

## Composition of Gaseous Combustion Products of Polymers

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### Synopsis

The gaseous products generated by the flaming combustion of ten kinds of synthetic polymers and a kind of wood (cedar) under the same conditions (sample weight, 0.1 g; temperature, 700°C; air flow rates, 50 and 100 l./hr) were quantitatively analyzed by infrared spectrophotometry, gas chromatography, and colorimetric tube method. The main hydrocarbons generated were methane, ethylene, and acetylene. The amount of acetylene generated by the flaming combustion of polymers was much larger than the amount of acetylene formed by pyrolysis at 700°C in nitrogen. Acetylene increased in quantity with increasing air. For nitrogen compounds, hydrogen cyanide was generated from every polymer containing nitrogen used, but ammonia was detected only for nylon 66 and polyacrylamide. Nitrogen monoxide and nitrogen dioxide were detected only in small amounts. Nitrous oxide was detected in the gaseous products generated by the nonflaming combustion of urea resin and melamin resin. It was also found that about 70% of the nitrogen in N-66 and PAA was converted into nitrogen gas ( $N_2$ ) by combustion under the conditions described above.

### INTRODUCTION

In recent years, the generation of the gaseous combustion products of synthetic polymers, especially poisonous gases due to fires, has been increasingly drawing attention as a serious problem. At present, experimental data<sup>1-13</sup> on the composition of gases produced by combustion are still lacking for many polymers, while there are many reports on the composition of gases generated by the pyrolysis of polymers in an inert gas atmosphere or under reduced pressure. Moreover, little comparative information<sup>3,12</sup> is available on the composition of gases generated by the combustion of several kinds of polymers under the same combustion conditions.

A combustion and collection apparatus was devised.<sup>11</sup> This apparatus made it possible to burn sample materials at a desired temperature and with a desired rate of air supply, and it also made it possible to collect the gaseous combustion products without substantial dilution. In this investigation, the composition of the gaseous combustion products that were produced by combustion under the same conditions of ten kinds of synthetic polymers and a kind of wood were quantitatively analyzed by infrared spectrophotometry, gas chromatography, and colorimetric tube method, and these components were compared with each gaseous pyrolyzate produced by pyrolysis at 700°C

in nitrogen atmosphere. The process of the formation of the acetylene which was produced by the combustion of most of the polymers was also discussed.

## EXPERIMENTAL

### Combustion and Collection Apparatus

The apparatus for burning and collecting gaseous combustion products is shown in Figure 1. This apparatus consists of the following four units: (1) a combustion unit (E-H) equipped with a quartz cylindrical combustion chamber G (inner diameter, 46 mm; height, 220 mm) and an electric furnace E (inner diameter, 60 mm; height, 200 mm); (2) a gas supply unit (A-C) for introducing air into the combustion chamber G; (3) a piston-cylinder-type gas collection unit (K-M); and (4) a driving unit (O and P) for operating the piston.

This apparatus is operated in the following sequence: (1) The combustion chamber G is heated to a fixed temperature (700° or 800°C) by the electric furnace E. (2) The air pump is set in motion to feed air into the combustion chamber at a fixed air flow rate (50 or 100 l./hr) (during this process, the sample inlet H is being opened). (3) Simultaneously with the operation of the suction stroke at a predetermined speed, 0.1 g sample (1 grain) material is dropped into combustion chamber G, and the sample inlet is closed. (4) The gaseous combustion products generated in the combustion chamber G are then introduced into gas collector K. The displacement of the piston used for suctioning the gaseous combustion products is measured for the purpose of getting the total volume of the gases collected; in this experiment, however, the piston was pulled to a fixed point so that the total volume might be constant (2000 ml). (5) Immediately after the gaseous combustion products are collected in gas collector K, a cylindrical gas cell (volume, 250 ml; path length, 10 cm; pressure, below 0.5 torr) for IR measurement is connected to end J which was disconnected after collecting the gases. The gases in the collector K are introduced into the cell under a temperature of 25°C and a pressure of 1 atmosphere.

### Pyrolysis and Collection Apparatus

The apparatus for pyrolyzing polymers and collecting gaseous pyrolyzates is shown in Figure 2. This apparatus consists of the pyrolysis unit equipped with a quartz pyrolysis tube D (inner diameter, 18 mm; height, 200 mm), an

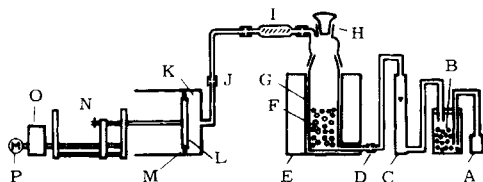


Fig. 1. Combustion and collection apparatus: (A) air pump, (B) silica gel, (C) flow meter, (D) connector, (E) electric furnace, (F) quartz beads, (G) combustion chamber, (H) sample inlet, (I) filter, (J) connector, (K) gas collector, (L) piston, (M) seal ring (Teflon), (N) stopper, (O) stepless speed change device, (P) motor.

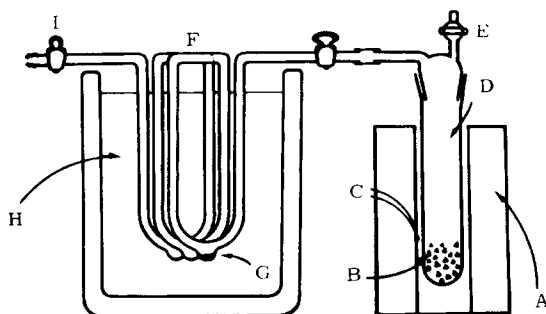


Fig. 2. Pyrolysis and collection apparatus: (A) electric furnace, (B) sample, (C) thermocouple, (D) quartz pyrolysis tube, (E) cock, (F) pyrex trap tube, (G) pyrolyzate, (H) methanol-Dry Ice freezing mixture, (I) cock.

electric furnace A (inner diameter, 20 mm; height, 200 mm), a trap unit equipped with a Pyrex trap tube F, and a Dewar vessel containing methanol-Dry Ice freezing mixture H.

This apparatus is operated in the following sequence. (1) A sample of predetermined weight (0.02–0.1 g) is put into pyrolysis tube D. (2) Air in the pyrolysis tube and the trap tube is replaced with nitrogen which is introduced through cock E or I. (3) After replacing the air with nitrogen, cocks E and I are closed. (4) The trap tube F is dipped in liquid nitrogen, and the pyrolysis tube D is put into electric furnace A which is heated at a fixed temperature (700°C). (5) After pyrolysis, the gas cell for IR measurement is connected with cock I. The trapped pyrolyzate is vaporized into the gas cell by pouring boiling water into trap tube F. In order to the gaseous pyrolyzate remaining in the pyrolysis tube into the gas cell, cock E is opened to introduce air into the pyrolysis tube.

### The Apparatus for Collecting the Components of Methane Flame and Ethylene Flame

The apparatus shown in Figure 3 was used for collecting the components of methane flame and ethylene flame. The components of the upper, the middle, and the lower parts of the flame were separately collected by syringe J shown in Figure 3, the extreme point of the needle being thrust into the center of each part of the flame. The suctioning of the flame components was conducted slowly, at a suction speed which kept the flame most nearly in shape.

### Analyses

Infrared spectrometry was the main method used in this analysis. The bands of the infrared spectra used for determining the components were as follows: hydrogen chloride, 2769  $\text{cm}^{-1}$ ; carbon dioxide, 2321  $\text{cm}^{-1}$ , nitrous oxide, 2229  $\text{cm}^{-1}$ ; carbon monoxide, 2165  $\text{cm}^{-1}$ ; carbonyl sulfide, 2078  $\text{cm}^{-1}$ ; sulfur dioxide, 1379  $\text{cm}^{-1}$ ; ammonia, 1122  $\text{cm}^{-1}$ ; hydrogen cyanide, 709  $\text{cm}^{-1}$ ; methane, 1305  $\text{cm}^{-1}$ ; ethylene, 949  $\text{cm}^{-1}$ ; acetylene, 728  $\text{cm}^{-1}$ .

Nitrogen gas ( $\text{N}_2$ ) generated by the combustion of polymers containing ni-

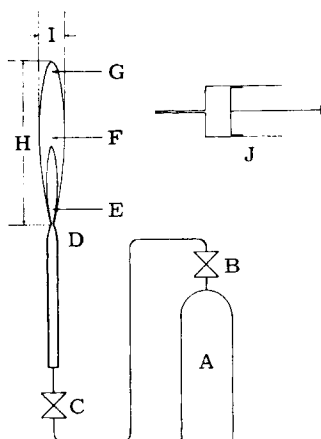


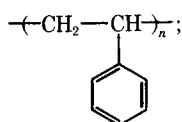
Fig. 3. Apparatus for collecting the components of methane flame or ethylene flame: (A) methane gas or ethylene gas, (B) and (C) valves, (D) quartz nozzle, (E) lower part of flame, (F) middle part of flame, (G) upper part of flame, (H) ca. 10 cm, (I) ca. 10 mm, (J) syringe for collecting the components of the flame.

trogen was analyzed by gas chromatography using a thermal conductivity detector, with a molecular sieve 5A packed column. In this experiment, a sample was burned in a mixed gas atmosphere consisting of argon and oxygen in the ratio of 79:21 instead of air.

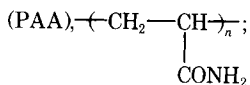
For nitrogen monoxide and nitrogen dioxide, colorimetric tubes having a range of 1 to 100 ppm were used.

### Samples

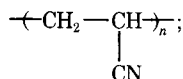
The following samples were used for the present studies: (1) polyethylene (PE),  $-(\text{CH}_2 - \text{CH}_2)_n$ ; (2) polystyrene (PS),



(3) nylon 66 (N-66),  $[\text{OC}(\text{CH}_2)_4\text{CONH}(\text{CH}_2)_6\text{NH}]_n$ ; (4) polyacrylamide

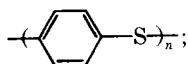


(5) polyacrylonitrile (PAN),



(6) three kinds of polyester-type polyurethanes (diisocyanate; tolylene diisocyanate, 1,5-naphthalenediisocyanate, diphenylmethane-4,4'-diisocyanate);

(7) poly(phenylene sulfide) (PPS),



(8) diaminodiphenylmethane-cured epoxy (bisphenol A-type) resin (ER); (9) urea-formaldehyde resin (UR); (10) melamine-formaldehyde resin (MR); and (11) cedar (WD). These polymers were all commercially available and do not contain submaterials of filler, plasticizer, pigment, and so forth.

## RESULTS AND DISCUSSION

The analytical results of the components of the gaseous combustion products of ten kinds of polymers and one kind of wood (cedar) which were burned under the same combustion conditions (sample weight, 0.1 g; temperature, 700°C; air flow rate, 50 and 100 l/hr) are shown in Table I. These results are based on means of three or more repeated tests. The combustion of each sample started immediately after dropping it into the combustion chamber, and the combustion continued with a constant flame from the start to the end under the conditions described above. However, MR alone burned without flame under these conditions. The quantities of the components other than ammonia shown in Table I could be determined within less than 10% of the coefficient of variation (*C.V.*). The reproducibility in determining ammonia is poor (*C.V.* ca. 20%), probably because ammonia was influenced in its generation quantity even by only a slight change in combustion conditions, and also because ammonia is a sort of water-soluble gas.

### Hydrocarbons

The main gaseous hydrocarbons produced by the flaming combustion of polymers were methane, ethylene, and acetylene.

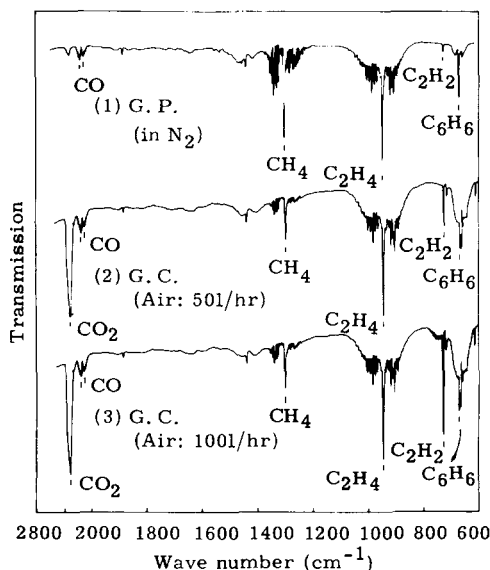


Fig. 4. Infrared spectra of gaseous pyrolyzate (G.P.) and gaseous combustion products (G.C.) of polyethylene: sample weight (1) 0.02 g, (2) and (3) 0.1 g; temperature, 700°C.

TABLE I  
Analytical Results of the Composition of Gaseous Combustion Products of Polymers by Infrared Spectrophotometry

Sample (0.1 g)	Air flow rate, l./hr	Composition, mg/g of sample										
		CO <sub>2</sub>	CO	COS	SO <sub>2</sub>	N <sub>2</sub> O	NH <sub>3</sub>	HCN	CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>2</sub>	
Polyethylene	100	738	210					72	185		34	
	50	502	195					65	187		10	
Polystyrene	100	619	178					7	18		13	
	50	590	207					7	16		6	
Nylon 66	100	590	205			10	31	40	94		15	
	50	563	194			4	26	39	82		7	
Polyacrylamide	100	796	157			17	18	16	10		9	
	50	738	173			32	21	20	13		4	
Polyacrylonitrile	100	556	108				56	6			7	
	50	630	132				59	8			4	
Polyurethane <sup>a</sup>	100	666	173				3	21	43		14	
	50	625	160				1	17	37		6	
Poly(phenylene sulfide) <sup>b</sup>	100	1,796	161	3	423						2	
	50	1,892	219	3	451						1	
Epoxy resin	100	1,138	153				2	16	2		7	
	50	961	228				3	33	5		6	
Urea resin <sup>c</sup>	100	1,193										
	50	980	80									
Melamine resin	100	576	194			34	22					
	50	702	190			27	96					
Cedar	100	1,573	16				59					
	50	1,397	66				2	1			2	

<sup>a</sup> Polyurethane: polyester type (diisocyanate: tolylene diisocyanate).

<sup>b</sup> Sample weight, 0.05 g.

<sup>c</sup> Temperature, 800°C.

TABLE II  
Analytical Results of Nitrogen Oxide and Nitrogen Dioxide

Sample	Composition, mg/g of sample	
	NO	NO <sub>2</sub>
Nylon 66	0.3	0.07
Polyacrylamide	0.6	trace
Polyurethane	0.3	0.06
Melamine resin	0.9	trace

<sup>a</sup> Polyurethane: polyester type (diisocyanate: tolylene diisocyanate).

Acetylene increased in quantity with increasing air. The ratio of acetylene to the hydrocarbons contained in the gaseous combustion products was much larger than that of gaseous pyrolyzates, as shown in Figure 4, for example. It was conceivable from these data that acetylene could be produced by the fur-

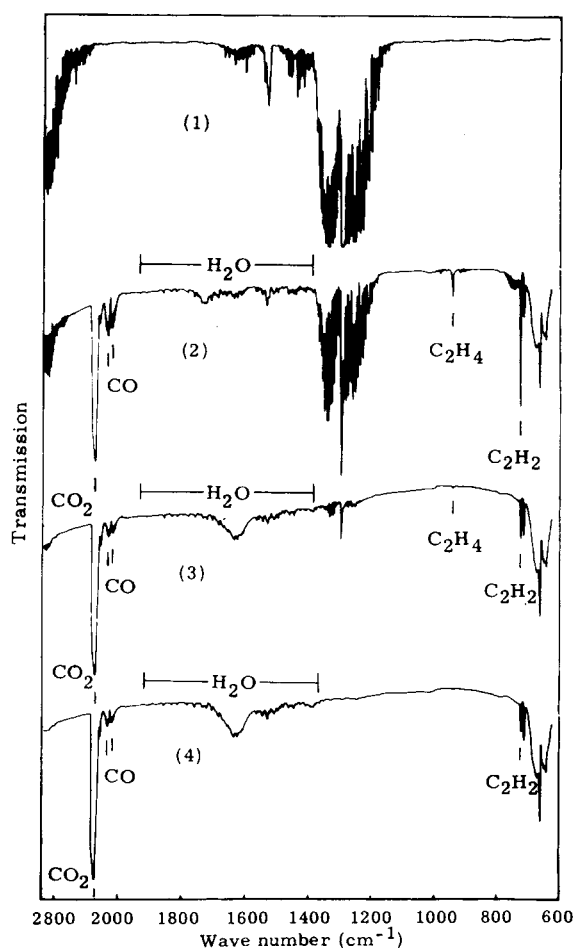


Fig. 5. Infrared spectra of methane gas and the components of methane flame: (1) methane gas (99.9% up), (2) component of the lower part of the flame, (3) component of the middle part of the flame, (4) component of the upper part of the flame.

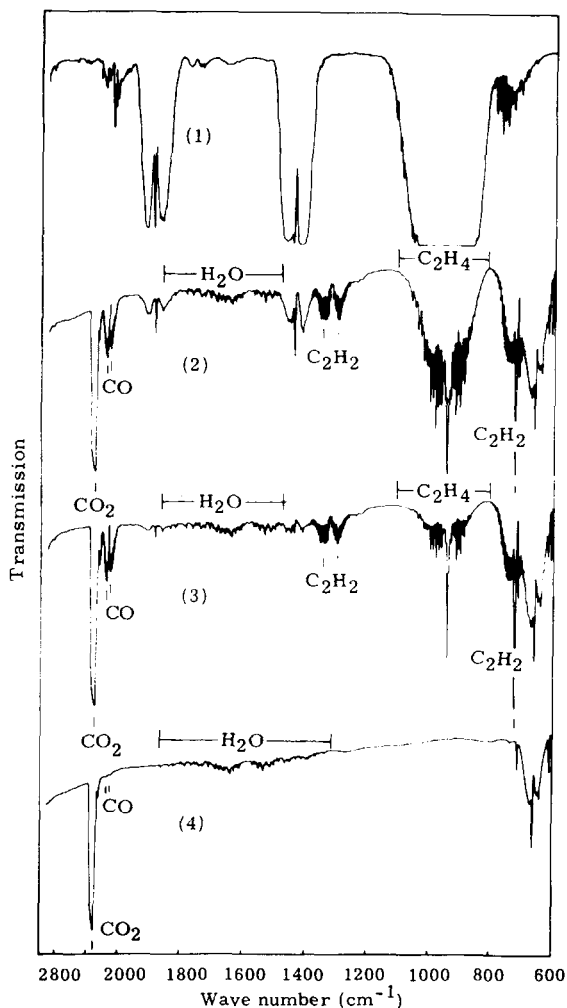


Fig. 6. Infrared spectra of ethylene gas and components of ethylene flame: (1) ethylene gas (99.9% up), (2) components of the lower part of the flame, (3) components of the middle part of the flame, (4) components of the upper part of the flame.

ther combustion of the hydrocarbons such as methane, ethylene, and so forth that were generated in the early stage of burning. In order to confirm this, the components of the methane flame and the ethylene flame obtained by using the apparatus shown in Figure 3 were analyzed by infrared spectrophotometry. It was found, as shown in Figures 5 and 6, that acetylene was formed by the combustion of both methane and ethylene. This shows that methane and ethylene are one of the major sources of acetylene. It is very interesting that acetylene and ethylene consisting of two carbons are contained in the component of the flame of methane consisting of only one carbon.

#### Nitrogen Compounds

Hydrogen cyanide was produced by the combustion of every polymer containing nitrogen as shown in Table I. For polyurethanes, hydrogen cyanide



was generated by the combustion of each of the three kinds of polyurethanes used, though the amount is small. Hydrogen cyanide was also detected in the gaseous pyrolyzates of above polymers except polyurethanes.

Ammonia was generated only from the combustion of PAA and N-66, while ammonia was detected in the gaseous pyrolyzates of every polymer containing nitrogen shown in Table I except PU.

For nitrogen oxides, as shown in Table II, only small amounts of nitrogen monoxide and nitrogen dioxide were detected in the gaseous combustion products of N-66, PAA, PU, and MR (nitrogen oxides in the gaseous combustion products of ER and PAN were not analyzed). Nitrous oxide was detected in the gaseous combustion products of MR and UR obtained at 700°C in the atmosphere, the air flow rate of which is not sufficient for them to burn with flame.

The total amount of nitrogen in the nitrogen compounds detected in the gaseous combustion products was much less than that of the nitrogen in each polymer, even if the rate (the ratio of the total amount of carbon detected in gaseous hydrocarbons and carbon oxides to the amount of carbon in each polymer) of conversion for each polymer to gaseous components was considered. Therefore, it was conceivable that a considerable amount of nitrogen in the polymers was converted to nitrogen gas ( $N_2$ ). In order to confirm it, the amount of  $N_2$  in the gaseous products generated by combustion under the conditions described above (sample weight, 0.1 g; temperature, 700°C; air flow rate, 100 l./hr) of N-66 and PAA, for example, was quantitatively analyzed. As a result, it was found that 69% and 73% of the nitrogen in N-66 and PAA, respectively, was converted to  $N_2$ . This result shows that a fairly large amount of the nitrogen in polymers containing nitrogen is converted to  $N_2$  by the flaming combustion.

### Sulfur Compounds

It was found that when PPS burned under the conditions described above, sulfur was converted into a considerably large quantity of sulfur dioxide (about 70% of the sulfur in PPS is accounted for as sulfur dioxide) and an extremely small quantity of carbonyl sulfide. On the other hand, only a trace amount of carbonyl sulfide was detected in the gaseous pyrolyzate of PPS obtained by burning in a nitrogen atmosphere at 700°C.

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