THE DISTRIBUTION OF PRODUCTS BETWEEN MAINSTREAM AND SIDESTREAM SMOKE[1]

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Distributions of several cigarette smoke components between the mainstream and sidestream smokes have been determined. These distributions have been used to define the differences in the physico-chemical factors that govern the formation of the two streams.

INTRODUCTION

Differences in the deliveries of many cigarette smoke components to the sidestream and mainstream smoke have been noted by several workers (4, 7, 8, 10-12, 14).

Examples of the ways in which components distribute themselves between the streams are given in **Table 1**. Qualitatively, there is general agreement that larger deliveries to the sidestream reflect the fact that more tobacco is consumed during the smoulder period than during the puffing cycle. However, there are those components (such as pyridine and 3-vinyl pyridine) which distribute themselves so predominately to one stream or the other that the distribution is obviously out of line with anything that would be predicted from differences in tobacco consumption. Water is another of these (**Table 2**). Williams and Hunt (14) observed 5781 micrograms of ammonia in sidestream smoke and 55 micrograms in the mainstream. Again, a small molecule is delivered almost exclusivey to the sidestream. **Table 3** gives some ammonia values which vary in the sidestream but remain constant and small in the mainstream. This delivery, as with water, is totally out of line with considerations of tobacco consumption in the two streams as determined from physical data. It was the object of this work to examine components which are delivered preferentially to either stream and those which are split in various proportions between the streams. From this examination, attempts would be made to obtain relationships which may define the nature of the differences in the physico-chemical factors that govern the formation of the two streams.

EXPERIMENTAL

Cigarettes employed in this study were 85 mm, machine-made all burley, all bright and all Turkish types. Additionally, the Kentucky Reference 1R1 cigarette was studied. These cigarettes, which were conditioned at 75°F and 60% RH prior to smoking, are described further in **Table 4**.

Smoking was accomplished by using a motor-driven syringe type smoking machine which took 35 ml puffs

Table 1. Some Sidestream (SS):mainstream (MS) ratios.

Substance	SS/MS	Reference
Nicotine	2.7	(10)
Phenol	2.6	(10)
Benzo(a)pyrene (mg)	3.4	(10)
Benzo(a)pyrene (ppm)	2.1	(10)
Dry Condensate	1.7	(10)
3-Vinyl Pyridine	43.0	(4)
Pyridine	10.0	(4)

Table 2. Water in cigarette smoke.

Investigator	SS	MS
Neurath (11)	344.7 mg	14.4 mg
Seehofer (12)	95%	5%

Table 3. Ammonia deliveries in cigarette smoke.

Cigarette	Ammonia Yields (μg/cigt)	
	SS	MS
Burley	8500	50
Bright	5600	50
Turkish	6400	50
Kentucky Reference 1R1	5300	50

Table 4. Cigarette physical characteristics.

Cigarette	Paper Porosity (sec)	Smoulder Rate (mm/min)	Puff Count	Tobacco Consumption[a] (mg/cigt)	
				Sidestream	Mainstream
Burley	21	6.0	6	320	290
Bright	21	3.84	11	580	280
Turkish	21	3.69	13	680	190
Kentucky Reference 1R1	40	4.31	10	490	230

[a]Calculated from **Table 5** and the weight of smoked rod.

of two second duration each minute. Mainstream smoke was collected in various ways, the smoke collection being a function of the analytical requirements for any given component. Sidestream smoke was directed onto a Cambridge pad and through a stainless steel cold trap which contained 40x80 mesh Polypak 2 (Hewlett Packard Company) by an 1150 ml/min vertical flow of air through a glass chimney fitted over the front of the cigarette. The cigarette was inserted horizontally into the chimney through a hole in the side of the chimney which was slightly larger in diameter than the cigarette. In this way any diffusional losses of the mainstream components through the paper would not be collected as sidestream smoke. In the analysis of sidestream components by gas chromatography, only one puffing interval (between the third and fourth puffs) was sampled. Larger samples led to difficulties because of the huge amount of water present in the sidestream smoke. The measured quantities were then multiplied by the averaged number of intervals per cigarette to obtain the quantities reported. Analysis of the sidestream components at different intervals between puffs showed no differences in smoke composition. Smoke from the entire cigarette was used in the mainstream analyses.

Table 5. Tobacco consumption in mainstream and sidestream smoke.

$$\text{Tobacco consumed in mainstream smoke} = nKv = \frac{W}{L_0}[L-s(n-1)(\frac{1}{f}-\frac{1}{30})]$$

n = puff count
Kv = weight of tobacco burned in a puff
W = weight of tobacco rod
L₀ = length of tobacco rod
L = burn length
s = smoulder rate (mm/min)
f = number of puffs per minute

Table 6. Sidestream:mainstream ratios.

Smoke Component	SS/MS			
	Burley	Bright	Turkish	Ky. Ref. 1R1
Methane	4.8	3.6	3.8	3.1
Acetylene	1.1	2.1	2.5	0.81
Propane-Propene	6.2	5.0	4.95	4.1
Methyl Chloride	1.7	2.7	3.3	2.1
Acetone	2.6	3.1	3.2	2.5
Methyl Furan	2.6	4.1	3.9	3.4
Propionaldehyde	2.8	2.6	2.5	2.4
2-Butanone	3.1	4.3	3.7	2.9
Butanedione	1.4	0.92	1.2	1.0
Nicotine	3.2	3.3	2.8	2.6
Pyridine	14.6	24.0	18.3	20.3
Carbon Monoxide	3.3	3.6	4.7	2.5
Carbon Dioxide	9.0	11.3	8.9	8.1
Toluene	8.3	6.7	5.9	5.6
SS/MS (calculated from Table 5)	1.1	2.1	3.6	2.1

Table 7. Carbon dioxide and carbon monoxide in sidestream and mainstream smoke.

Cigarette	Delivery (mg/cigt)			
	CO₂		CO	
	SS	MS	SS	MS
Burley	448	50	46	14
Bright	759	67	57	16
Turkish	695	78	61	13
Ky. Ref. 1R1	617	76	56	22

Cigarette	SS/MS		CO₂/CO	
	CO₂	CO	SS	MS
Burley	9.0	3.3	9.8	3.6
Bright	11.3	3.6	13.2	4.2
Turkish	8.9	4.7	11.4	6.0
Ky. Ref. 1R1	8.1	2.5	11.0	3.5

Table 8. Nitriles in cigarette smoke.

Cigarette	(µg/cigt)					
	Acetonitrile		Hydrogen Cyanide		Acetonitrile Hydrogen Cyanide	
	SS	MS	SS	MS	SS	MS
Burley	1025	190	14	160	73	1.2
Bright	575	160	16	260	36	0.6
Turkish	735	210	25	230	29	0.9
Ky. Ref. 1R1	820	210	17	305	48	0.7

Table 9. Calculation of smoke formation temperatures.

From Figure 3:

$$\log T(°K) = -0.11 \log \frac{\Phi CH_3}{\Phi H} + \log 980$$
$$\log T_f = -0.11 \log \gamma + 2.991$$
$$T_f = 980\,\gamma^{-0.11}$$
$$T_f\,(°C) = 707\,\gamma^{0.15}$$

Boyd, et al (2)
$$T(°C) = 785\,\gamma^{-0.06}$$
$$\gamma = \frac{O_2}{N_2} \times \frac{CO_2}{CO}$$

Table 10. Toluene:benzene ratios in cigarette smoke.

Cigarette	SS	MS
Burley	2.1	1.8
Bright	2.1	1.8
Turkish	2.1	2.1
Ky. Ref. 1R1	2.0	1.7

The gas phase of each stream was collected at dry ice temperature in a stainless steel trap containing 40x80 mesh Polypak 2. The trap was connected to the injection port of a Varian model 1860 gas chromatograph which contained a 22 ft. x 0.125 in. stainless steel column containing the same packing and, also, maintained at dry ice temperature. The trap was provided with a helium flow of 75 ml/min while heating tapes were used to elute the components onto the cold column. The dry ice was removed from the column and the column oven was heated to 40°C. The

temperature was programmed at 10°/min to 140°C and held 4.5 min. The temperature was raised 6°/min until 240°C was reached. The temperature was held here until the end of the analysis. The injector temperature, detector temperature and filament current were 200°C, 270°C and 165 ma, respectively. Components separated in this manner were methane, acetylene, propane-propene, methyl chloride, acetone, methylfuran, propionaldehyde, 2-butanone, butanedione, carbon dioxide, benzene, toluene, pyridine and acetonitrile. Identities were based on retention times of authentic samples and mass spectrometry. Calibrations based on the Disc integrated peaks of known samples provided quantitation.

Sidestream carbon monoxide was measured by the passage of the gases which exited the cold trap, through a Unor nondispersive infrared analyzer. Mainstream carbon monoxide was measured by conventional infrared techniques.

Nicotine was determined by a cyanogen bromide technique (3) and hydrogen cyanide by the analysis of cyanide ion using an ion-selective electrode (13). Caution was used in the analysis of these two smoke components in that the mainstream nicotine resided mainly in the particulate phase but the sidestream nicotine was found equally in the gas and particulate phases. Hydrogen cyanide, as is well known, is found in both phases of mainstream smoke in varying proportion but we found it to reside exclusively in the particulate phase of sidestream smoke.

Pyrolysis apparatus and procedures have been described elsewhere (9).

RESULTS AND DISCUSSION

Backhurst and Hughes (1) proposed an equation (Table 5) from which cigarette consumption during mainstream and sidestream smoking can be calculated. The consumptions derived from this equation are given in Table 4.

Sidestream to mainstream ratios for several smoke components are given in Table 6, along with the ratios of consumption as determined by the Backhurst and Hughes equation.

Methyl chloride delivery followed cigarette consumption very well, and, with the exception of "propane-propene", deviations from consumption predictions may be considered small for most substances in Table 6.

The sidestream:mainstream ration of pyridine was found to be unusually high (15-24), much like that reported by Glock; 10 for pyridine, 43 for 3-vinyl pyridine (4), quite out of line with consumption data. This preference for sidestream delivery is to be expected on the basis of at least two observations:

(a) Alkaloid decomposition can lead to pyridine formation. Glock (4) showed that cigarettes containing added nicotine showed increased 3-vinyl pyridine delivery; most of the increase occurring in the sidestream. Nornicotine gave increases in the yields of both vinyl pyridine and pyridine, mainly in the sidestream.

(b) Nicotine has been shown to undergo essentially no decomposition during mainstream smoking (6). However, some nicotine was "lost" during our studies and, thus, decomposition took place preferentially in the sidestream. Neither nicotine nor nornicotine degrades extensivley in the mainstream. Perhaps the air flow is such that these stable, volatile tobacco components are swept ahead of the advancing coal during the puff that they actually "see" lower temperatures than they do during the comparative static conditions
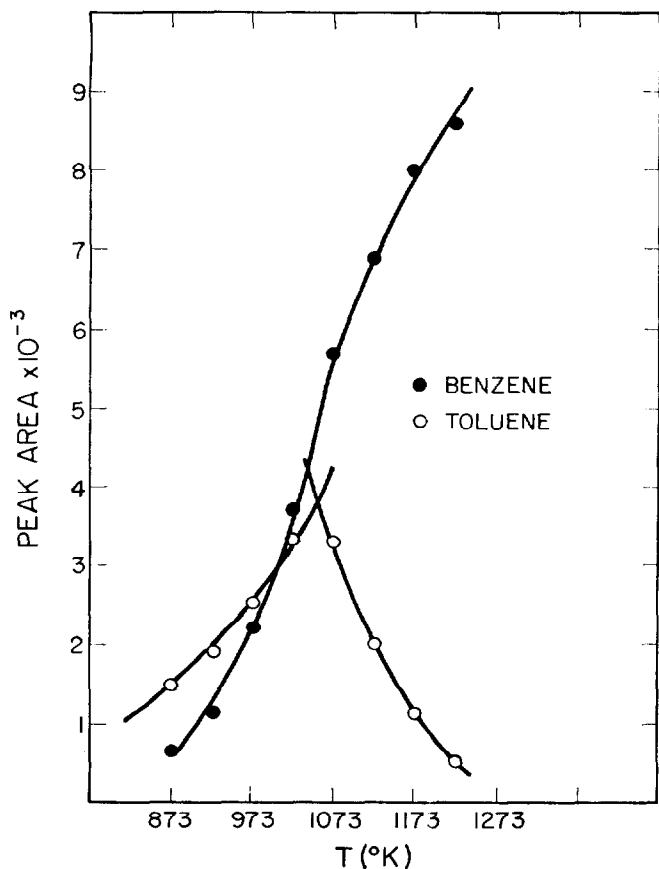
Figure 1. Benzene and toluene from the pyrolysis of Kentucky 1R1 tobacco.
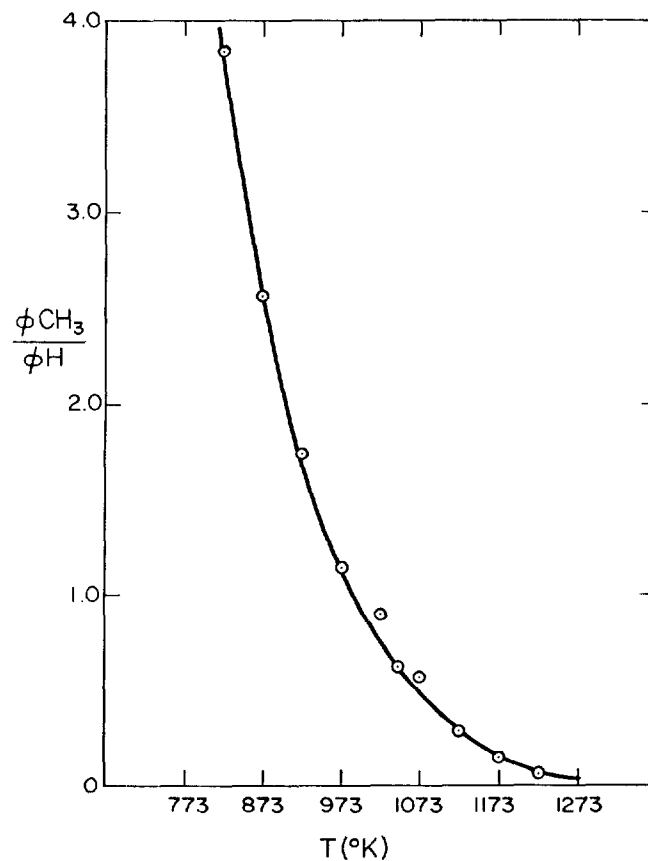

Figure 2. Toluene: bnezene ratios from the pyrolysis of Kentucky 1R1 tobacco.

between puffs. Similar behavior has been found to occur with the volatile tobacco additive menthol (7).

Carbon dioxide was found to prefer the sidestream far more than carbon monoxide. Implied then, is a far more complete combustion occurring during smoulder than during the puff. **Table 7** presents CO_2/CO data in varying ways which show:

(1) The higher actual deliveries of CO_2 to both streams.

(2) The much greater preference for the sidestream shown by CO_2 as compared with CO.

(3) The CO_2/CO ratios for the two streams. These are high and nearly constant in the sidestream despite the differences in cigarette types. We believe the ratios to be characteristic of the oxidizing conditions prevailing in the two streams.

Two nitriles worthy of mention are hydrogen cyanide and acetonitrile. Hydrogen cyanide is unique in that it is delivered almost exclusively to the mainstream. The closely related acetonitrile, however, prefers the sidestream **(Table 8)**. The resulting CH_3CN/HCN ratios are typically high in the sidestreams and low in the mainstream. Pyrolysis of the tobaccos yielded high CH_3CN/HCN values at low temperatures and low values at high temperatures. In fact, hydrogen cyanide was difficult to detect below 600°C. It would appear then, that the nitrile precursors are exposed to much higher temperatures of about 600°C for the high sidestream ratios and 700° for the low ratios of the mainstream. Though the high values of the sidestream and the low values of the mainstream are thought to be quite characteristic, the wide variation in the sidestream ratios (29-73) indicates a strong dependency of the ratios on tobacco types. As a result, no further correlations with physical data were sought.

Pyrolytic yields of toluene and benzene were found

to be independent of tobacco types and characteristic of temperature. Yields of these aromatics from the pyrolysis of Kentucky Reference 1R1 tobacco are given as functions of temperature in **Figure 1** and a plot of the toluene:benzene ratios *versus* temperature is shown in **Figure 2**. The ratios are shown to be large at low temperatures and small at high temperatures. A plot of log T *versus* the log of the toluene:benzene ratio that we will call gamma **(Figure 3)** gives a straight line which is of a form similar to that obtained by Boyd, *et al.*, from thermocouple measurements of coal temperature and mainstream gas phase components **(Table 9)**. Using this chemical thermometer, we determined that the precursors of benzene and
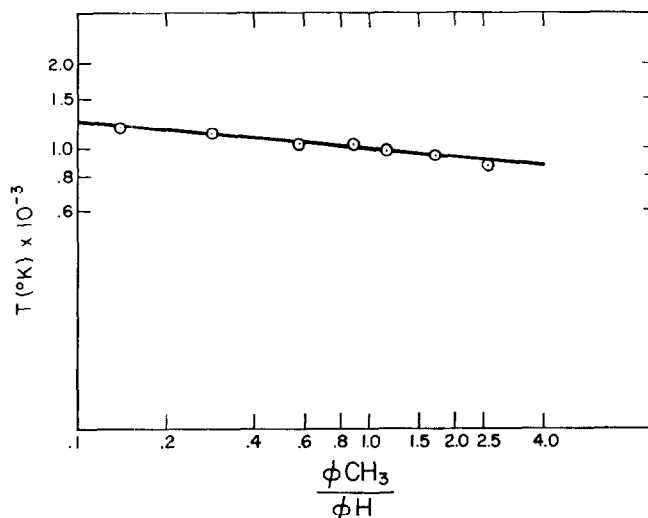

Figure 3. A plot of the log of the absolute temperature versus the log of the toluene: benzene ratio.

toluene were exposed to identical temperatures in the sidestream of all cigarettes studied and except for the Turkish cigarette, a characteristic ratio was obtained for the mainstream (Table 10).

Using the equation in Table 9, an average temperature of 633°C can be calculated for the sidestream and 647°C for the mainstream except that of the Turkish cigarette which was identical to the average sidestream temperature. The high puff count of the Turkish cigarette and other data in Table 4 are consistent with the notion of a cooler mainstream smoke for this cigarette.

As expected, the formation temperatures, T_f, that might be estimated from either the nitrile or toluene: benzene ratios are lower than the maximum mean temperatures measured physically. For example, Hook (5) obtained average maximum temperatures of 850°C in mainstream smoke and 780°C in the sidestream for a difference of 70° which is to be compared with 100° and 14° for the differences in the formation temperatures of the nitriles and the two aromatics, respectively.

We would like to suggest then, that the temperatures which are of importance to any given compound in cigarette smoke are the temperatures to which that compound's precursors are effectively subjected during the smoking process. For most compounds, these temperatures will be well below peak coal temperatures determined by physical methods. It follows though, that changes in the peak coal temperature can well mean changes along the entire temperature profile. However, any given change may affect different classes of compounds in different ways.

Inspection of the product ratios of selected members of a given class of compounds from different cigarettes and the comparison of these ratios with pyrolysis data is offered as a method of determining the extent to which observed differences within that class across different cigarettes may be attributed to thermal factors.

SUMMARY

Comparisons of smoking results with pyrolysis results indicate that for any given coal condition different portions of the tobacco substrate respond to different portions of the temperature profile. Stable volatiles such as nicotine and nornicotine degrade more during the formation of sidestream smoke than they do during the formation of the mainstream. Hydrogen cyanide and acetonitrile behavior, on the other hand, suggests that higher temperatures act on their precursors during mainstream formation. Benzene and toluene act as if similar average conditions prevail in both streams. It would appear that temperatures are available during the formation of both smoke streams sufficiently above the formation threshold of smoke products that the substrate and the egress of distillation-pyrolytic products become the controlling factors in the determination of product distribution in cigarette smoke.

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