, it is seen from radial sections that only after several weeks will the nicotine added down the rod center approach total radial equilibration. Upon smoking these two types of nicotine- ^{14}C (U) labelled cigarettes, differences in their total smoke distribution were noted, as shown in Table 1. The sidestream gas yield has increased, primarily at the expense of the mainstream total particulate matter (TPM) in the sprayed *versus* the spiked cigarettes. There is not enough difference in the mainstream gas or sidestream TPM to imply any meaning.

Nicotine is known to undergo considerable migration toward equilibration in cigarettes before they are lit and, being a semi-volatile distillable component of to-

Table 1. Distribution of radioactivity (%) in smoke from cigarettes labelled with nicotine- ^{14}C (U).

Smoke phase	Mode of addition	
	Sprayed	Spiked
Sidestream gas	21.7	25.0
Sidestream particulate	52.6	53.5
Sidestream total	74.3	78.5
Mainstream gas	2.2	1.6
Mainstream particulate	23.5	20.0
Mainstream total	25.7	21.6

bacco, may also undergo some vapor phase equilibration in the hot zones behind the approaching coal. The nicotine present in the vapor state could be expected to diffuse not only axially but also radially. This would, in effect, take non-uniformly labelled cigarettes and, by vapor phase equilibration, tend to cause a uniform distribution of the nicotine in the zone behind the coal. Therefore, nicotine would not be expected to show large differences in smoke distributions as cigarettes prepared by both techniques would be essentially uniformly labelled. Another mitigating consideration is that of possible chemical reactivity of the nicotine with other tobacco constituents. Thornton (8) has shown that when large amounts of exogenous sugar were added to filler, a lower transference of nicotine takes place, presumably due to the chemical reaction of nicotine and the pyrolysis products of the sugar.

Dotriacontane is a relatively inert tobacco constituent known to distill into smoke (9), but possesses such a low vapor pressure so as to preclude migration equilibration before the cigarette is smoked. Cigarettes were prepared by spraying (uniform) and syringe-spiking of dotriacontane-16,17- ^{14}C down the center of the rod (non-uniform). The smoke distribution data are shown in Table 2. The increase in contribution of the center portion of the rod to the sidestream gas phase is apparent. This sidestream gas phase contribution increases as the dotriacontane is located more in the center. This sidestream gas phase increase appears to have originated at the expense of both the sidestream and mainstream particulate phases. As with nicotine, no apparent change occurs in the contribution to the mainstream gas phase

Table 2. Distribution of radioactivity (%) in smoke from cigarettes labelled with dotriacontane-16,17- ^{14}C .

Smoke phase	Mode of addition	
	Sprayed	Spiked
Sidestream gas	9.8	17.1
Sidestream particulate	46.0	42.4
Sidestream total	55.8	59.5
Mainstream gas	1.3	1.3
Mainstream particulate	42.9	39.2
Mainstream total	44.2	40.5

Table 3. Distribution of radioactivity (%) in smoke from cigarettes labelled with β -proline- ^{14}C (U).

Smoke phase	Mode of addition		
	Sprayed	Spiked	^{14}C -sheet blend*
Sidestream gas	68.4	69.6	77.1
Sidestream particulate	8.2	10.3	4.8
Sidestream total	76.6	79.9	81.9
Mainstream gas	12.1	12.2	12.7
Mainstream particulate	11.3	7.9	5.4
Mainstream total	23.4	20.1	18.1

* 15 % sheet containing β -proline- ^{14}C , placed in center of rod.

indicating that radial positioning is not a major factor in these small mainstream gas yields. Nicotine and dotriacontane are both distillable compounds and one explanation for the lack of a decrease in mainstream gas deliveries is that the mainstream gas yields from the distillables are formed mainly during the static burn between puffs, and they enter the mainstream smoke upon the turn-around of the air at the beginning of the puff. Gaseous diffusion along the rod during the static burn period is also a contributor of unknown magnitude.

Proline is an amino acid present in tobacco and readily sublimates as was found from radiothermogravimetric studies on tobacco labelled with ^{14}C -proline (10). Proline would have a tendency to equilibrate (via sublimation) in the approaching combustion zone and not remain to undergo combustion/pyrolysis. It can escape ahead of the coal at the appropriate thermal gradient and, because of this, would be expected to act similar to distillable compounds. Proline, on the other hand, has a lower thermal stability and should undergo pyrolysis and combustion in a lower thermal zone than nicotine or dotriacontane. Cigarettes labelled in three ways with proline- ^{14}C (U) were prepared. They were prepared by spraying (uniform distribution), syringe-spiking (reasonably centered) and by hand-lacing individual strands of blended sheet containing ^{14}C -proline (very centered). The ^{14}C -sheet material (15% by weight) was placed only in the center zone of the rod (~10%). These smoke results (Table 3) are in general agreement with those of nicotine and dotriacontane. A definite increase in the sidestream gas phase is noted as the label is more radially centered. A decrease in mainstream particulate is apparent with too much scatter in the sidestream particulate to indicate any trend. There is no change in mainstream gas yields as the labelled material is more centrally located, again indicating that the origin of the mainstream gas phase is not position dependent and may be mainly due to the pyrolysis/combustion taking place during the static burn and carried into the mainstream by the puff reversal.

A clearer answer to the effects of the peripheral tobacco on mainstream smoke formation was obtained by studying compounds not capable of distillation or sublima-

Figure 2. Radial distribution of radioactivity from cigarettes syringe-spiked with ^{14}C -invert sugar (U).

tion. These materials cannot re-equilibrate ahead of the high temperature zones and must necessarily remain stationary to undergo pyrolytic reactions. Cigarettes were smoked which contained ^{14}C -invert sugar (U) added by spraying onto the filler (uniform) and by the syringe-spiking of an aqueous solution (centered). The distribution of the radioactivity radially in these cigarettes was also investigated by taking cigarettes labelled by syringe-spiking, removing the tobacco from the center of the rod by drilling the frozen cigarette with a special slow-speed hollow drill bit very similar to a conventional cork-borer, and then measuring the activity per gram of tobacco. These data were compared to the specific activity obtained from the peripheral filler only. This distribution of radioactivity radially from cigarettes which were syringe-spiked with invert sugar- ^{14}C (U) down the center of the rod is shown in Figure 2. The data show that the syringe-spiking technique (20 μl solvent per cigarette) applies 87.6% of the radioactivity in the central 9% of the rod. The remaining 91% of the tobacco outside of the center possessed only 12.4% of the total radioactivity. These data also show that cigarettes prepared by the syringe-spiking of non-volatile materials essentially have the labelled materials located in the central 10% of the rod. Invert sugar- ^{14}C (U) was added uniformly by spraying the filler and subsequently making it into cigarettes. The distribution of the radioactivity into total smoke from these two types of invert sugar- ^{14}C (U) labelled cigarettes is shown in Table 4. These data (Table 4) again reinforce the findings that the sidestream gas yields increase and the sidestream particulate shows little change when the material is more centered. In mainstream, again the particulate decreases and here, for the first time, a decrease is seen in mainstream gas yields as the material is more centered. The invert sugar is not capable of equilibrating in front of the thermal gradient and remains to undergo pyrolysis/combustion giving rise to a radial position dependency to the smoke distribution. The mainstream gas yield for the sprayed sample represents the contribution from combustion/pyrolysis occurring during puffing plus the static burn gaseous diffusion and turn-around effects. The spiked sample (centered) represents mainly the diffusion and puff turn-around contribution from the static burn.

Table 4. Distribution of radioactivity (%) in smoke from cigarettes labelled with invert sugar-¹⁴C (U).

Smoke phase	Mode of addition	
	Sprayed	Spiked
Sidestream gas	67.6	75.0
Sidestream particulate	8.3	8.1
Sidestream total	75.9	83.1
Mainstream gas	14.5	9.9
Mainstream particulate	9.6	7.0
Mainstream total	24.1	16.9

Invert sugar is a single exogenously added cigarette component and may or may not be representative of the major tobacco constituents. Therefore, cigarettes were handmade using cellulose-¹⁴C (U) that had been incorporated into blended sheet. Cigarettes were prepared in three ways: one with the radioactivity only in the central 20% of the rod, one with the central 20% containing no radioactivity but with the periphery (80%) containing the ¹⁴C-label, and one with the uniform addition of the ¹⁴C-label throughout the rod. Smoking data (Table 5) show a dramatic increase in sidestream gas yields as the radioactivity is more localized in the center. A decrease in both sidestream and mainstream particulate yields is observed. Also, the mainstream gas values showed marked decreases. These data from ¹⁴C-cellulose sheet labelled cigarettes, coupled with the data from the other labelled cigarettes, lead to the following conclusions regarding the effect of the radial position of ¹⁴C-labelled material in the cigarette rod on the contributions to the formation of total smoke:

1. The theories put forth by *Keith* (3), *Wakeham* (4) and *Osdene* (5) are substantiated.
2. The periphery plays a large contributing role (though not the sole role) in the formation of:
 - a. Mainstream particulate phase,
 - b. Sidestream particulate phase (non-distillable/non-sublimable materials),
 - c. Mainstream gas phase (non-distillable/non-sublimable materials).
3. The central portion of the cigarette rod plays a large contributing role in:
 - a. Sidestream gas phase,
 - b. Sidestream particulate phase (distillable/sublimable compounds).
4. The mainstream gas phase yields of the distillable/sublimable compounds are due in large part to the pyrolysis/combustion products formed during the static burn period. These products are carried into mainstream smoke by the incoming air at the beginning of the puff turn-around and by diffusion due to the pressure gradient existing in the cigarette during static burning.

These experiments have demonstrated the significant effects that the central portion of the cigarette rod has on sidestream smoke formation and, conversely, the

Table 5. Distribution of radioactivity (%) in smoke from cigarettes labelled with cellulose-¹⁴C (U).

Smoke phase	Position of label		
	Periphery (80%)	Blended (100%)	Center (20%)
Sidestream gas	69.5	74.8	80.4
Sidestream particulate	8.7	7.0	5.9
Sidestream total	78.1	81.8	86.3
Mainstream gas	14.3	11.6	8.2
Mainstream particulate	7.6	6.6	5.5
Mainstream total	21.9	18.2	13.7

effects of the periphery on mainstream smoke. Future experiments are needed on cigarettes prepared with a smaller labelled periphery (in the order of 10–20%). These types of cigarettes should dramatically demonstrate the effects of the periphery on mainstream smoke, but must wait until the expertise for this type of cigarette preparation can be developed and refined.

SUMMARY

The effects of the cigarette periphery on smoke formation have been experimentally studied. A series of cigarettes was prepared with carbon-14 labelled materials placed in different radial positions within the rods. These cigarettes were smoked and the distribution of the radioactivities into total smoke was measured. These data lead to the following conclusions: [1] The periphery plays a large contributing role (though not the sole role) in the formation of a) the mainstream particulate phase, b) sidestream particulate phase (derived from non-distillable/non-sublimable materials), and c) mainstream gas phase (derived from non-distillable/non-sublimable materials); [2] The central portion of the cigarette rod plays a large contributing role in a) sidestream gas phase and b) sidestream particulate phase (derived from distillable/sublimable compounds); and [3] The mainstream gas phase yields from the distillable/sublimable compounds are due in large part to the pyrolysis/combustion products formed during the static burn period. These products are carried into mainstream smoke by the incoming air at the beginning of the puff and by diffusion due to the pressure gradient existing in the cigarette during static burn.

These experiments have demonstrated the significant effects that the central portion of the cigarette rod has on sidestream smoke formation and, conversely, the effects of the periphery on mainstream smoke.

ZUSAMMENFASSUNG

Die Wirkungen der Zigarettenperipherie auf die Rauchbildung wurden experimentell untersucht. In einer Reihe von Zigaretten wurden ¹⁴C-markierte Substanzen inner-

halb des Tabakstranges an verschiedenen radial angeordneten Stellen plazierte. Die Zigaretten wurden abgeraucht, und die Verteilung der Radioaktivität im Gesamtrauch wurde gemessen. Die Ergebnisse führen zu den folgenden Schlußfolgerungen: [1] Die Randzone des Tabakstranges leistet (wenn auch nicht als einziger Faktor) einen erheblichen Beitrag bei der Bildung von a) der Partikelphase des Hauptstromrauches, b) der Partikelphase des Nebenstromrauches (nachgewiesen anhand nicht destillierbarer oder nicht sublimierbarer Stoffe) und c) der Gasphase des Hauptstromrauches (nachgewiesen anhand nicht destillierbarer oder nicht sublimierbarer Substanzen); [2] Die Mitte des Tabakstranges leistet einen großen Beitrag bei der Bildung von a) der Gasphase des Nebenstromrauches und b) der Partikelphase des Nebenstromrauches (nachgewiesen anhand destillierbarer oder sublimierbarer Verbindungen); [3] Die Ausbeute der Gasphase des Hauptstromrauches an destillierbaren oder sublimierbaren Verbindungen ist zum großen Teil auf Pyrolyse- bzw. Verbrennungsprodukte zurückzuführen, die während des statischen Abrennens entstehen. Diese Stoffe gelangen in den Hauptstromrauch mit der einströmenden Luft am Anfang des Zuges und durch Diffusion aufgrund des Druckgefälles, das während des statischen Abrennens in der Zigarette vorliegt.

Diese Untersuchungen zeigen den bedeutenden Einfluß, den die Mitte des Zigarettenstranges auf die Bildung des Nebenstromrauches ausübt, und andererseits die Beeinflussung des Hauptstromrauches durch die Zigarettenperipherie.

RÉSUMÉ

On a étudié expérimentalement l'influence de la périphérie de la cigarette sur la formation de la fumée. On a préparé une série de cigarettes avec des matériaux marqués au carbone 14 que l'on a placés dans différentes orientations radiales dans les boudins de tabac. Ces cigarettes ont été fumées et on a mesuré la distribution de la radioactivité dans la fumée totale. Ces données nous ont amenés aux conclusions suivantes: [1] la périphérie joue un rôle contributif important (quoique pas le seul) dans la formation de a) la phase particulaire du flux principal, b) la phase particulaire du flux secondaire (ce qui dérive de composés non distillables ou non sublimables) et c) la phase gazeuse du flux principal (ce qui dérive de matières non distillables ou non sublimables); [2] la portion centrale du boudin de tabac joue un rôle contributif important dans la formation de a) la phase gazeuse du flux secondaire et b) la phase particulaire du flux secondaire (ce qui dérive de composés distillables ou sublimables); et [3] les rendements de la phase gazeuse du flux principal en composés distillables

ou sublimables sont dûs pour une large part aux produits de pyrolyse/combustion se formant pendant l'intervalle de combustion statique. Ces produits sont transportés dans le flux principal de fumée par l'air pénétrant au début de la bouffée et par diffusion due au gradient de pression dans la cigarette durant la combustion statique.

Ces expériences ont démontré l'influence significative de la portion centrale du boudin de tabac sur la formation du flux secondaire de fumée et, de même façon, l'influence de la périphérie sur le flux principal de fumée.

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Acknowledgements

The authors wish to thank Mr. R. A. Comes, Miss M. T. Core and Mr. M. D. Edmonds for their assistance in the isolation and purification of the ^{14}C -labelled materials and Mr. G. C. Newell for his assistance in the labelled cigarette preparation.

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