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PRODUCTS OBTAINED DURING COMBUSTION OF POLYMERS UNDER SIMULATED INCINERATOR CONDITIONS

I. POLYETHYLENE

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SUMMARY

An apparatus permitting the combustion of large (2 g) polymer samples at high temperature is described. Effluents from combustion are collected in cold traps (liquid nitrogen) and on glass wool for analysis by capillary gas chromatography and gas chromatography-mass spectrometry. Products from polyethylene combustion at four temperatures (800, 850, 900, 950°C) are determined.

INTRODUCTION

In 1975 it was estimated that between 130 and 135 million tons of refuse were generated by the people of the United States, or *ca.* 3.4 pounds per person per day. Of these 130 million tons, approximately 69% is disposed of in dumps, 22% in sanitary landfills, 8% by incineration, and 1% is recovered for further use^{1,2}. Other statistics suggest that between 2.3 and 2.7 pounds per person per day of refuse is generated, leading to between 94 and 113 million tons of municipal waste every year³⁻⁵.

Incineration of wastes has the advantage of significantly reducing the volume of collected material, by as much as 90-95%³. However, incineration and combustion processes in general have been shown to release hazardous or toxic materials. For example, polycyclic aromatic hydrocarbons (PAHs) have been associated with coal combustion, automobile exhaust, and municipal incineration⁶⁻¹¹ and are produced during the combustion of hydrocarbons and various polymers¹²⁻¹⁵.

Municipal waste consists largely of paper, with food, wood, fabrics, plastics

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and other substances making up the remainder. Plastics account for 4–5% of the total, although the exact composition of the plastics incinerated is unknown. Low density polyethylene is the leading thermoplastic polymer produced in the United States, and as such is expected to be one of the major plastics present in municipal waste. The annual production of polyethylene was 7.5 billion pounds in 1982, with 8 billion pounds expected in 1983^{2,16,17}.

The pyrolysis and combustion of polyethylene has not been studied extensively. In 1965, Kolb *et al.*¹⁸ reported on the use of pyrolysis gas chromatography for the analysis of the degradation products of polyolefins. Polyethylene (4 mg) was pyrolysed at 1000°C and the pyrolysis products hydrogenated before analysis by gas chromatography (GC). Their work focussed on the less volatile, more characteristic components of polyethylene pyrolysis. Pyrolysis was found to produce triplets of peaks, corresponding to the α , ω -olefin, α -olefin, and n -hydrocarbon, in a 1:2:1 ratio. The carbon number associated with the various pyrolysis products was not indicated, although compounds with at least 12 carbons were formed.

More recent work has been carried out by Hodgkin *et al.*¹⁹ on the degradation of polyethylene under varying oxidative conditions. Combustion temperatures of 500–800°C were investigated on samples of 3 g or more, with products identified consisting of mixtures of compounds expected from both pyrolysis and oxidative degradation. Again, the triplets of α -, ω -olefin, α -olefin and n -hydrocarbon were identified, with chain lengths of 8 to 23 carbons. In addition, lower molecular weight species such as acetaldehyde, acrolein, 2-methylpropenal and benzene were identified.

Boettner *et al.*²⁰ have investigated the combustion products of polyethylene at temperatures below 580°C and air flows of 100 ml/min. The effluents from combustion were collected in Saran[®] bags for analysis by GC and IR. Sample size was from 1 to 3 g heated at rates of 5–50°C/min, and combusted in atmospheres of air or air enriched with excess oxygen. Combustion products identified contained six carbons or less, and included saturated hydrocarbons, alkenes and dienes. When oxygen was added to the gas stream, the amount of carbon dioxide produced increased and hydrocarbon production decreased.

Thermo-oxidative degradation of polyethylene at 264–289°C has been found to produce large numbers of low-molecular-weight oxygen-containing species. Conditions were chosen to approximate industrial processing conditions, and the investigation was designed to identify possible toxic species produced. Several aldehydes, acids, ketones and lactones were found, along with various hydrocarbons. The heaviest compound identified was valerolactone (C₅H₈O₂, mol. wt. 100). A mechanism involving radical production and recombination was proposed to explain the observed compounds²¹.

Although previous work has involved oxidative thermal degradation, almost no data is available on the degradation products obtained under incinerator conditions. An apparatus has been constructed in our laboratories to permit the combustion of relatively large (2 g) samples, and to collect the chemical products obtained in liquid nitrogen cold traps and particulates on glass wool. Analysis by capillary column GC and gas chromatography–mass spectrometry (GC–MS) allows us to acquire both qualitative and quantitative information concerning the species produced.

EXPERIMENTAL

Chemicals

Low-density polyethylene was obtained from Aldrich (Milwaukee, WI, U.S.A.). Polyethylene was in pellet form, having a density of 0.92 g/ml and a melting temperature of 115°C. Three standard solutions containing *n*-hydrocarbons, alcohols, phthalates and PAHs were used to evaluate GC and GC-MS performance. Straight, chained alcohols and hydrocarbons were from standard kits (Poly-Science, Niles, IL, U.S.A.), phthalates were from Matheson, Coleman and Bell (Norwood, OH, U.S.A.) and selected PAHs were obtained from Aldrich. Five PAH standards in benzene were prepared for use in GC-MS analysis. The PAHs were obtained as a standard kit from Chem-Service (Westchester, PA, U.S.A.).

Combustion apparatus

The apparatus used for polymer combustion is shown in Fig. 1. The combustion chamber consisted of a 57 × 3 cm O.D. quartz tube, narrowing to 1.25 cm O.D. at one end and fitted with an outer $\text{\textcircled{S}}$ 34/45 joint at the other. The quartz combustion tube was equipped with two thermocouple wells, positioned immediately over the combustion zone and approximately 18 cm downstream near the exit from the combustion tube.

A pyrex tube, 9 × 1.25 cm O.D., loosely packed with pyrex wool was placed at the exit of the combustion tube to trap particulate material and prevent it from entering the cold traps. Two liquid nitrogen cold traps constructed from pyrex glass were placed in series with the combustion train, followed by a trap containing activated charcoal. All glassware was joined using 0.5-in. swagelock unions equipped with Teflon[®] ferrules (Arizona Valve and Fitting, Phoenix, AZ, U.S.A.).

Temperature was measured directly above the combustion zone and near the exit from the chamber by means of two type K chromel-alumel thermocouples. Thermocouples were connected to calibrated chart recorders with full scale values set at 50 mV in order to monitor temperature changes during combustion. Air flow through the combustion apparatus was maintained at 1.8 l/min (4 ft.³/h), resulting in the combustion tube being swept out in *ca.* 13 sec.

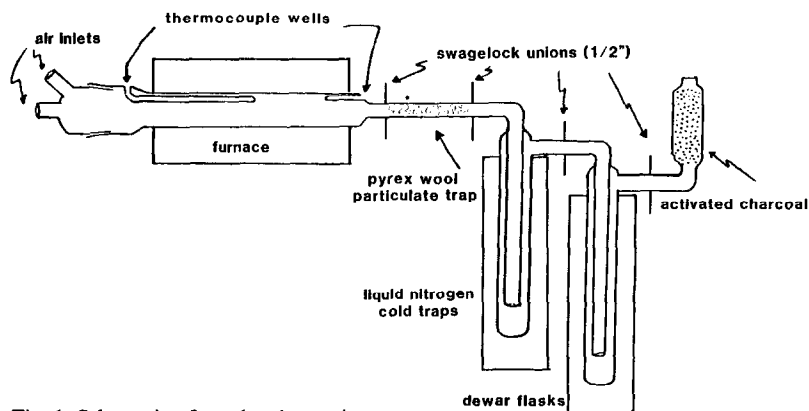


Fig. 1. Schematic of combustion train.

After the combustion apparatus was assembled and reached the desired temperature, a nickel sample boat containing 2 g of polyethylene was inserted through the 34/45 outer joint and the inner joint replaced. The sample was allowed to remain in the tube furnace for 3–4 min, after which time the furnace was turned off and the quartz tube quickly cooled to room temperature. The cold traps were removed from the dewars and warmed to room temperature, and were then washed with 40 ml dichloromethane (Burdick and Jackson, distilled-in-glass grade, Muskegon, MI, U.S.A.) and the dichloromethane washes combined. The pyrex wool filter was washed with 100 ml dichloromethane and the cold trap and glass wool extracts kept separate for concentration and analysis.

The extracts were concentrated to *ca.* 3 ml by rotary evaporation at room temperature, transferred to 25 ml pear-shaped flasks and further concentrated to *ca.* 700 μ l. Samples were then transferred to 1 ml reacti-vials (Wheaton Scientific, Millville, NJ, U.S.A.) equipped with Teflon-lined screw caps. Samples were stored in a freezer at 0°C until analysis.

Capillary GC and GC-MS analysis

A Hewlett-Packard 5880 gas chromatograph equipped with HP5880A level four data station and flame ionization detector was used for capillary GC analysis (Hewlett-Packard). GC conditions were: initial temperature, 70°C; initial time, 1 min; ramp rate, 4°C/min; final temperature, 300°C; final time, 5 min; detector temperature, 320°C; He carrier flow, 3 ml/min; cold on-column injection.

GC-MS analyses were performed on a Hewlett-Packard 5992 GC-MS calculator system, using software developed at the University of Waterloo^{22,23}. The effluent from the gas chromatograph was admitted into the mass spectrometer by means of a capillary restrictor. In addition to mass spectra taken at the top of the GC peaks, six ions were monitored: *m/e* 57, 71, 85 for hydrocarbons, 149 for possible phthalate contamination, 252 for benzpyrene isomers, and 460 for octachlorodibenzo-*p*-dioxins. Chromatographic conditions were: initial temperature, 70°C; ramp rate, 6°C/min; final temperature, 300°C; final time, 5 min; solvent time out, 2 min; injection port, 70°C; He carrier gas flow, 3 ml/min. Columns used for both GC and GC-MS analysis were 30 m \times 0.32 mm I.D. DB-5, film thickness 0.25 μ m (Chromatographic Specialties, Brockville, Canada). All GC and GC-MS analysis were performed at the University of Waterloo, Waterloo, Ontario, Canada.

RESULTS AND DISCUSSION

Cold traps

The total ion chromatograms (TIC) of the cold trap extracts at each combustion temperature are given in Fig. 2. At 800, 850, and 900°C, hydrocarbons are the main constituents of the combustion products. At 950°C, hydrocarbons are also produced but are overlapped by PAHs in the total ion chromatogram. The hydrocarbon species present in the lower temperature combustions consist of α , ω -olefins, α -olefins, and the corresponding *n*-hydrocarbons with the diene present in the largest quantities. The hydrocarbon species identified ranged in chain length from C₁₀ to C₃₅. At lower chain lengths, species containing all levels of unsaturation were observed, but as chain length increased, saturated hydrocarbons and the diunsaturated species appeared to no longer be formed.

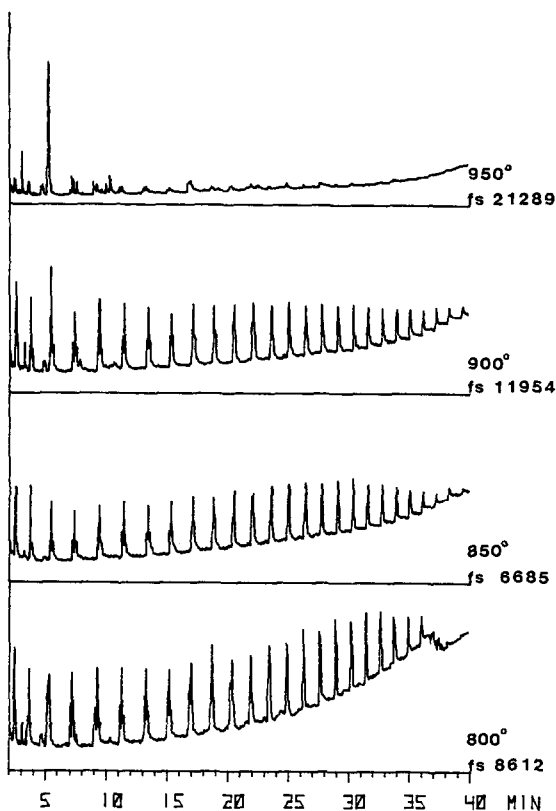


Fig. 2. Total ion chromatograms of polyethylene cold trap extracts. Combustion temperatures and full scale ion abundances are given to the right of each TIC.

Some PAHs were identified in the lower temperature extracts. Indane, indene, naphthalene, two $C_{10}H_{10}$ isomers, and 1-methyl naphthalene were found in trap extracts at 800–900°C. However, it is not until a temperature of 950°C that PAHs are produced in any quantity. The total ion chromatograph of the 950°C cold trap extract is shown at the bottom of Fig. 3. Above it are single ion traces of ions 57, 71, 85, 149, 252, and 460. Ions 57, 71, and 85 were monitored to determine the presence of hydrocarbons; 149 was a check for phthalate contamination; 252 is the molecular ion for the benzo[fluoranthenes, benzopyrenes and perylene; and 460 is the most abundant ion of the eight-chlorine isotope cluster at the molecular weight of octachlorodibenzo-*p*-dioxin. Ion 460 was monitored in conjunction with other studies being performed concurrently. Some of the compounds identified from mass spectra and retention index are alkyl benzenes, indane, indene, methyl styrenes, naphthalene, substituted methyl and vinyl naphthalenes, phenanthrene, methyl phenanthrene, fluoranthene, pyrene, benzofluorenes and higher condensed species. The two major compounds of *m/e* 252 are benzo[*b*]fluoranthene and benzo[*a*]pyrene. Although the TIC does not possess a typical hydrocarbon pattern, the hydrocarbon fragment ions monitored show that hydrocarbons from C_{10} to approximately C_{33} are produced.

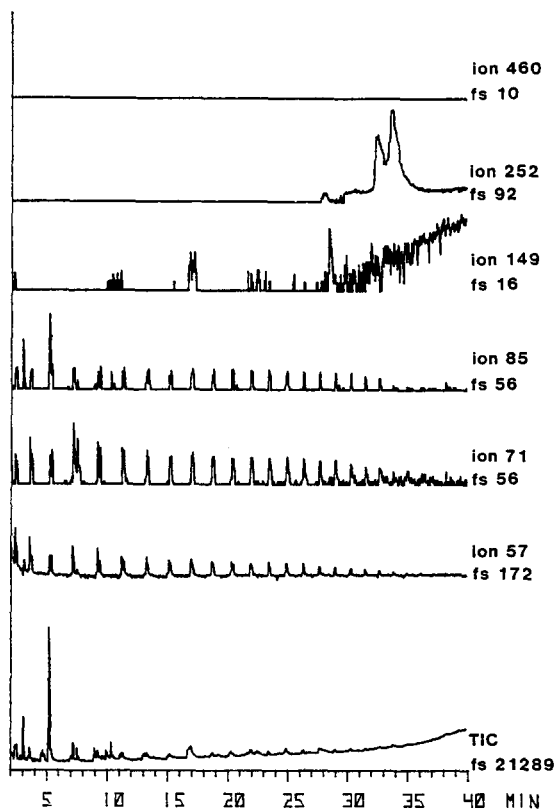


Fig. 3. Total ion chromatogram and six monitored ions from polyethylene 950°C cold trap extracts.

Glass wool traps

The TIC's of the polyethylene glass wool trap samples are shown in Fig. 4. Once again, a hydrocarbon pattern is easily recognized at temperatures of 800–900°C. The large peak at approximately 39 min in the 900°C samples is column bleed. Because of the high concentrations of large numbers of compounds in the samples, capillary column performance had begun to degrade. Improved performance was achieved by removing the first 30 cm of the column and then conditioning for 5 h, followed by analyses. The 900°C polyethylene glass wool trap sample was the first sample analysed after this procedure, and the large peak at 39 min is believed to be column bleed from the freshly exposed surface at the end of the column.

The TIC of the 950°C glass wool combustion sample is again unique when compared with the lower temperature combustions. The major peaks observed in the TIC consist of PAHs, although inspection of the monitored ions indicated the presence of hydrocarbon species, beginning at C_{13} and continuing to C_{35} . A small amount of naphthalene and 1- and 2-methylnaphthalene are observed; in general, the glass wool extracts for any of the polyethylene combustion samples did not contain large amounts of compounds eluting before 9 min (temperature of 124°C, boiling points of approx. 250°C). The PAHs identified in the glass wool trap sample include phenanthrene as the major component, with acenaphthylene second. Other com-

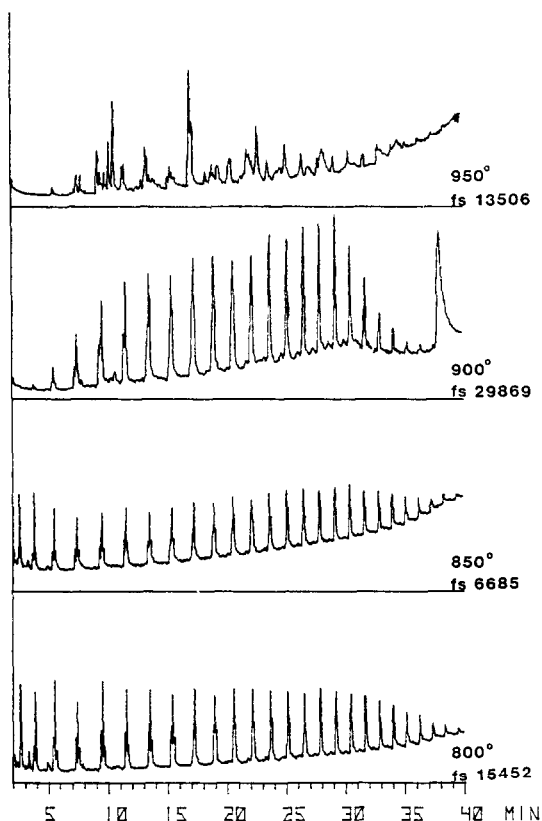


Fig. 4. Total ion chromatograms from polyethylene glass wool extracts.

TABLE I

COMPOUNDS IDENTIFIED IN COMBUSTION OF POLYETHYLENE

× means present in that sample. T = liquid nitrogen cold traps; GW = pyrex glass wool trap.

Compound	800°C		850°C		900°C		950°C	
	T	GW	T	GW	T	GW	T	GW
2-Propenylbenzene	×				×		×	
<i>n</i> -Propylbenzene	×				×			
C ₁₀ H ₁₈	×		×		×			
C ₁₀ H ₂₀	×		×		×			×
C ₁₀ H ₂₂	×		×		×			
<i>m</i> -Methylstyrene								×
<i>p</i> -Methylstyrene								×
Indane	×		×		×		×	
Indene	×		×		×		×	
C ₁₁ H ₂₀	×		×		×	×	×	

(Continued on p. 270)

TABLE I (continued)

Compound	800°C		850°C		900°C		950°C	
	T	GW	T	GW	T	GW	T	GW
C ₁₁ H ₂₂	x		x		x	x	x	
C ₁₁ H ₂₄	x		x		x		x	
C ₁₀ H ₁₀ , isomer No. 3							x	
C ₁₀ H ₁₀ , isomer No. 4							x	
C ₁₀ H ₁₀ , isomer No. 5	x				x		x	
C ₁₀ H ₁₀ , isomer No. 6	x				x		x	
C ₁₀ H ₁₀ , isomer No. 7							x	
C ₁₂ H ₂₂			x		x	x		
Naphthalene	x				x		x	x
C ₁₂ H ₂₄	x		x		x	x		
C ₁₂ H ₂₆	x		x		x	x		
C ₁₃ H ₂₄			x		x	x	x	x
C ₁₃ H ₂₆	x		x		x	x	x	x
C ₁₃ H ₂₈	x		x		x	x		
2-Methylnaphthalene							x	x
1-Methylnaphthalene	x				x	x	x	x
C ₁₄ H ₂₆	x		x		x	x		
C ₁₄ H ₂₈	x		x		x	x	x	x
C ₁₄ H ₃₀	x		x		x	x		x
1-Vinylnaphthalene						x	x	x
2-Vinylnaphthalene						x	x	x
Acenaphthylene					x	x	x	x
C ₁₅ H ₂₈	x		x		x	x	x	x
4-Methylbiphenyl							x	x
C ₁₅ H ₃₀	x		x		x	x	x	x
C ₁₅ H ₃₂	x		x		x	x		
Unknown, MW 168						x		
1-Methylacenaphthylene						x		
Fluorene						x	x	x
C ₁₆ H ₃₀	x		x		x	x	x	x
C ₁₆ H ₃₂	x		x		x	x	x	x
C ₁₃ H ₃₄	x		x		x	x		
-1-H phenalene					x			
Methylacenaphthylene (3- or 4-)						x		
C ₁₇ H ₃₂	x		x		x	x	x	x
C ₁₇ H ₃₄	x		x		x	x	x	x
C ₁₇ H ₃₆						x	x	x
Phenanthrene						x	x	x
C ₁₈ H ₃₄	x		x		x	x	x	x
C ₁₈ H ₃₆	x		x		x	x	x	
C ₁₈ H ₃₈	x		x		x			
1-Phenylnaphthalene						x		x
C ₁₉ H ₃₆	x		x		x	x		x
C ₁₉ H ₃₈	x		x		x	x	x	x

TABLE I (continued)

Compound	800°C		850°C		900°C		950°C	
	T	GW	T	GW	T	GW	T	GW
C ₁₉ H ₄₀	x		x					
3-Methylphenanthrene						x		
4,5-Methylenephenanthrene						x		
2-Phenylnaphthalene						x	x	x
C ₂₀ H ₃₈	x		x		x		x	x
C ₂₀ H ₄₀	x		x		x	x		x
C ₂₀ H ₄₂	x		x					
Fluoranthene					x	x		
Unknown, MW 204						x		
C ₂₁ H ₄₀	x		x		x	x		x
C ₂₁ H ₄₂	x		x		x	x	x	x
C ₂₁ H ₄₄	x		x					
Diphenyldiacetylene						x		
Pyrene						x	x	x
C ₂₂ H ₄₂	x		x		x		x	
C ₂₂ H ₄₄	x		x		x	x	x	x
C ₂₂ H ₄₆	x							
Benzo[<i>a</i>]fluorene						x		
Benzo[<i>b</i>]fluorene						x		
1-Methylpyrene					x	x		
C H	x		x		x			
C H	x		x		x	x	x	x
Unknown, MW 228								x
C H	x		x		x			
C H	x		x		x	x	x	x
Benzo[<i>c</i>]phenanthrene								x
C H	x		x		x	x		x
Chrysene							x	
C H	x		x		x	x		x
C H	x		x		x	x		x
C H	x		x		x	x		x
Benzo[<i>b</i>]fluoranthene							x	
C H	x		x		x			x
C H	x		x		x			x
Benzo[<i>a</i>]pyrene							x	
Perylene								x
C H	x		x		x			x
C H	x				x			x
Benzo[<i>ghi</i>]perylene								x
C H	x				x			
C H					x			

pounds were: methylacenaphthylenes, fluorene, vinylnaphthalenes, phenylnaphthalenes, fluoranthene, pyrene, and the benzofluorenes. Ion 252 shows the presence of two components, although only one was present at quantities sufficient for detection during mass spectral scanning. The compounds are a benzofluoranthene isomer and perylene, with perylene present sufficiently for detection during scanning. A summary of the compounds identified in the polyethylene combustion is given in Table I.

CONCLUSIONS

Under the conditions attained in this study, it appears that complete combustion of polyethylene is not accomplished. Instead, combustion combined with pyrolytic degradation takes place. It is of interest to note that oxygen-containing species are not detected from polyethylene combustion, although they have been observed at lower temperatures^{19,21}. The air flow used was selected as sufficient to initiate and maintain flaming combustion. When compared with air flows used in municipal incinerators, the ratio of air flow to incinerator volume is approximately 10 times greater for our system.

Except at the highest temperature, polyethylene yielded hydrocarbons, alkenes and dienes, with a few PAHs such as naphthalene, fluorene, or phenanthrene also

TABLE II

TOTAL AMOUNTS (mg) OF SELECTED COMPOUNDS IDENTIFIED IN COLD TRAP EXTRACTS

Compound	Temperature (°C)			
	800	850	900	950
Indene	0	0	0	3.61
Naphthalene	1.91	1.35	3.17	13.5
C ₁₂ H ₂₄	2.56	0.507	2.06	0.672
2-Methylnaphthalene	0	0.145	1.68	1.23
1-Methylnaphthalene	0	0.140	0.425	1.01
Biphenyl	0	0	0.284	0.935
Acenaphthylene	0	0	0.386	1.92
Fluorene	0.0891	0	0	0.425
9-Methylfluorene	0	0	0	0.185
Dihydroanthracene	0	0	0	0.169
Phenanthrene	0.506	0	0.312	1.56
C ₁₉ H ₃₈	1.46	0.883	1.008	0.204
2-Phenylnaphthalene	0	0	0	0.204
Fluoranthene	0.0749	0	0	0.406
Pyrene	0	0	0	0.528
Benzo[c]phenanthrene	0	0	0	0.164
Chrysene	0.0419	0	0	0.155
C ₂₆ H ₅₂	0.932	0.609	0.386	0
Total HC*	47.76	23.19	33.71	—**
Total PAH*	—***	—***	—***	54.9

* Total amounts in sample of all compounds.

** Hydrocarbons present at levels too low for identification by GC alone.

*** PAHs present at levels too low for identification by GC alone.

present. These and other PAHs were minor components of polyethylene combustion until a temperature of 950°C, at which point PAHs become the dominant species produced with hydrocarbons decreasing in abundance. The PAHs formed in polyethylene combustion at 950°C are mainly simple fused rings, with occasional substituted compounds identified, but a complex mixture of PAHs is not present. The total amounts of selected species identified in the cold trap extracts at the varying combustion temperatures are given in Table II. There appears to be a trend of increased amounts of PAHs at high temperatures along with a decrease in formation of alkenes. However, a definite pattern is not readily observed, as production of some species appears to peak at 900°C and then decrease at 950°C.

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