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Combustion Products from Burning Polyethylene

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ABSTRACT

Thermal degradation of polyethylene was studied under a wide range of oxidative degradation conditions including flaming combustion. The collection techniques described were designed to isolate the product mixtures so that secondary reactions were minimized. Both pyrolytic and oxidative degradation products were generally obtained. The pyrolysis products included a range of saturated and unsaturated hydrocarbons from C_2 to C_{23} which did not vary greatly in product ratio with conditions. The oxidative degradation products, including mainly acetone, acetaldehyde, acetic acid and a small amount of acrolein, varied considerably in relative yield.

INTRODUCTION

In recent years there has been a lot of research activity directed at an understanding of the smoke and gaseous materials produced from polyolefins in fire situations. This has been brought about by reports [1-3] of toxic gases such as acrolein being produced in large amounts when polyolefins are heated in air under certain conditions. The toxic hazards associated with these materials in fires is very difficult to assess because of the well-known variations in combustion chemistry under different conditions and also the lesser-known problems of obtaining reliable analytical results.

The use of chemical analysis systems such as Draëger tubes, or other methods where the gases are not separated, is often unreliable because of the complex and often interfering product mixture. Gas chromatography, especially when coupled with mass spectrometry (GC/MS), has been used with great success for product analysis in small-scale pyrolysis [4] and mild oxidative degradation of polyolefins [5, 6]. In these cases gas samples have been analyzed either by direct injection into a gas chromatograph or by adsorption of gases onto a cross-linked polymer support and subsequent high temperature desorption into a chromatograph. This paper describes the use of GC/MS techniques to study products from larger-scale burning experiments. In this work, interest centered on analysis of the range of organic compounds produced and the product ratios, without considering the total yield of each product.

Preliminary experiments on the analysis of volatile products from larger-scale burning and oxidatively pyrolyzed polyolefins indicated that previous techniques [5-7] were not completely satisfactory. First, the composition of samples collected changed drastically if kept more than a few minutes at room temperature. They could, however, be kept at -20°C in a solvent for a few days without great change. High-temperature desorption from an organic surface caused even greater changes. Second, because of large amounts of water produced from burning polymers, direct sampling by syringe and subsequent injection into a GC/MS column was not practicable. The most satisfactory technique for this work was low-temperature effluent trapping, solvent recovery, and GC/MS injection similar to that detailed by Chatfield et al. [8].

EXPERIMENTAL

Samples

Four commercial polyethylenes (PE) were used: (a) low-density PE foams of densities 0.15 g/cm^3 and 0.05 g/cm^3 from Pilon Plastics Pty. Ltd., Sydney, Australia; (b) low-density PE pellets of Alkathene XJG 143 from ICI Australia Ltd., Melbourne, Australia; (c) high-density PE pellets GF 7660 from Hoechst Australia Ltd., Melbourne, Australia.

Apparatus

The simple combustion apparatus used for the majority of our experiments is shown in Fig. 1. The sample tube was a 4-cm diameter by 20 cm length of Pyrex or silica tube connected directly to various

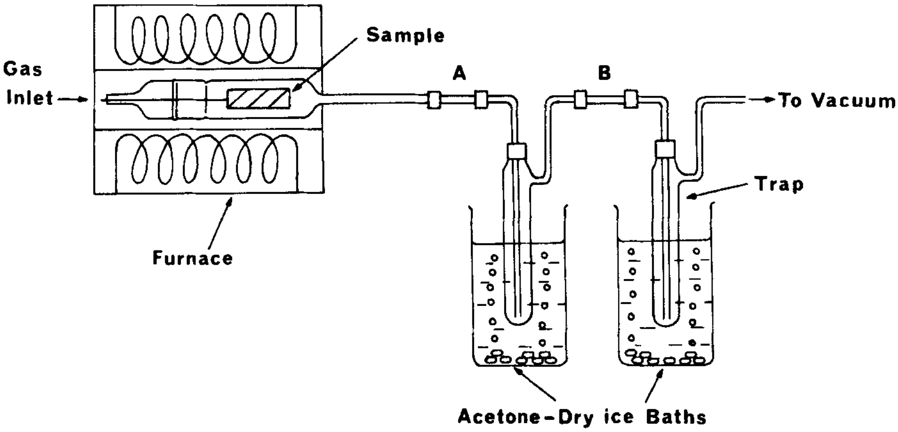

FIG. 1. Combustion apparatus.

traps. The furnace was a Chemelec muffle furnace with controlling thermocouples adjacent to the sample tube. In the experiments reported in this paper the inlet gas was air, so the flow was controlled by variations in gas inlet size and the vacuum outlet.

Spectroscopy

Infrared (IR) spectra were recorded on a Unicam Model SP1000 grating infrared spectrometer in methylene chloride solution. Nuclear Magnetic Resonance (NMR) spectra were recorded on a Varian T-60 instrument in $CDCl_3$ solution using tetramethylsilane as the internal standard.

Gas Chromatography and GC/MS

Gas chromatography was carried out using Hewlett-Packard 5710A and Perkin Elmer 900 instruments fitted with a 1.8 m × 2 mm ID glass column packed with 80-100 mesh Porapak Q and a 50-m SE-30 SCOT column, respectively. Nitrogen and helium were used as carrier gases. For GC/MS, analysis was carried out on a Finnigan 3300F instrument fitted with a chemical ionization source and columns identical to those employed for gas chromatography. Helium was used as carrier gas and the reagent gas for mass spectrometry, yielding spectra equivalent to those obtained by electron impact. Mass spectra were recorded on a Finnigan 6100 Data System at 2-s intervals at an electron energy of 120 V and a beam current of 0.4 mA.

The identity of the degradation products was established by comparison of their mass spectra with spectra recorded in the EPA/NIH Mass Spectral Data Base [9], and checked by comparison of retention times with that of a known sample.

RESULTS AND DISCUSSION

Experimental Design

One of the major problems encountered in the study of burning polymers is the extreme variability of the experimental conditions. No one study can expect to cover all possible burning modes, so restrictions have to be placed on the experimental conditions. Early in our work a range of experimental techniques for studying the burning of polyethylene was tried, including that of Sumi and Tsuchiya [10]. Although we found that this worked reasonably for other polymers, the products obtained from polyolefins were more variable and could not be correlated well with larger scale burning tests. Later experiments showed that the sample weight to heating surface (especially for the less dense polyethylene) ratio was too low. Sample weights of 3 g or more in our glass or silica tube furnace apparatus (Fig. 1) gave a mixture of pyrolysis and oxidative degradation products. As each sample was placed in the furnace (heated to a preset temperature), the sample temperature increased rapidly and consistently; hence the degradation conditions remained the same. For larger sample sizes in other furnace types there were greater reproducibility problems and minor problems of keeping the condensing surfaces cool and maintaining reliable temperature control. However, the range of products found was the same.

Combustion Products

The organic products from all the combustion/pyrolysis experiments were obtained as waxy, oily, mists (condensed in the cold trap) which could be extracted from the particulate and water residues with methylene chloride or methanol. The NMR spectra indicated that the bulk of the products were long-chain hydrocarbons but the infrared spectra (Fig. 2) showed that there were also considerable proportions of carbonyl-containing materials present. The latter were present as low molecular weight products, as the carbonyl peak intensity decreased rapidly with time when recorded on a sodium chloride plate. GC/MS analysis of the products on a SE 30 SCOT column gave the very regular triplet pattern shown in Fig. 3. This pattern is almost identical in major peaks to that obtained by a number of previous workers [11, 12], including most recently Sugimura and Tsuge [4], as the products of micropyrolysis of polyethylene. The research

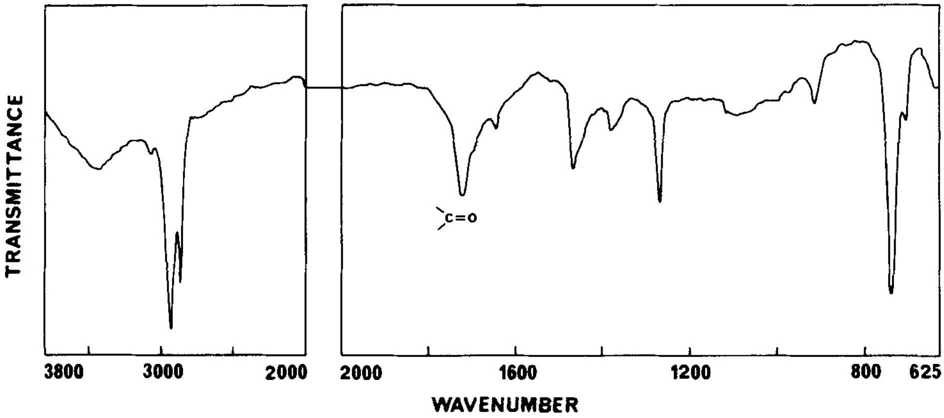

FIG. 2. IR spectrum of combustion/pyrolysis products.

of the latter workers showed that the three peaks consisted of the long-chain saturated hydrocarbons (at highest retention time), α-unsaturated hydrocarbons (medium retention), and α,ω-diolefins (lowest retention) at each level from C_8 to C_{23}. Our GC/MS results confirmed that we had obtained the same series of compounds.

Our chromatogram also included a number of other small peaks, such as those at spectrum numbers 21, 30, 44 and 108, which were more variable depending on the type of column used, the burning conditions, and the nature of the polyethylene sample. The mass spectra of these extra peaks indicated that they were long-chain mono-unsaturated hydrocarbons with the double bonds in nonterminal positions. These have not been fully characterized.

The combustion/pyrolysis experiments were carried out at furnace temperatures of 500, 600, 700, and 800°C with a range of polyethylene samples including high and low densities and various foams. The air flow in these experiments was also varied over a wide range. Surprisingly, the product pattern showed extremely little variation with these different conditions and only the total yield of organic volatiles changed. Previous work on pyrolysis of polyethylene [4] showed that only the minor peaks changed with the different samples of polymer. Figure 3 shows the products from a sample heated at 600°C; at 800°C the same triplet pattern is present except that the diene peak in each group is considerably higher, and a number of the unidentified small peaks between C_{10} and C_{12} are much larger. At this higher temperature the polyethylene samples burst into flames soon after being placed in the furnace; at 600°C the time interval before this happens is longer.

As shown in Fig. 3, the SE 30 SCOT column was not very useful in identifying materials below the C_8 hydrocarbons, so simultaneous

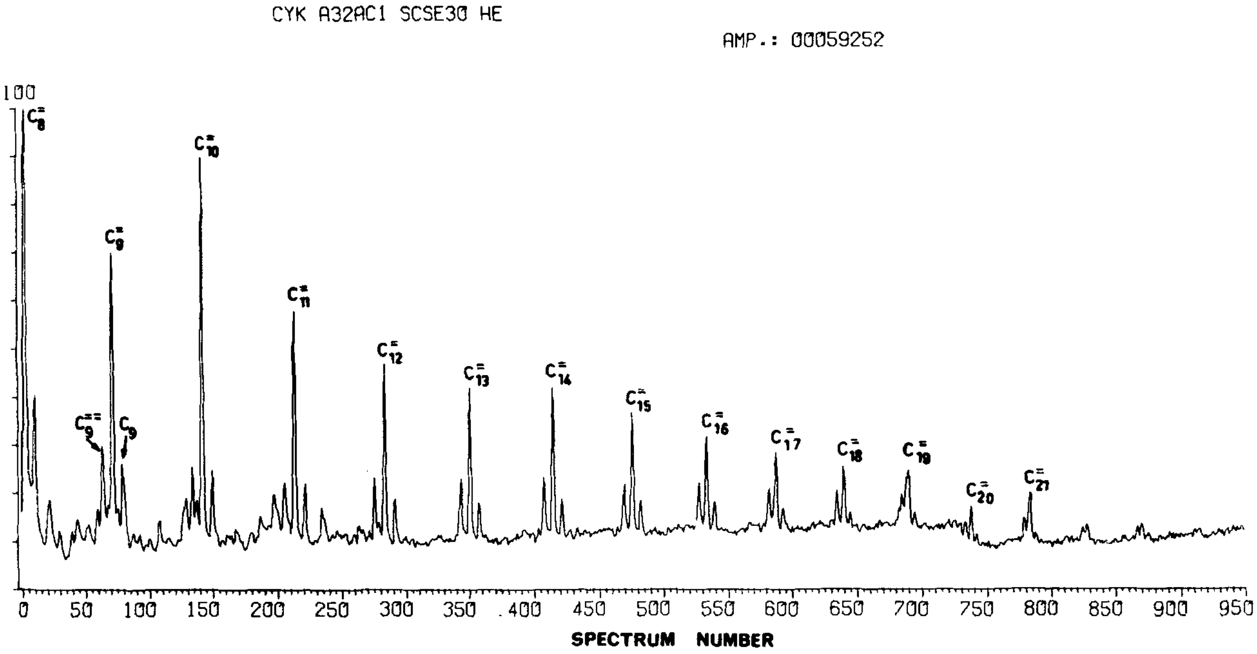

FIG. 3. Total ion chromatogram from GC/MS of high boiling products (G.C. conditions: 50 m SE-30 SCOT column programmed from 50 to 200° at 4°C/min)

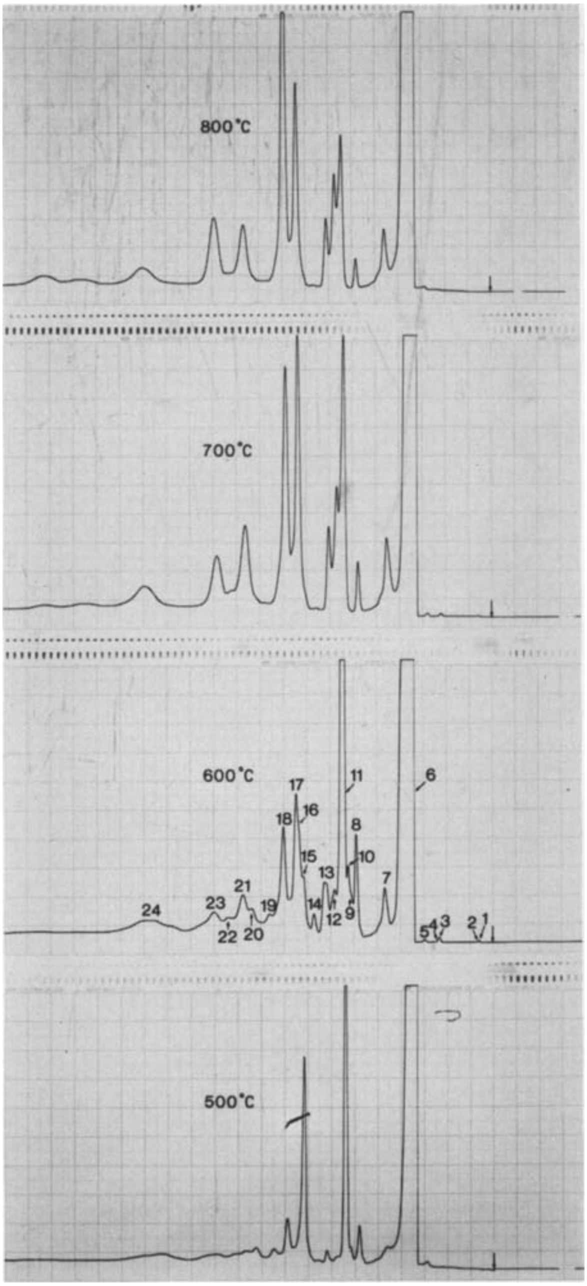

FIG. 4. Combustion temperature vs product composition (G.C. conditions: 1.8 m × 2 mm ID Porapak Q column programmed from 50 to 180° at 8°C/min).

TABLE 1. Low Molecular Weight Products from Burning Polyethylene (Porapak Q Column)

Peak no.	Name	GC/MS[a]	GC[b]
1	Ethylene	-	+
2	Ethane	-	+
3	Propene	-	+
4	Propane	-	+
5	Butene	-	+
6	Methanol (solvent)	+	+
7	Acetaldehyde	+	+
8	Unknown	-	-
9	Acrolein	+	+
10	Propionaldehyde	+	+
11	Acetone	+	+
12	C_5H_6	+	-
13	C_5H_8	+	-
14	2 propenal, 2 methyl	+	-
15	Methyl ethyl ketone + C_5H_{10}	+	+
16	Hexene	-	+
17	Acetic acid	+	+
18	Benzene	+	+
19	Unknown	-	-
20	Unknown	-	-
21	Heptene	-	+
22	Unknown	-	-
23	Toluene	+	+
24	Octene	-	+

[a] + Identified by mass spectral library search [9].

[b] + Identified by direct gas chromatographic comparison with known sample.

analysis was carried out on Porapak Q columns. These have been extensively used in the past for identifying the low molecular weight volatile and polar products from the oxidation of hydrocarbon polymers [5, 6]. In contrast to the higher molecular weight products, those analyzed on the Porapak Q column varied more extensively with changes in the combustion conditions and with the collection methods. Addition of polymer or inert silica traps at A or B (Fig. 1) gave fewer and a more variable range of products than completely open tubes through the cold traps. The products were recovered by washing down the traps with cold methanol and drying with molecular sieves at low temperatures. Other solvents such as acetone and methylene chloride could be used, but they did not appear to recover all the products and obscured several major peaks.

An important variable which has been shown by a number of workers [1, 2] to affect the yield of combustion products such as acrolein from polyethylene is the temperature of oxidative pyrolysis. Similar results were also found in the present combustion/pyrolysis experiments. The change in product composition with temperature is shown in Fig. 4. for samples recovered in methanol. The list of products identified by GC/MS and associated retention times are shown in Table 1. The major changes include the large decrease in acetone as the temperature increased and the simultaneous increase in the aromatic hydrocarbons, benzene, and toluene. The series of unsaturated hydrocarbon products identified in Fig. 3 is continued with heptene, hexene and small peaks at the start of the trace, butene, propene, and ethylene. No carboxylic acids other than acetic were identified, even when the pyrolysis products were recovered in ether/diazomethane mixtures and product retention times identified by known samples. This is at variance with the results of Morikawa [1]. The presence of formaldehyde was determined chemically but could not be determined by gas chromatography. Acrolein, of major toxic concern in the literature, was generally a very minor component in our traces. Chromatographic results obtained on a Porapak Q column from large polyethylene foam samples burnt in the open were similar to those shown in Fig. 4 for the 500°C furnace sample, with major peaks for acetic acid, acetone, and acetaldehyde only.

A surprising feature of these results was the repeatability of the gas chromatography analyses even with quite large variations in the air flows and with different samples of polyethylene including foams, high and low densities, and filled and unfilled samples. Total product yields of course varied more noticeably. Considering this, our results contrast somewhat with those obtained by Michal et al. [7] who obtained much higher yields of long-chain oxidation products during thermal oxidation and combustion. The differences may be due to sample collection methods or polyethylene sample size. The general conditions encountered in our furnace experiments should be close to those found when large amounts of polyethylene burn and smoulder in a moderately restricted environment, such as in clad insulation, and hence give a good indication of the type of products formed in these situations.

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