Cigarette Smoke Formation Studies

VI. The Carbon Contribution to Total Smoke from Each Individual Component in the 1R1-Type Cigarette*

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INTRODUCTION

The tobacco industry has spent considerable time and effort over the years researching every possible avenue regarding cigarette smoke composition and its formation. In spite of this, some relatively basic questions have apparently gone unnoticed for many years and can be stated as follows: 1. What is the distribution of carbon into all of the portions of total cigarette smoke? 2. Is the assumption correct that each cigarette ingredient contributes its proportionate share of carbon to each phase of smoke? In other words, does a cigarette which contains 40% Bright lamina reflect an equivalent 40% of the total carbon to mainstream total particulate matter (MS-TPM), MS gas phase, sidestream total particulate matter (SS-TPM), SS gas phase and butt filtration as being derived from the Bright lamina portion of the blend?

To answer these questions, carbon-14 labelled cigarettes were utilized. The desired labelled Bright, Burley and Oriental tobaccos were grown in a $^{14}\text{CO}_2$ chamber. These tobaccos were then cured and utilized in the fabrication of a laboratory copy of the 1R1 Kentucky reference cigarette. These cigarettes were made individually with each major ingredient being labelled with carbon-14. The smoke distribution of the radioactivity from each of these labelled cigarettes was multiplied by the actual amount of carbon consumed during burning, resulting in the carbon contribution of each cigarette blend component to total smoke.

EXPERIMENTAL

Radiochemicals

The labelled Bright, Burley and Oriental tobaccos were produced by growing the tobacco from the transplant stage to maturity in a $^{14}\text{CO}_2$ growth chamber as described by Bass (1). These tobaccos were cured and then stemmed and shredded by hand. The ^{14}C -cigarette paper was pre-

pared by the Schweitzer Division of Kimberly-Clark utilizing ^{14}C -cellulose (U^{**}) isolated from the ^{14}C -Bright (U) tobacco grown in the growth chamber. ^{14}C -glycerol was purchased from the New England Nuclear Corporation. ^{14}C -sucrose (U) was purchased from the New England Nuclear Corporation and reacted with invertase to produce ^{14}C -invert sugar (U).

Uniformity of Labelling

The biosynthetically produced ^{14}C -tobaccos were assayed by an instrumental method to determine the degree of uniformity of carbon-14 labelling (2) and in all cases were found to fall within the limits of accuracy established for the assay method.

Labelled Cigarette Preparation

The proper weight percentage of each labelled ^{14}C -tobacco type was mixed with the remaining components of the 1R1-type cigarette in the same composition as present in the University of Kentucky 1R1 cigarette (3). The proper amounts of glycerol and invert sugar were always added. The ^{14}C -glycerol and ^{14}C -invert sugar were used to prepare separate batches of labelled cigarettes. These materials were added by spraying using the techniques reported elsewhere for the preparation of labelled cigarettes (4). The cigarette paper had the same chemical and physical parameters as the 1R1 cigarette paper and was prepared on a conventional bobbin. The control and ^{14}C -labelled papers were processed through a conventional cigarette making machine, the tobacco was then pulled from the paper and the paper tubes were then used in the hand-making process. Cigarettes were made to weight as previously described (4). All cigarettes were equilibrated at 24°C and 60% relative humidity for one week prior to their use. Cigarettes were checked for uniformity of labelling by taking cigarettes of each type, sectioning into four parts, and subsequently making radioactivity determinations. In all cases, the uniformity was within established limits (4).

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** uniformly labelled

Smoke Distribution of Radioactivity

The distribution of the radioactivity into smoke was determined by using a carbon-14 total recovery smoking machine (5). The total particulate matter (TPM) was removed from the Cambridge filter pads by extraction in either an appropriate solvent or dissolution in a commercial liquid scintillation solubilizing agent (Hyamine-10X®*). Sectioned cigarettes, as well as the smoked butts, were dissolved in Hyamine-10X®, and aliquots taken for radioactivity counting.

Liquid Scintillation Counting

A Packard Tricarb model 3390 liquid scintillation spectrometer with optimized gain and window settings was used. The Hyamine-10X® aliquots were counted in an Insta-Gel (Packard) scintillator cocktail. Other aliquots were counted in conventional cocktail formulations.

RESULTS AND DISCUSSION

Cigarettes were prepared to be identical with the 1R1 except that in each batch a different cigarette component was added in a radioactive form. Each ¹⁴C-tobacco was blended separately by weight into the normal 1R1 blend composition. The ¹⁴C-glycerol and ¹⁴C-invert sugar were added at the same concentration levels as in the 1R1. The

Table 1. Weight and carbon content of the 1R1 Kentucky reference cigarette.

Components	% by weight	Carbon content (%)
Bright		
lamina*	38.19	40.88
stem*	13.52	32.90
Burley* (Includes 1.1% Maryland)	24.76	37.34
Oriental*	11.05	37.88
Glycerol	2.67	40.00
Invert sugar	5.05	39.12
Paper*	4.76	34.87

* Equilibrated weight at 60% relative humidity and 24 °C.

cigarette paper was composed of ¹⁴C-cellulose and was specially prepared by the Schweitzer Division of Kimberly-Clark to be identical with that of the 1R1 cigarette. The weight percentages used are listed in Table 1. Also listed is the carbon content of each ingredient as determined by Galbraith Laboratories.

* Rohm and Haas Company

Table 2. Carbon contribution of each ingredient of the 1R1-type cigarette.

(carbon weight percent × dry cigarette weight × 62/85)

Component	Carbon consumed (mg)
Bright	
lamina	113.96
stem	32.47
Burley (Includes 1.1% Maryland)	67.49
Oriental	30.56
Glycerol	7.80
Invert sugar	14.42
Paper	12.12

The actual amount of carbon from each ingredient consumed during the smoking process can be calculated by multiplying the dry cigarette weight by the carbon weight percent of each cigarette ingredient times 100, reduced by 62/85 to compensate for the unsmoked butt portion. These results are shown in Table 2.

The amount of carbon left in the ash has been determined to be quite small in all cases (less than 0.3%) and, thus, is ignored in this discussion.

Each of the separate types of labelled cigarettes was smoked on our total recovery smoking machine and the smoke distributions of radioactivity were measured. These data are shown in Table 3.

From these transference values (Table 3), multiplied by the amount of carbon consumed (Table 2), the carbon contribution of each cigarette component to each smoke phase can be calculated. These calculations require an accurate determination of the radiotransferences of carbon into all smoke phases. In order to verify the validity of our radiotracer techniques, the carbon balance of mainstream total particulate matter (MS-TPM) was calculated by multiplying the amount of carbon consumed by the radio-carbon transference to MS-TPM ($\text{Carbon consumed}_A \times \% \text{ Transference of } ^{14}\text{C}_A \text{ to MS-TPM} \div 100 = \text{Amount of carbon contributed to MS-TPM by ingredient A}$). This calculation thus shows the mg of carbon delivered by each ingredient. The total should equal the total carbon content for the 1R1 MS-TPM as analytically determined. Listed in Table 4 is this calculation of MS-TPM carbon balance using our radioactivity transference values. Listed also is the analytically determined carbon content for the MS-TPM delivered by the total smoke machine. The 27.99 mg C as determined by our radiotracer techniques is in excellent agreement with the 27.54 mg C determined using normal analytical techniques for total carbon in MS-TPM.

Table 3. Percentage of carbon transferred to total smoke from each ¹⁴C-component of the 1R1-type cigarette (based on tobacco consumed).

Smoke phase	Bright lamina	Bright stem	Burley	Oriental	Glycerol	Invert sugar	Paper (cellulose)
Mainstream gas phase	13.7	15.6	13.0	12.1	8.6	13.6	20.4
Mainstream total particulate matter	11.5	5.3	7.7	12.3	22.0	9.1	9.7
Sidestream gas phase	60.2	71.1	62.6	58.5	38.9	63.8	38.3
Sidestream total particulate matter	11.2	5.8	11.4	12.9	24.5	7.8	28.2
Butt	3.3	2.1	5.3	4.4	5.7	5.7	3.2

Table 4. Carbon mass balance of mainstream total particulate matter (MS-TPM).

	Radioactive transference (based on dry cigarette weight)
Bright	
lamina	13.10 mg
stem	1.72
Burley	5.20
Oriental	3.76
Glycerol	1.72
Invert sugar	1.31
Paper	1.18
Total	27.99 mg C in mainstream total particulate matter

Direct analysis of the mainstream total particulate matter of 1R1-type cigarette:

$$(TPM - H_2O) \times (\% C) \div 100 = 27.54 \text{ mg C in mainstream total particulate matter}$$

$$\text{error} = \pm 1.6$$

These data verified the use of radiocarbon in determining the percentage contribution of each cigarette ingredient into smoke.

Table 5. Mainstream (carbon) contribution from 1R1 cigarette components in percent.

	Experimental		Theoretical
	Total particulate matter	Gas phase	Total particulate matter or gas phase
Bright			
lamina	46.8	40.9	40.9
stem	6.1	13.4	11.7
Burley	18.6	23.1	24.2
Oriental	13.4	9.7	11.0
Glycerol	6.1	1.0	2.8
Sugar	4.7	5.3	5.2
Paper	4.1	6.6	4.3

Table 6. Sidestream (carbon) contribution from 1R1 cigarette components in percent.

	Experimental		Theoretical
	Total particulate matter	Gas phase	Total particulate matter or gas phase
Bright			
lamina	41.0	40.7	40.9
stem	6.1	13.7	11.7
Burley	24.7	25.0	24.2
Oriental	12.5	10.6	11.0
Glycerol	1.3	1.8	2.8
Sugar	3.5	6.6	5.2
Paper	10.9	2.7	4.3

The expected distribution of carbon into smoke is determined by calculating strictly on the weight percentage of each ingredient incorporated, and assuming that all ingredients contribute proportionally to the smoke. This theoretical carbon contribution is therefore the same for all smoke phases (SS, MS-gas; SS, MS-TPM; butt filtration). The comparison of this theoretical contribution to the actually determined carbon contribution for mainstream and sidestream smoke as well as that smoke removed by the unburned tobacco butt is shown in Tables 5, 6 and 7.

In examining the MS-TPM data, there are several obvious differences from our earlier assumptions of proportionate delivery from each component. Bright lamina delivers in the MS-TPM considerably more carbon than expected (Table 5). The stem does the opposite. In fact, stem contributes only 52% of that expected to MS-TPM. The Burley delivery is only 77% of what was expected. The Oriental tobacco delivers some 121% of the expected carbon to the MS-TPM. The sugar is a little less than the theoretical, whereas glycerol is some 218% higher. This is not unexpected as glycerol is readily distilled ahead of the thermal gradient in a burning cigarette. The paper delivers the predicted yield, but this fact is surprising when one considered its apparent ease in going to the sidestream smoke versus being drawn into the mainstream.

Similar comparisons can be made to the sidestream (Table 6) and butt (Table 7) results. Some of the more surprising results are the large contribution to the sidestream TPM from the paper and the large butt filtration value for Burley. The paper, with its apparently large availability of oxygen, was thought to contribute very little if any to SS-TPM, but these data show that paper does contribute 10.9% of the SS-TPM carbon content. The butt filtration values, coupled with reduced MS-TPM contribution for Burley, imply that Burley contributes smoke components which are easily condensable and show a large condensation on the tobacco column. The converse is apparent from the Bright tobacco which shows a large contribution to those ingredients in MS-TPM which are not easily condensable, perhaps more in the non-volatile particulate aerosol. Glycerol, as expected, is easily condensable and shows a large butt filtration as well as a large TPM contribution. The Bright stem shows only about one half the MS-TPM contribution thought previously, and also a reduced butt filtration value. These results show stem to

Table 7. Tobacco column filtration (carbon) from 1R1 cigarette components in percent.

	Experimental	Theoretical
Bright		
lamina	34.2	40.9
stem	6.3	11.7
Burley	32.4	24.2
Oriental	11.7	11.0
Glycerol	4.5	2.8
Sugar	7.2	5.2
Paper	3.6	4.3

contribute more heavily to the gas phase than any of the other blend components in the cigarette.

SUMMARY

Shown for the first time is the contribution of carbon into each smoke phase from each ingredient in the 1R1-type cigarette. In many cases, the actual percentage contribution is greatly different from the theoretical contribution assumed correct for many years. The Bright lamina is a larger carbon contributor to mainstream total particulate matter (MS-TPM) than expected and the Bright stem contributes considerably less. These data imply that Burley tobacco contributes more than the expected amounts of carbon to those smoke components which are more easily condensable, as compared to Bright tobacco, which contributes more than expected to the non-volatile particulate phase and less to the condensable phase. The cigarette paper was shown to contribute a disproportionate share of carbon to the sidestream total particulate matter (SS-TPM). Glycerol was shown to contribute heavily to the MS-TPM, in keeping with what would be expected for distillable materials.

ZUSAMMENFASSUNG

An der Tabakmischung der 1R1-Versuchscigarette (Kentucky) wurde erstmalig nachgewiesen, wie sich der Kohlenstoffgehalt der einzelnen Tabakarten anteilig auf die verschiedenen Rauchphasen verteilt. Es zeigte sich in vielen Fällen, daß sich die tatsächlich beobachtete Verteilung prozentual stark von jener unterscheidet, die auf Grund theoretischer Berechnungen jahrelang als richtig angesehen wurde. Bei Virginia-Tabak (Bright) trägt das entrippte Blattgut mehr und das Rippengut erheblich weniger als erwartet zum Kohlenstoffgehalt der Partikelphase des Hauptstromrauches (MS-TPM) bei. Die Ergebnisse lassen auch erkennen, daß Burley-Tabak mehr Kohlenstoff als erwartet zu dem leichter kondensierbaren Rauchanteil beiträgt, während Virginia-Tabak dagegen mehr als erwartet zum Kohlenstoffgehalt der nichtflüchtigen Partikelphase und weniger zu der kondensierbaren Phase beiträgt. Das Cigarettenpapier trägt unverhältnismäßig stark zum Kohlenstoffgehalt der Partikelphase des Nebenstromrauches (SS-TPM) bei. Glycerin trägt sehr stark zum Kohlenstoffgehalt der Partikelphase des Hauptstromrauches (MS-TPM) bei, welches auch nach den Kenntnissen über destillierbare Stoffe zu erwarten war.

RÉSUMÉ

La contribution de carbone de chaque ingrédient du mélange de tabac de la cigarette de type 1R1 (Kentucky) à

chaque phase de la fumée est démontrée pour la première fois. La part de la contribution effective diffère souvent largement de la contribution théorique estimée correcte dans le passé. Les limbes de tabac Bright contribuent une part de carbone plus grande qu'escomptée à la phase particulaire de la fumée principale (MS-TPM) alors que les côtes de tabac Bright en contribuent nettement moins. Il en découle que le tabac Burley contribue plus de carbone que les quantités escomptées aux composants de la fumée facilement condensables que le tabac Bright qui, lui, apporte une contribution plus grande qu'escomptée au carbone de la phase particulaire non volatile et moins grande au carbone de la phase condensable. Le papier à cigarette contribue dans une mesure nettement plus que proportionnelle au carbone de la phase particulaire de la fumée secondaire (SS-TPM). Selon ce qui était à prévoir pour les substances distillables, la glycérine contribue une très grande part de carbone à la phase particulaire de la fumée principale (MS-TPM).

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