Fractionation and Phenol Composition of Cellulose Cigarette Smoke Condensate[†]

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Fractionation of smoke condensate and a detailed analysis of phenols in the cellulose cigarette smoke were performed during the course of systematic compositional studies of the smoke. Nearly equal yields of phenolic, acidic and neutral fractions were obtained in fractionation of cellulose cigarette smoke condensate. Thirtyseven phenols were newly identified in the smoke of cellulose cigarette in addition to six phenols ever found in pyrolysis products of cellulose. Semi-quantitative determination of some of these phenols revealed that dihydric phenols, such as catechol, hydroquinone, resorcinol and their alkyl derivatives were the main phenols and monohydric phenols were the minor phenols.

Cellulose on burning produces a pungent smoke and the so-called "paper burning aroma." The products formed by pyrolysis or combustion of cellulose have been studied^{2~10)} by many investigators to examine the mechanism of thermal cellulose decomposition, the ignition of cellulose kindling, and to develop and evaluate better flame-retardants. None of these studies have comprehensively examined the products of cellulose, and the components identified or quantitatively determined have been small.

For the purpose of clarifying factors affecting harshness and the "paper burning aroma" of tobacco cigarette smoke, we began to study the composition of cellulose cigarette smoke systematically. In the present paper, analyses were performed on cellulose cigarette smoke, fractionation of the smoke condensate and a detailed analysis of phenols in the smoke condensate.

EXPERIMENTAL

Sample. Toyo filter paper No. 2 (ca. 98% α -

cellulose) was sprayed with 0.5% (w/w) aqueous KNO_3 and made into cigarettes (70 mm length and 25 mm circumference). The cigarettes were equilibrated at 60% relative humidity at 20°C and those to be used in the subsequent experiments were selected on the basis of draw resistance (30 ± 3.0 mm H_2O pressure) and weight (0.7 ± 0.3 g).

Smoking conditions. The smoking machine was operated to take a single 35 ml puff of 2 seconds duration per minute, and the cellulose cigarettes were smoked to a butt length of 30 mm. (Puff No. 5.0)

Some analyses of cellulose cigarette smoke. Total particulate matter (TPM),¹¹⁾ water in TPM,¹²⁾ pH ,¹³⁾ carbonyl compounds¹⁴⁾ and total volatile phenols¹⁵⁾ were determined according to methods for analyzing these components in cigarette smoke.

Fractionation of smoke condensates. The smoke condensate of 20 cellulose cigarettes collected in a cold trap cooled with dry ice-methanol was fractionated into phenolic, acidic and neutral fraction according to the usual manner. The phenolic fraction was reextracted with aqueous 3% NaHSO_4 solution to separate the phenolic aldehydes from simple phenols, as shown in Fig. 1. The ether solution of each fraction was dried over anhydrous Na_2SO_4 and concentrated with rectifying column at 38~39°C, then the ether-free fractions were weighed.

Preparation of phenol samples for identification. The ether solution of the smoke condensate of 200 cellulose cigarettes was extracted with 5% NaHCO_3 containing a small quantity of ascorbic acid as an

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FIG. 1. Fractionation of Cellulose Cigarette Smoke Condensate.

antioxidant, and the extract was discarded. After about one-fifth of the ether layer was removed for extracting catechols, the remainder was extracted with 5% NaOH again containing a small quantity of ascorbic acid. The extract was acidified to pH 1 with 50% H_3PO_4 and extracted with ether. About a quarter of the ether extract was dried over anhydrous Na_2SO_4 and concentrated to dryness. About one-half of the residue was trimethylsilylated with trimethylsilylation reagent, BSTFA, and pyridine and the other half of the residue was methylated with diazomethane. The remaining extract was further extracted with 3% NaHSO_3 . The extract was adjusted to pH 1 with 50% H_2SO_4 and extracted with ether. The ether extract was dried over anhydrous Na_2SO_4 and concentrated to dryness. The phenolic aldehydes thus obtained were trimethylsilylated.

Catechols¹⁶⁾ were obtained from 5% NaHCO_3 treated ether solution by extracting the solution with 5% $\text{K}_2\text{B}_4\text{O}_7$, acidifying the extract and extracting the

acidic solution with ether, and then trimethylsilylated.

Preparation of phenol samples for semi-quantitative analysis. The smoke condensate of 5 cellulose cigarettes collected in a cold trap cooled with dry ice-methanol was dissolved in 25 ml of ether, to which 100 μg *o*-hydroxyacetophenone was added as an internal standard, and extracted with 30 ml of 5% NaHCO_3 containing a small quantity of ascorbic acid as an antioxidant. After washing with saturated NaCl solution, the ether layer was extracted with 20 ml of 5% NaOH containing a small quantity of ascorbic acid as an antioxidant. After washing with 20 ml of ether, the aqueous layer was acidified to pH 1 with 50% H_3PO_4 under ice-cooling and extracted twice with 20 ml of ether each time. The combined ether layers were washed with saturated NaCl solution, dried over anhydrous Na_2SO_4 and evaporated to release the free phenols, which were subsequently converted to trimethylsilyl (TMS) derivatives with BSTFA and pyridine.

Calibration curves for each phenol were obtained by using a mixture of each phenol and internal standard (*o*-hydroxyacetophenone), which was trimethylsilylated.

Identification of phenols. Phenols in the smoke were identified by comparing their gas chromatography and gas chromatography-mass spectrometry data with those of authentic compounds and by examining their chemical behaviors (selective reactivity with sodium hydrogen sulfite or potassium borate).

Gas chromatography (GC). Each solution of TMS derivatives was analyzed with a Hitachi Model 063 gas chromatograph equipped with a flame ionization detector. A ϕ 0.25 mm $\times$ 20 m glass capillary column coated with silicone oil OV-101 was used. The column oven temperature was programmed from 60°C to 200°C at a rate of 2°C/min. The injection port was kept at 250°C. Helium was used as a carrier gas at a flow-rate of 1.0 ml/min with a split ratio of 1:30.

With methyl ethers of phenols, a ϕ 0.25 mm $\times$ 30 m glass capillary column coated with PEG 20 M was used and the column oven temperature was programmed from 60°C to 170°C at a rate of 2°C/min. Other conditions were identical with those of the TMS derivatives mentioned above.

Gas chromatography-mass spectrometry (GC-MS). GC-MS was conducted with a Hitachi Model RM-50GC GC-MS. Gas chromatography was conducted under the same conditions described above except that the carrier gas was controlled with an inlet pressure of 0.2 kg per cm². The mass spectrometer was operated at an ionization voltage of 70 eV and an ion source temperature of 200°C.

RESULTS AND DISCUSSION

Chemical analysis

Results of smoke analysis of cellulose cigarette are shown in Table I. As references, the values for the smoke of flue-cured tobacco of Ishiguro *et al.*¹⁷⁾ are also shown. Cellulose cigarette smoke pH (3.81) was considerably lower than tobacco cigarette smoke pH (6.03). The total amount of TPM was lower in cellulose cigarette smoke than in tobacco cigarette smoke, but no significant difference was present in the moisture content of either TPM.

Cellulose cigarette smoke was approximately two times higher in carbonyl compounds content than tobacco cigarette smoke, but the amount of total volatile phenols in cellulose cigarette smoke was only about one-

TABLE I. SMOKE ANALYSIS OF CELLULOSE CIGARETTE

	Cellulose cigarette smoke	Cigarette smoke ^{b)}
pH	3.81	6.03
TPM	16.17 mg/cigarette	32.21 mg/cigarette
Water in TPM	3.06 "	3.20 "
Dry TPM	13.11 "	28.01 "
Carbonyl compounds ^{a)}	4.09 "	2.34 "
Total volatile phenols	28.0 μ g/cigarette	284.0 μ g/cigarette

^{a)} The amount of carbonyl compounds obtained as 2,4-dinitrophenylhydrazone was calculated as acetaldehyde.

^{b)} Flue-cured tobacco (A Leaf 1).¹⁷⁾

TABLE II. FRACTIONATION OF CELLULOSE CIGARETTE SMOKE CONDENSATE

Fraction	Yield (mg/cigarette)	Ratio in dry TPM (%)
Total phenolics	1.50	11.4
Phenolics A ^{a)}	0.17	1.3
Phenolics B ^{b)}	0.85	6.5
Acidic	1.61	12.3
Neutral	1.56	11.9
Total	4.67	35.6

^{a)} The phenolic fraction soluble in 3% NaHSO₃.

^{b)} The phenolic fraction insoluble in 3% NaHSO₃.

tenth that of tobacco cigarette smoke.

Fraction yields of smoke condensate

Table II shows the yields of each fraction of cellulose cigarette smoke condensate. No significant differences were observed in the yields of phenolic, acidic and neutral fraction, and the total amount of these three fractions was 35.6% of the dry TPM amount (Table I). In tobacco cigarette smoke,¹⁸⁾ neutral compounds are abundant to a marked degree, and therefore the yield of phenolic fraction was only about one-fifth that of neutral fraction and the yield of the acidic fraction was about two-thirds the phenolic fraction. In addition to these three fractions, tobacco cigarette smoke contained fair amounts of basic fraction, and the sum of these four fractions reached 93.8% the weight of dry TPM.

As seen by these results, the recovery of cellulose cigarette smoke components through

the fractionation procedure was considerably lower than that of tobacco cigarette smoke. This seems to indicate that ether insoluble components are more abundant in cellulose

cigarette smoke than in tobacco cigarette smoke.

The ratio of phenolic aldehydes soluble in aqueous 3% sodium hydrogen sulfite to total

FIG. 2. Gas Chromatograms of TMS Derivatives of Phenols in Cellulose Cigarette Smoke.

(a): Total phenols soluble in 5% NaOH

(b): Phenolic aldehydes soluble in 3% NaHSO₃

TABLE III. PHENOLS IDENTIFIED BY GC AND GC-MS IN CELLULOSE CIGARETTE SMOKE

Peak No.	Phenols	Methods of identification		References
1	Phenol	GC ^{a)}	MS ^{a), d), e)}	9, 19, 23
2	<i>o</i> -Cresol	" ^{a), e)}	" ^{a), d), e)}	9, 19, 23
3	<i>m</i> -Cresol	" ^{a), e)}	" ^{a), d), e)}	9, 19, 23
4	Unknown			
5	<i>p</i> -Cresol	GC ^{a)}	MS ^{a), d), e)}	9, 23
6	Unknown			
7	Unknown			
8	<i>o</i> -Ethylphenol	GC ^{a)}		20, 24
9	2,5-Xylenol	" ^{a)}	MS ^{d)}	9, 20, 23
10	<i>o</i> -Methoxyphenol	" ^{a)}	" ^{a)}	20, 23
"	<i>m</i> -Ethylphenol	" ^{a)}	" ^{a)}	20, 23
"	2,4-Xylenol	" ^{a)}	" ^{a)}	20, 23
11	3,5-Xylenol	" ^{a)}	" ^{a), d)}	20, 22
12	2,6-Xylenol	" ^{a)}	" ^{a), d)}	20, 23
13	<i>p</i> -Ethylphenol	" ^{a)}	" ^{a), d)}	20, 23
14	2,3-Xylenol	" ^{a)}	" ^{d)}	20, 24
15	3,4-Xylenol	" ^{a)}	" ^{a), d)}	9, 20, 23
16	Unknown			
17	<i>p</i> -Vinylphenol	GC ^{a)}	MS ^{d)}	20, 23
18	<i>m</i> -Methoxyphenol	" ^{a)}	" ^{d)}	20, 23
19	<i>p</i> -Methoxyphenol	" ^{a)}	" ^{a), c)}	20, 23
20	Salicylaldehyde	" ^{a), b)}	" ^{a), b)}	23
21	Catechol	" ^{a), b), c), e)}	" ^{a), b), c), d), e)}	20, 23, 24
22	<i>p</i> -Hydroxybenzaldehyde	" ^{a), b)}	" ^{a), b)}	26
23	<i>o</i> -Hydroxyacetophenone	" ^{a)}		22
24	3,4,5-Trimethylphenol	" ^{a)}		18
25	2,6-Dimethoxyphenol	" ^{a)}	MS ^{a)}	21
26	Resorcinol	" ^{a), b), e)}	" ^{a), b), e)}	22, 23, 24
27	<i>m</i> -Hydroxyacetophenone	" ^{a)}	" ^{b), d)}	22
"	4-Methylcatechol	" ^{a), c), e)}	" ^{a), c), d), e)}	16
28	3-Methylcatechol	" ^{a), c), e)}	" ^{a), c), e)}	16
29	Hydroquinone	" ^{a), b), c), e)}	" ^{a), b), c), d), e)}	20, 23, 24
30	<i>p</i> -Hydroxyacetophenone	" ^{a)}	" ^{c)}	22
31	Orcinol	" ^{a), e)}	" ^{d), e)}	18
32	2-Methylresorcinol	" ^{a), c)}	" ^{b), d), e)}	18
33	4-Ethylcatechol	" ^{a), c), e)}	" ^{a), c), e)}	16
"	Methylhydroquinone	" ^{a)}	" ^{a), d)}	18
34	Vanillin	" ^{a), b)}	" ^{b)}	26
35	4-Ethylresorcinol	" ^{a), b)}	" ^{a), b)}	18
36	α -Naphthol	" ^{a)}	" ^{d)}	22, 23
37	β -Naphthol	" ^{a)}	" ^{d)}	22, 23
38	Pyrogallol	" ^{a), b), c)}	" ^{a), b), c)}	16
39	Unknown			
40	3,4-Dihydroxybenzaldehyde	GC ^{a), b), d), e)}	MS ^{a), b), d), e)}	23, 26
41	1,2,4-Trihydroxybenzene	" ^{a), d)}	" ^{e)}	
42	2,5-Dihydroxybenzaldehyde	" ^{a), b)}	" ^{a), b)}	
43	Syringaldehyde	" ^{a), b)}		26
"	2,4-Dihydroxybenzaldehyde	" ^{a), b)}		

a) TMS derivatives of all phenols soluble in 5% NaOH.

b) TMS derivatives of phenols soluble in 3% NaHSO₃.c) TMS derivatives of phenols soluble in 5% K₂B₄O₇.d) TMS derivatives of phenols insoluble in both 3% NaHSO₃ and 5% K₂B₄O₇.

e) Methyl ethers of all phenols soluble in 5% NaOH.

phenols was slightly lower in cellulose cigarette smoke (11%) than in tobacco cigarette smoke (14%).

Gas chromatograms of phenols

Chromatograms of TMS derivatives of all phenols extracted with sodium hydroxide solution and phenolic aldehydes extracted with sodium hydrogen sulfite solution are shown in Fig. 2 (a) and 2 (b).

Among about 200 peaks in Fig. 2 (a), peaks identified by GC and GC-MS and the chemical reactivities for potassium borate or sodium hydrogen sulfite are shown in Table III. Although only six kinds of phenols (phenol, *o*-, *m*-, *p*-cresol, 2,5- and 3,4-xyleneol,) have been reported^{9,10)} in cellulose pyrolyzate, 37 phenols were positively or tentatively newly identified in addition to the six mentioned phenols in this study.

Semi-quantitative analysis of phenols

The approximate amounts of each identified

phenol are shown in Table IV. Most individual phenols through the sample preparing process for semi-quantitative analysis were recovered at 70~90%, but monohydroxybenzaldehydes were recovered as low as *ca.* 20%. On the other hand, the recovery of dihydric phenols, such as catechols and hydroquinones was nearly zero when ascorbic acid, antioxidant, was not added, and the recovery of trihydric phenols, such as pyrogallol was nearly zero even when ascorbic acid was added.

As evident from Table IV, the predominant phenols in cellulose cigarette smoke were dihydric phenols such as catechol, hydroquinone, resorcinol and their alkyl derivatives. The total amount of these dihydric phenols was *ca.* 160 $\mu\text{g}/\text{cigarette}$, which accounted for nearly 80% of the total amount of phenols determined by gas chromatography. On the other hand, monohydric phenols were generally quantitatively small, and their total amount was *ca.* 45 $\mu\text{g}/\text{cigarette}$, but this value was larger than that of total volatile phenols ob-

TABLE IV. SEMI-QUANTITATIVE DETERMINATION OF PHENOLS IN CELLULOSE CIGARETTE SMOKE

Phenols	Amount ($\mu\text{g}/\text{cigarette}$)	Phenols	Amount ($\mu\text{g}/\text{cigarette}$)
Phenol	12.2	<i>p</i> -Hydroxyacetophenone	tr
<i>o</i> -Cresol	6.8	2,6-Dimethoxyphenol	3.3
<i>m</i> -Cresol	4.6	α -Naphthol	0.6
<i>p</i> -Cresol	2.6	β -Naphthol	^{c)}
<i>o</i> -Ethylphenol	0.6	Catechol	75.0
<i>p</i> -Ethylphenol	0.3	Resorcinol	6.6
2,3-Xyleneol	1.8	Hydroquinone	31.4
2,5-Xyleneol	1.1	Orcinol	1.3
2,6-Xyleneol	0.5	4-Methylcatechol	11.9
3,4-Xyleneol	0.5	3-Methylcatechol	12.3
3,5-Xyleneol	1.9	2-Methylresorcinol	^{c)}
<i>o</i> -Methoxyphenol	5.5 ^{a)}	Methylhydroquinone	19.4 ^{b)}
<i>m</i> -Ethylphenol		4-Ethylcatechol	
2,4-Xyleneol		4-Ethylresorcinol	1.4
<i>m</i> -Methoxyphenol	^{c)}	2,4-Dihydroxybenzaldehyde	^{d)}
<i>p</i> -Methoxyphenol	2.2	2,5-Dihydroxybenzaldehyde	^{d)}
Salicylaldehyde	^{c)}	3,4-Dihydroxybenzaldehyde	^{d)}
<i>p</i> -Hydroxybenzaldehyde	tr	Vanillin	^{d)}
<i>p</i> -Vinylphenol	tr	Syringaldehyde	^{d)}
3,4,5-Trimethylphenol	0.6	Pyrogallol	^{d)}
<i>m</i> -Hydroxyacetophenone	^{c)}	1,2,4-Trihydroxybenzene	^{d)}

^{a)} Determined as *o*-methoxyphenol which was predominant.

^{b)} Determined as methylhydroquinone.

^{c)} Not determined because of their insufficient separation.

^{d)} Not determined in this study.

tained by the colorimetric method.

Of these monohydric phenols, phenol was largest, followed by *o*-cresol; other monohydric phenols, such as *p*-cresol, xylenol, *etc.* were found at relatively low quantitative levels.

The levels of phenolic isomers were estimated to increase in general in the order of *m*-, *p*-, *o*-substituted phenols but in the case of cresol isomers, *p*-substituted phenol indicated the lowest level. In this study, phenolic aldehydes and trihydric phenols were not estimated, but Fig. 2 (b) shows that the levels of dihydroxybenzaldehyde isomers increased in the order of *m*-, *p*-, *o*-diphenol.

The sum of these mono- and dihydric phenols amounted to *ca.* 0.2 mg/cigarette, which was considerably lower than 1.5 mg/cigarette obtained as phenol weight fraction. This indicates that in addition to phenols determined in this study, considerable components, for example, polyhydric phenols, which could not be analyzed by gas chromatography, might be present in the phenol fraction of cellulose cigarette smoke.

When these phenols in cellulose cigarette smoke are compared with phenols in tobacco cigarette smoke,¹⁸⁾ a relatively close relationship is seen in the phenol types and relative concentrations. For example, dihydric phenols, such as catechol, hydroquinone and their alkyl derivatives, which are the major phenols in cellulose cigarette smoke, are also predominant in tobacco cigarette smoke.

However, different points were evident as follows: phenols having vinyl group which are contained in relatively large quantity in tobacco cigarette smoke were hardly found in cellulose cigarette smoke; the amount of *p*-substituted phenols in isomers was relatively small in cellulose cigarette smoke compared with tobacco cigarette smoke; and the total amount of mono- and dihydric phenols in cellulose cigarette smoke was about one-third that of tobacco cigarette smoke per weight of consumed cigarette.

While cellulose is the main component of tobacco leaves, many other components, such as starch, hemicellulose, pectin, lignin, protein

and resinous material are also present in considerable amounts.

It has been reported^{19~21)} that considerable amounts of phenol and cresols were produced on pyrolysis of some of these other tobacco components, but no comprehensive study has been reported to date.

In the present study, many types of phenols were found to be present in cellulose cigarette smoke, but the fact that the total amount of phenols in cellulose cigarette smoke was considerably lower than that in tobacco cigarette smoke may indicate that cellulose is not a good precursor of phenols in tobacco cigarette smoke.

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